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MECHANICALLY DRIVEN DISORDER AND PHASE TRANSFORMATIONS IN ALLOYS

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CONTENTS

1. INTRODUCTION	160
2. ATOMIC (CHEMICAL) DISORDERING OF INTERMETALLIC COMPOUNDS IN THE EARLY STAGE OF BALL MILLING	161
2.1. <i>Experimental procedures</i>	161
2.2. <i>Anti-site disorder in B2 compounds</i>	163
2.2.1. <i>Thermal disorder in B2 compounds</i>	163
2.2.2. <i>Mechanically induced disorder in B2 compounds</i>	164
2.3. <i>Anti-site disorder in L1₂ compounds</i>	167
2.4. <i>Anti-site disorder in A15 compounds</i>	167
2.4.1. <i>Introduction</i>	167
2.4.2. <i>Thermal disorder and disorder by irradiation in A15 compounds</i>	168
2.4.3. <i>Mechanically induced disorder in A15 compounds</i>	171
2.5. <i>Triple-defect disorder in group VIII–group IIIA compounds crystallising in the B2 structure</i>	174
2.5.1. <i>Introduction</i>	174
2.5.2. <i>Thermal disorder in VIII–IIIA compounds</i>	175
2.5.3. <i>Mechanically induced disorder in VIII–IIIA compounds</i>	179
2.6. <i>Atomic disorder in B8 compounds</i>	181
2.6.1. <i>Introduction</i>	181
2.6.2. <i>Mechanically induced disorder in B8₂ compounds with composition T₁Z</i>	182
2.6.3. <i>Mechanically induced disorder in B8₂ compounds with composition T₂Z and related orthorhombic phases</i>	185
2.7. <i>Discussion</i>	188
3. PHASE TRANSFORMATIONS IN INTERMETALLIC COMPOUNDS INDUCED BY BALL MILLING	190
3.1. <i>Amorphisation</i>	190
3.2. <i>Phase transformations to the solid solution: The Au–Nb system</i>	195
3.3. <i>Phase transformations in the Ni–V system</i>	199
3.4. <i>Phase transformations in compounds with the B8₂ structure and related orthorhombic structure</i>	204
3.5. <i>Mechanically induced disorder and phase transformations in L1₂ compounds</i>	210
3.6. <i>Phase transformations in σ-phases</i>	216
3.7. <i>Prediction of phase transformations in intermetallic compounds induced by milling</i>	220
3.8. <i>Discussion</i>	223
4. NEW MATERIALS SYNTHESISED BY MECHANICAL MILLING	225
4.1. <i>Introduction</i>	225
4.2. <i>Novel spin-glass materials by ball milling of intermetallic compounds</i>	225
ACKNOWLEDGEMENTS	231
REFERENCES	231
APPENDIX A. ESTIMATE OF THE DISORDERING ENTHALPY IN COMPLETELY ORDERED COMPOUNDS	234
APPENDIX B. ESTIMATE OF THE ENTHALPY OF THE COMPOUND, THE SOLID SOLUTION AND THE AMORPHOUS STATE	236
APPENDIX C. ESTIMATE OF THE ENTHALPY OF PARTLY ORDERED B2 AND L1 ₂ STRUCTURES	237

1. INTRODUCTION

Milling by the action of moving balls has long been known as a technique for refining minerals and in fact for refining particles of all kinds of materials. The first ball milling experiment for synthesis of special configurations, in which metals were involved, was performed at INCO Research Laboratories in the early 1960s. In this experiment fine oxide particles were coated by ductile metals, such as nickel and aluminium, in a high energy vibratory mill.⁽¹⁾ A later development was the dispersion by milling of oxide particles in a metal matrix to produce oxide-dispersion-strengthened (ODS) alloys for high temperature applications.⁽²⁾ For this process vibratory mills, stirred attrition mills or large conventional ball mills could be used. This technique of producing composite metal powders with controlled microstructures in a ball mill is known as "mechanical alloying" (MA).

A further important progress in mechanical alloying was the discovery by Koch *et al.*⁽³⁾ that, during mechanical alloying of powders of elemental niobium and nickel in a SPEX mill, the final product became an amorphous alloy. This was demonstrated by the disappearance of the crystalline reflections in X-ray diffraction and the appearance of a broad peak, characteristic of amorphous material. Moreover, differential scanning calorimetry revealed an exothermic crystallisation peak. Already in this early stage it was recognised that by ball milling the size of the crystallites, constituting the powder particles before amorphisation, was reduced to nanocrystalline dimensions. This was assessed by applying the Scherrer formula. Further early investigations of amorphisation by mechanical alloying were carried out by Schwarz *et al.*⁽⁴⁾ in the Ni-Ti system, Hellstern and Schultz⁽⁵⁾ for a number of transition metal-zirconium systems and by Weeber *et al.*⁽⁶⁾ for the Ni-Zr system. In the latter investigation it was shown that nickel almost lost its magnetic moment after long milling times, which clearly demonstrated the mixing on an atomic scale by ball milling.

Moreover, MA could be related to a different type of experiment, namely amorphisation of alternating thin crystalline layers of lanthanum and gold by interdiffusion, when such configuration was annealed well-below the crystallisation temperature.⁽⁷⁾ This reaction is known as the solid-state amorphisation reaction (SSAR). It could be shown by scanning electron microscope (SEM) observations that by repeated fracture and cold welding of powder particles during ball milling a multilayered structure of both metals is also generated.^(4,5,8) Eventually amorphisation occurs by interdiffusion, i.e. by the SSAR. The driving force for the SSAR is the gain of free energy upon mixing of the two metals, while apparently nucleation and growth of crystalline intermetallic compounds with an even lower free energy is avoided. The thermodynamic and kinetic aspects of these reactions were analysed by Johnson,⁽⁹⁾ while an early review of amorphisation by milling is found in Weeber and Bakker.⁽¹⁰⁾

In the first years following the discovery by Koch *et al.*,⁽³⁾ a relatively small number of research groups started ball milling experiments. The number of published papers grew gradually with, as an indication, about 10 papers on ball milling at a conference in Los Alamos in 1987 and about 20 papers at the RQ7 conference in Sweden in 1990.⁽¹²⁾ At the latter conference it seemed that the consequence of the production of nanocrystalline alloys by ball milling was fully realised. In nanocrystalline materials ductility is highly enhanced, so that by using powder metallurgy routes originally brittle materials can be shaped. This could be a promising technique for the production of, for example, engine parts from Ti-Al, Ni-Al or Nb-Al intermetallics, whose materials are light in weight and exhibit high hardness and corrosion

resistance at high temperatures. These promising technical applications may have led to the explosive growth of research in the field around 1991, which became manifest at a specialised conference in Japan in 1992, where over 100 papers were presented.⁽¹³⁾ A recent review of mechanical alloying and related topics was written by Koch.⁽¹⁴⁾

Even two years before the publication by Koch *et al.*⁽³⁾ a paper was published by Yermakov *et al.* on the amorphisation of a number of Y–Co compounds as a result of grinding.⁽¹⁵⁾ The material was examined by X-ray diffraction and Mössbauer methods and exhibited the characteristics of amorphous material. However, Yermakov *et al.* did not start from elemental powders, but from pre-alloyed intermetallic compounds. Later on, such experiments were termed by Koch “mechanical milling”(MM). There is a striking difference between MA and MM. In a MA experiment free energy is gained due to the mixing of the elements. In contrast, in a MM experiment free energy is lost, because evidently the intermetallic compound has a lower free energy than the amorphous alloy. Thus there is an increase in energy during MM and thus there must be a way of storing free energy in the material by ball milling, where extra energy eventually leads to amorphisation. Amorphisation of intermetallic compounds can also be induced by electron irradiation⁽¹⁶⁾ or by irradiation by ions.^(17,18) It was already known for a long time that irradiation by energetic particles generates atomic (chemical) disorder in compounds, i.e. atoms are transferred to the other (‘wrong’) sublattice, which results in a decrease of the Bragg–Williams long-range-order parameter. These findings were interpreted theoretically by Zee and Wilkes.⁽¹⁹⁾ Johnson⁽⁹⁾ suggested that atomic (chemical) disorder could also provide a mechanism for amorphisation by mechanical impact. However, Johnson⁽⁹⁾ concludes in his review from 1986 that at that time the statement is speculative and that “clearly more work will be required before an understanding emerges”. At present, less than a decade later, the occurrence of atomic (chemical) disorder as a result of mechanical milling has been demonstrated in a large number of intermetallic compounds. It is the aim of the present review to present evidence for atomic (chemical) disorder in the early stage of milling and to show that an intermetallic compound may undergo a phase transformation during the later stage of milling. We will see that such transformations may be not only transformations to the amorphous state, but also transformations to a different crystal structure. In this way MM turns out to drive phase transformations far from equilibrium.

The present review paper is naturally organised as follows: In Section 2 we examine what is occurring on an atomic scale in an intermetallic compound in the early stage of milling. It turns out that compounds are disordering indeed. This can be monitored not only directly by disappearance of superlattice reflections in X-ray and neutron diffraction, but also indirectly by changes of any appropriate physical parameter. A condition for the use of changes in physical parameters for monitoring the process is that one should know how the chosen parameter is influenced by disorder. Therefore, in cases where such knowledge exists, for example by knowledge of atomic disorder at higher temperatures frozen-in by rapid quenching or disorder induced by irradiation, we first discuss these experiments before proceeding to the effect of MM. In Section 3 we discuss mechanically induced phase transformations, while in Section 4 we discuss some special topics.

2. ATOMIC (CHEMICAL) DISORDERING OF INTERMETALLIC COMPOUNDS IN THE EARLY STAGE OF BALL MILLING

2.1. *Experimental Procedures*

Intermetallic compounds for ball milling experiments are usually prepared by arc-melting weighed amounts of the pure metals in a purified argon atmosphere. Arc-melting is repeated

several times to ensure homogeneity. Sometimes it is necessary to anneal the button for periods up to one month to obtain homogeneous single-phase material. The anneal is performed in sealed quartz ampoules under argon atmosphere and precautions are taken to avoid a reaction with quartz. The sample is crushed, for example by a mortar and pestle, and the powder is annealed again to anneal-out plastic deformation.

A variety of ball mills is used in the experiments. These have been reviewed by Koch:⁽¹⁴⁾ tumbler ball mills, attrition mills, shaker mills (SPEX), planetary ball mills (Fritsch), rod mills⁽²⁰⁾ and vibratory mills. One big ball or several smaller balls from various materials can be applied. The variety of types of ball mills and milling intensity may cause differences in the results of different research groups. As an example, the vibratory ball mill used at the Van der Waals–Zeeman Laboratory is presented in Fig. 1. The device consists of a stainless steel vial with a hardened steel bottom, the central part of which consists of a tungsten carbide disk (diameter 2 cm). Inside the vial a single hardened steel ball with a diameter of 6 cm is kept in motion by a vibrating frame upon which the vial is mounted. The amount of milled sample is in the order of a few grams. The device is evacuated during the milling down to a pressure of 10^{-6} Torr in order to avoid reactions with a gas atmosphere. It is not advisable to perform milling in air, because the fresh surfaces, continuously produced by fracture, easily react with oxygen or nitrogen even at ambient temperature. If a type of mill is used which cannot be evacuated, for example a planetary mill, usually the vials are filled in a glove box under purified argon atmosphere. Subsequently the vials are tightly sealed and the milling is either performed outside the glove box or, in case of a small mill, inside the glove box. Utmost care should always be taken to avoid reactions with reactive gases, because the results obtained can give rise to erroneous interpretations. A warning example is the milling of a LaCo compound in a glove

Fig. 1. Vibratory ball mill for milling under high vacuum.

box under argon atmosphere purified for water and oxygen, which we performed some years ago. What we observed was a decomposition of the compound in cobalt and a second component, which had exactly the same lattice parameter as f.c.c. (β) lanthanum. The elemental character of cobalt in the mixture was assessed by measuring the magnetic moment, which turned out to be equal to the magnetic moment of pure cobalt. The result was erroneously interpreted as demixing of the compound in the pure metals. However, deeper inspection showed that the second component was not pure lanthanum, but LaN. Apparently the lanthanum in the compound was reactive enough to react with nitrogen impurities in the argon atmosphere. Also, the effect of crystallisation of amorphous material in a ball mill after long periods of milling, as sometimes is reported, may be suspect and could be a slow reaction with, for example, nitrogen. This is the reason, why milling under high vacuum is advisable.

Another source of contamination is formed by the milling tools. If there is a tungsten carbide contamination, tungsten carbide reflections are observed in the X-ray pattern. However, contamination by iron is more serious, because iron as an impurity will mechanically alloy and thus iron atoms will occupy lattice sites in the compound. This can be serious in case conclusions are drawn about the milling process based on magnetic measurements. Elemental analysis and annealing of the sample after the experiment in order to obtain the starting material back are necessary. After such an anneal the sample should exhibit identical (magnetic) properties to the original starting compound.

Numerous techniques are used to examine the sample after milling: X-ray diffraction, neutron diffraction, transmission electron microscopy (TEM), scanning electron microscopy (SEM), elemental analysis, differential scanning calorimetry (DSC) and differential thermal analysis (DTA) are all commonly employed. Furthermore, much can be learnt from a.c. magnetic susceptibility measurements, magnetisation measurements in high fields and as function of temperature at low and high temperatures (Faraday balance), Mössbauer spectra, microhardness, powder size and shape analysis etc. In fact, the measurement of any physical property that is sensitive enough to changes in the structure is appropriate. Several techniques should be combined for a full characterisation of changes occurring in the material during milling.

2.2. Anti-Site Disorder in B2 Compounds

2.2.1. Thermal disorder in B2 compounds

The intermediate phase β CuZn, crystallising in the B2 structure (Fig. 2), is a classical example of a compound that exhibits anti-site atomic disorder at higher temperatures and even an order–disorder transition at a certain temperature, called order–disorder temperature or critical

Fig. 2. The B2 or CsCl structure.

temperature (1015 K). Below the critical temperature two simple cubic interpenetrating sublattices can be distinguished in the structure, one (mainly) occupied by Cu atoms and one (mainly) occupied by Zn atoms. Above the critical temperature the long-range order is lost and Cu and Zn atoms are distributed in equal amounts over both sublattices. In fact, sublattices can no longer be distinguished. The degree of order of such a compound varies with temperature and there is some decrease already below the critical temperature. It can be measured, in principle, by X-ray diffraction or neutron diffraction.⁽²¹⁾ If the material is completely disordered, i.e. at higher temperatures, the B2 structure is identical to the body centred cubic structure and the diffraction pattern will be the one characteristic of the b.c.c. structure. However, in the ordered state at lower temperatures additional reflections, so-called superlattice reflections, appear. The reason for this can be understood from Fig. 2. In the disordered state, for example, the (100) reflection is absent, because the scattered waves from subsequent (100) planes cancel. In contrast, in the completely ordered structure the (100) planes are not occupied by just 'average' atoms, but the structure then consists of alternating layers consisting of Cu and Zn atoms. If the scattering factors of both species for X-rays or neutrons are sufficiently different, the scattered waves from subsequent planes will not cancel, but will give rise to a superlattice reflection. We call the alloy *AB* and distinguish between two sublattices α and β . We define the long-range-order (l.r.o.) parameter η as (we use η instead of the more usual S in order to avoid confusion with entropy S):

$$\eta = \frac{c_A^\alpha - c_A^\beta(\text{complete disorder})}{1 - c_A^\beta(\text{complete disorder})}, \quad (1)$$

where c_A^α is the fraction of the α sublattice sites occupied by A atoms. The l.r.o. parameter varies from $\eta = 1$ for complete order to $\eta = 0$ for complete disorder. It has been shown that the l.r.o. parameter can be derived from the intensity of a superlattice reflection relative to that of a fundamental line by:⁽²²⁾

$$\frac{\eta}{\eta_0} = \sqrt{\frac{(I_s/I_f)_\eta}{(I_s/I_f)_{\eta_0}}}, \quad (2)$$

where $(I_s/I_f)_\eta$ is the intensity of the superlattice reflection relative to the fundamental line at a value η of the l.r.o. parameter and η_0 is, for example, equal to unity, when starting from complete order. Equation (2) has been used to follow the disordering process by milling.

2.2.2. Mechanically induced disorder in B2 compounds

An early example of the application of X-ray diffraction to monitor the state of order during ball milling is an experiment on ordered AlRu.⁽²³⁾ Figure 3 shows the diffraction pattern of the as-prepared compound and after 32 h milling. The superlattice lines are those with an odd number for the sum of the Miller indices $h + k + l$. It is seen that all lines broaden as a result of strain and refinement of the crystallites in the powder particles. Analysis of the effect of strain and crystallite size on line broadening makes an evaluation of both phenomena possible. The final crystallite size was 7 nm and the strain as a function of reciprocal average crystallite size is given in Fig. 4. Strain increases rapidly in the early stage, passes through a maximum and then decreases. This decrease is interpreted as a decrease of dislocation density when the crystallites become very small. By use of eq. (2) the l.r.o. parameter could be calculated. This parameter is presented in Fig. 5, again as a function of reciprocal crystallite size. It decreases and reaches a constant value of about 0.7 for long milling periods. The material does not disorder completely. Still an appreciable part of the strain will reside in the disorder, because

Fig. 3. X-ray diffraction patterns of AlRu before milling and after milling for 32 h [23].

atoms on the 'wrong' sublattice are to be accommodated on lattice sites, where they do not fit. This gives rise to strain. The total heat evolved in a DSC experiment by samples, milled for long times, turned out to be about $6 \text{ kJ (mole of atoms)}^{-1}$. Apparently this amount of heat is stored in the material by milling. Let us attempt to explain this quantity. Energy is stored in various forms: strain by disorder and dislocations and further lattice defects, 'chemical' energy by disorder and grain boundary energy. In Appendix C it is shown how, based on Miedema's semi-empirical model, the enthalpy due to disordering can be estimated. This enthalpy turns out to be equal to about $9 \text{ kJ (mole of atoms)}^{-1}$. A usual estimate of grain boundary energy in nanocrystalline intermetallic compounds is $1\text{--}2 \text{ kJ (mole of atoms)}^{-1}$. Summing up these different contributions we arrive at a value that overestimates the magnitude of the total energy (heat evolved $6 \text{ kJ (mole of atoms)}^{-1}$), but yields at least the correct order of magnitude. Important conclusions from this experiment on AlRu are that ball milling introduces atomic disorder in intermetallic compounds and that the crystallite size is reduced to nanometre scale.

Fig. 4. Strain in AlRu as a function of reciprocal crystallite size. ⁽²³⁾

Fig. 5. Long-range-order parameter η of AlRu as a function of reciprocal crystallite size.⁽²³⁾

Experiments that raise some doubt on the unambiguous character of the information on the state of long-range order obtained by using eq. (1) have been conducted on the intermetallic compound CoZr.^(24,25) In both investigations^(24,25) it is concluded that, although the intensities of all X-ray lines decrease with milling time and all peaks broaden, the intensities of the superlattice reflections relative to the fundamental lines do not show a significant decrease within experimental error. An obvious conclusion is that there is no measurable decrease of the l.r.o. parameter. However, in the early stage of milling the magnetisation, measured at 4.2 K increases by about a factor of 3, as is shown in Fig. 6.⁽²⁵⁾ (The decrease upon further milling will be explained later.) The lattice parameter increases, whereas the crystallite size decreases (Fig. 7). Why does the magnetisation increase? In the completely ordered compound all Co atoms are surrounded by Zr atoms, which makes the magnetisation low. However, when Co atoms are substituted on the Zr sublattice, these anti-site Co atoms have Co atoms on the Co sublattice as nearest neighbours and this leads to an increase of the magnetisation.⁽²⁶⁾ The increase of the lattice parameter points in the same direction: by substituting both atomic species on the wrong sublattice, where the atoms do not fit, size mismatch will lead to an increase of the lattice parameter. (In following sections we will see more examples of this.)

Fig. 6. Magnetisation of CoZr at 4.2 K and 21 T as a function of milling time.⁽²⁵⁾

Fig. 7. Relative change of the lattice parameter (open squares and left-hand-side scale) and average crystallite size (filled squares and right-hand-side scale) of CoZr as a function of milling time.⁽²⁵⁾

Simultaneously the crystallite size decreases, and one could ask whether this could be the reason for the observed effects. However, both nanocrystalline pure iron prepared following Gleiter's method⁽²⁷⁾ and ball milled pure Ni⁽²⁸⁾ exhibit a *lower* magnetisation than normal polycrystalline material. Thus, on the one hand the intensity of superlattice reflections in X-ray diffraction does not indicate atomic disordering, whereas on the other hand lattice parameter measurements and magnetic measurements show all the characteristics of atomic disorder. Therefore, it seems that there is a discrepancy between the results based on eq. (1) and measurements of lattice parameter and magnetisation. Probably magnetic properties are more sensitive to, and a better probe for, disordering than relative intensities of low intensity and broadened X-ray lines. The conclusion is that also in CoZr a certain degree of disordering is generated by mechanical impact. Consequences for the amorphisation of this material after long milling times will be discussed later.

2.3. Anti-Site Disorder in $L1_2$ Compounds

There is extensive evidence that ball milling induces atomic (chemical) disorder in $L1_2$ compounds, reducing the long-range-order parameter even to a value of zero. However, such a large reduction of the l.r.o. parameter automatically means a phase transformation from the $L1_2$ structure to the f.c.c. structure. Therefore, the treatment of disordering in this class of compounds is postponed to Section 3.5, where phase transformations will be described.

2.4. Anti-Site Disorder in $A15$ Compounds

2.4.1. Introduction

Among the about 700 binary intermetallic compounds there are only a few compounds, such as CuZn and Cu₃Au, that exhibit in equilibrium an order-disorder transition before melting. Most intermetallics are assumed to be *completely* ordered up to the melting temperature. In the next section we report experiments for investigating the validity of this statement for compounds crystallising in the $A15$ (Cr₃Si) structure. Moreover, we discuss the effect of

irradiation by neutrons. Thereafter, we will use this knowledge to find out what occurs in these compounds during milling.

2.4.2. Thermal disorder and disorder by irradiation in A15 compounds

The A15 (Cr_3Si) structure is presented in Fig. 8. It is a cubic structure. Compounds crystallising in this structure were relatively intensively investigated, because among these compounds there are good superconductors, i.e. compounds with a relatively high superconducting transition temperature T_c and a high critical magnetic field. Examples are Nb_3Sn , Nb_3Au , V_3Ga and Nb_3Ge . The latter compound was known as the material with the highest superconducting transition temperature (T_c of 23 K) until the discovery of the so-called high T_c superconductors. Much effort was given to develop ingenious techniques for the production of wires from these materials for the construction of superconducting magnet coils. Superconducting magnets made from Nb_3Sn are commercially available. Let us inspect the structure of such a compound A_3B (Fig. 8) more closely. The B atoms form a b.c.c. structure, where the A atoms are located in the cube faces. The A atoms form long linear chains in three perpendicular directions. The chains do not intersect. Attention has been given to this chain structure in relation to the superconductivity of these compounds.⁽²⁹⁾ In this linear chain model the integrity of the chains is important for good superconducting properties.^(30,31) Indeed, if impurity atoms are substituted into these chains the superconducting transition temperature T_c degrades. In a similar way the substitution of B atoms in the A chains, i.e. atomic disorder, will affect superconductivity. This indicates that for these materials we have a physical property in hand for monitoring (small) degrees of disorder, namely the value of T_c . The only problem is that T_c cannot be measured, of course, at high temperature, so that we have to quench the material rapidly from high temperature, hoping to quench-in the state of order at this high temperature. To achieve this aim a special quenching device for quenching powders into water was developed.⁽³²⁾ Not bulk material but powders were quenched in order to obtain a homogeneous quenching rate throughout the material. At ambient temperature the material remains in the quenched-in high temperature state, because atomic mobility is too low to restore the state of order belonging to ambient temperature. Powders, quenched from different high temperatures to ambient temperature, were cooled down to near liquid helium temperature and the superconducting transition temperature was found by measuring the step in a.c. magnetic susceptibility at T_c , where the material transforms from weak (para)magnetic to diamagnetic. Figure 9 shows the decrease of T_c for Nb_3Au as function of quenching temperature,⁽³³⁾ revealing violation of the chain integrity by 'wrong' atoms (gold atoms in the niobium chains).

Let us attempt to interpret the result quantitatively starting from the concept of anti-site disorder. The 'chemical' (disordering) reaction can be written in self-explanatory notation as:

Fig. 8. The A15 or Cr_3Si structure.

Fig. 9. The superconducting transition temperature of Nb₃Au vs quenching temperature.⁽³³⁾

Let c_B^α be the fraction of B atoms on the α sublattice (similar notation for the other fractions), then the mass-action law for this reaction is in the (almost) completely ordered state:

$$\ln \frac{c_B^\alpha c_A^\beta}{c_A^\alpha c_B^\beta} = c - \frac{2W}{kT}, \quad (4)$$

where c is a constant containing entropy contributions, $2W$ is the disordering energy, i.e. the energy for transferring an A atom to the β -sublattice and a B atom to the α -sublattice, k is the Boltzmann constant and T is the absolute quenching temperature. For almost complete order $c_A^\alpha = 1$, $c_B^\beta = 1$, and evidently $c_A^\beta \propto c_B^\alpha$, so that:

$$\ln c_A^\beta = c' - \frac{W}{kT}. \quad (5)$$

Let us assume that in first-order T_c degrades proportionally to the number of wrong atoms in the chains, then:

$$\frac{\Delta T_c}{T_{c \max}} \propto c_B^\alpha, \quad (6)$$

where $T_{c \max}$ is the transition temperature for complete order. Then we expect:

$$\ln \frac{\Delta T_c}{T_{c \max}} = c'' - \frac{W}{kT}, \quad (7)$$

so that a plot of the logarithm of the relative decrease of T_c versus reciprocal quenching temperature should give a straight line. Figure 10 is such a plot. Clearly the agreement with the above theoretical considerations is good. The plot shows directly that the quenching procedure is adequate, otherwise deviations from the straight line behaviour would be manifest. From the slope of the line we find the disordering energy as 1.72 eV (pair of wrong atoms)⁻¹. Similar results were obtained before on V₃Ga.⁽³⁴⁾ A full review of literature is given by Flükiger.⁽³⁵⁾

So far we assumed tacitly the occurrence of anti-site disorder of both components. However, a different possibility that needs attention is the formation of vacancies. These may be formed on both sublattices in a ratio of 3:1 in order to keep the number of sublattice sites in the correct

Fig. 10. The logarithm of the relative degradation of the superconducting transition temperature of Nb_3Au vs reciprocal quenching temperature.⁽³³⁾

proportion. Alternatively, these may be formed on one of the sublattices only, in combination with anti-site defects on the other sublattice. In one of the following sections we will discuss a class of compounds that exhibits such disordering behaviour. However, in the A15 compounds studied, no detectable amount of vacancies was found.⁽³⁴⁾ The detection limit was 0.05%.

Also from irradiation experiments there is evidence for anti-site disorder in A15 compounds. The effect of irradiation on A15 superconductors was extensively studied because of the use of superconducting magnet coils in radiation fields. Föhnle⁽³⁶⁾ used a modified linear chain model for the description of the effect of anti-site disorder on T_c and applied this theory to evaluate neutron irradiation results. His result for niobium compounds is:

$$\frac{T_c(\eta)}{T_c(\eta=1)} = 0.17 + 0.83 \exp\{-7.78 \cdot (1 - \eta)\}, \quad (8)$$

where η is the long-range-order parameter defined by:

$$c_B^2 = \frac{1}{4} (1 - \eta). \quad (9)$$

Thus $\eta = 1$ means complete order and $\eta = 0$ means complete disorder. The long-range-order parameter as a function of neutron fluence Φ is given by the Aronin equation:⁽³⁷⁾

$$\eta = \eta_0 \exp(-K\Phi), \quad (10)$$

where K is a constant and η_0 is the starting order parameter ($\eta_0 = 1$). Using eqs (8) and (9), a universal curve can be constructed for the relative decrease of T_c for niobium-based A15 compounds as a function of neutron fluence. The theoretical curve and data points for four compounds are presented in Fig. 11. The agreement is good. Another indication of anti-site disorder by irradiation is the increase of the lattice parameter with neutron fluence. Big B atoms have to be accommodated on small α -sublattice sites and therefore such an increase is expected, whereas, as we will see for a different class of compounds, the formation of large amounts of vacancies would lead to a decrease of the lattice parameter.

A full survey of irradiation experiments is found in Flükiger.⁽³⁵⁾ It is not the aim of the present paper to describe quenching and irradiation experiments in length. In this context the most important conclusion is that 'completely ordered' compounds, such as the A15 compounds, show some disorder at higher temperatures and a high degree of disorder after irradiation and that we are able to monitor disorder in A15 compounds by means of the value of the superconducting transition temperature and an increase of the lattice parameter.

Fig. 11. Dependence of the superconducting transition temperature of some A15 Nb compounds on neutron fluence.

2.4.3. Mechanically induced disorder in A15 compounds

If, as a result of mechanical action, anti-site disorder is created in A15 compounds, an equation similar to the Aronin relation, eq. (8), can be derived. We start from the assumption by Bellon and Martin⁽³⁸⁾ that neighbouring *A* and *B* atoms on both sublattices are exchanged with a ballistic jump frequency Γ_b . Then we write for the change of the number of *A* atoms on the α -sublattice N_A^α per unit time:

$$\frac{dN_A^\alpha}{dt} = -N_A^\alpha z^\alpha c_B^\beta \Gamma_b + N_A^\beta z^\beta c_B^\alpha \Gamma_b, \quad (11)$$

where z^α is the number of nearest-neighbouring sites of an α sublattice site on the β sublattice ($z^\alpha = 4$ and $z^\beta = 12$ for the A15 structure). The first term in the right-hand side of the equation describes the loss of *A* atoms from the α -sublattice due to an exchange with neighbouring *B* atoms on the β sublattice. Here c_B^β is the probability in the Bragg–Williams approximation of finding a *B* atom on a specified nearest-neighbouring β position. The second term accounts in a similar way for the gain of *A* atoms on the α -sublattice. It is not difficult to demonstrate that eq. (11) leads in terms of the long-range-order parameter η to:

$$\frac{d\eta}{dt} = -16\Gamma_b\eta, \quad (12)$$

with solution:

$$\eta = \eta_0 \exp(-16\Gamma_b t). \quad (13)$$

This is the analogue of the Aronin equation. One could argue that most probably the jumping of atoms will take place via vacancies (*V*). However, this leads to the same eq. (11) via:

$$\frac{dN_A^\alpha}{dt} = -N_A^\alpha z^\alpha c_V^\beta W_{AV}^{\alpha\beta} + N_A^\beta z^\beta c_V^\alpha W_{AV}^{\beta\alpha}, \quad (14)$$

where $W_{AV}^{\alpha\beta}$ is the exchange frequency of A^α and V^β . In detailed balance $c_V^\beta W_{AV}^{\alpha\beta} = c_V^\alpha W_{AV}^{\beta\alpha} = \Gamma_b$. In terms of η eq. (14) leads also to eq. (12). In this derivation it was assumed that the temperature

is low enough to neglect thermal mobility of atoms. Only ballistic mobility is operative. The problem of combined thermal and ballistic mobility is worked out in Bellon and Martin⁽³⁸⁾ and in Appendix D.

By means of eqs (8) and (13) we obtain the relation between the superconducting transition temperature and milling time as:

$$Y \equiv \ln \left[\ln \left\{ \frac{T_c(t)}{T_c(0)} - 0.17 \right\} + 7.966 \right] - 2.051 = -16\Gamma_b t, \quad (15)$$

so that the rather complex function Y should be a linear function of time.

In order to check the validity of eq. (15), and thereby the occurrence of anti-site disorder of both components due to milling, the following experiments were carried out on the A15 compounds Nb_3Sn and Nb_3Au .^(39,40) Since milling time in a ball milling experiment is a somewhat tricky quantity, because milling efficiency may depend on the amount of sample, all experiments of different milling periods were started from fresh alloy powder (0.5 grams). After milling, the low temperature a.c. magnetic susceptibility was measured. When a sample goes from the normal paramagnetic to the superconducting diamagnetic state a dramatic change in susceptibility is observed. In this way it was possible to assess the superconducting transition temperature as a function of milling period. Figure 12 shows a.c. susceptibility curves for Nb_3Sn as function of temperature after various milling periods. Up to milling periods of about 60 min two transition temperatures were observed, namely 18 K, the T_c of the starting material, and a lower T_c . By using TEM it was checked that, during those milling times, the sample contained the original unmilled powder, which consisted of single or bicrystals, and the processed powder particles, consisting of very small crystallites. After 60 min of milling the curves in Fig. 12 indicate a homogeneous superconductor with a gradual decrease of T_c with milling time. Similar results were obtained for Nb_3Au . The function Y from eq. (15) for the latter material is plotted in Fig. 13. A similar behaviour was found for Nb_3Sn . Figure 13 shows that a linear behaviour of Y as function of t was obtained as expected, if anti-site disorder of both components occurs. Moreover, from the slope of the line the ballistic jump frequency Γ_b is obtained as $5 \cdot 10^{-7} \text{ s}^{-1}$ for Nb_3Sn and as $4.3 \cdot 10^{-7} \text{ s}^{-1}$ for Nb_3Au . It turns out that the ballistic jump frequencies are very

Fig. 12. Temperature dependence of the a.c. magnetic susceptibility of Nb_3Sn after various milling periods.⁽³⁹⁾

Fig. 13. Dependence of Y in eq. (15) on milling time for Nb_3Au .⁽⁴⁰⁾

similar in value for both compounds. Figure 14 gives the long-range-order parameter for Nb_3Au obtained from eq. (8). The l.r.o. parameter is much lower after prolonged periods of milling than can be obtained by quenching from high temperatures. Another indication for anti-site disorder is the increase of the lattice parameter such as is also found in irradiation experiments. The increase in the lattice parameter due to the accommodation of big Sn atoms on small Nb sites in Nb_3Sn is given in Fig. 15. A similar behaviour for Nb_3Au is presented in Fig. 16. The increase of the lattice parameter in Nb_3Sn is much larger than in Nb_3Au due to the fact that Nb and Au atoms are more similar in size than Nb and Sn atoms.

It is imaginable that the degradation of T_c could be the result of, for example, iron contamination during milling. It is well-known that the superconducting transition temperature is very sensitive to ferromagnetic impurities. Therefore, after ball milling for 8 h the Nb_3Sn sample was annealed at 1000°C for various periods. The result is given in Fig. 17. After 24 h of annealing, T_c is completely restored, which would not have been possible if the degradation had been the result of contamination. From these results it is also clear that by appropriate milling and annealing procedures, all T_c s between 4.2 and 18 K can be obtained in this material.

Fig. 14. Dependence of the long-range-order parameter η of Nb_3Au on milling time as calculated from eq. (8).⁽⁴⁰⁾

Fig. 15. The relative increase of the lattice parameter of Nb₃Sn as a function of milling time.⁽³⁹⁾

A result that could not be explained was the dependence of T_c on very small magnetic measuring fields (in the order of tenths of a mT). These measuring fields are many orders of magnitude smaller than critical fields. Most probably the effect has to do with the shape and size of the nanocrystals in the milled powder particles. Because of this field dependence different measuring fields were applied (0.001–0.6 mT) and the result of Fig. 13 was obtained by extrapolation to zero field.

2.5. Triple-Defect Disorder in Group VIII–Group IIIA Compounds Crystallising in the B2 Structure

2.5.1. Introduction

In the previous section it was shown that in A15 compounds (A₃B) both by high temperature and irradiation on the one hand and by ball milling on the other hand anti-site disorder is introduced, i.e. substitution of both atomic species on the ‘wrong’ sublattices. Moreover, it

Fig. 16. The relative increase of the lattice parameter of Nb₃Au as a function of milling time.⁽⁴⁰⁾

Fig. 17. The temperature dependence of the a.c. susceptibility of Nb₃Sn, milled for 8 h and annealed at 1000°C for various periods.⁽³⁹⁾

turned out that the degree of disorder that could be introduced by irradiation and mechanical milling is much higher than can be generated by high temperatures. It is remarkable that the material disorders by all three techniques in the same way. Apparently a type of disorder is generated that is characteristic of the particular class of compounds. In order to investigate the validity of the latter statement more generally experiments were carried out on equiatomic VIII–IIIA compounds crystallising in the B2 structure (Fig. 2), such as CoGa and CoAl. From previous experiments it was known that at high temperatures these materials exhibit a special type of disorder, so-called triple-defect disorder, in which the transition metal atoms are able to substitute on the ‘wrong’ sublattice, whereas the other component remains on its own sublattice. This gives rise to the formation of anti-site transition metal atoms combined with the formation of vacancies on the transition metal sublattice in a ratio of 1:2. Such a combination of one anti-site atom with two vacancies is called a triple defect. However, the three defects are not necessarily in nearest-neighbour configuration, but may be distributed rather randomly over the corresponding sublattices. In A15 compounds we were able to monitor the degree of disorder by the degradation of the superconducting transition temperature and the increase of the lattice parameter. In the present compounds magnetic properties, macroscopic volume and lattice parameter are influenced by the disorder, which makes it possible to monitor the degree of disorder by measuring these quantities. As in the case of A15 compounds, we start with a brief survey of the effect of high temperature on disorder and after that we discuss results of mechanical milling.

2.5.2. Thermal disorder in VIII–IIIA compounds

The special type of thermal disorder in VIII–IIIA compounds with the B2 structure was first established by Wasilewski *et al.*⁽⁴¹⁾ for NiGa. A detailed investigation of triple-defect disorder was undertaken by Van Ommen *et al.*⁽⁴²⁾ on CoGa. First macroscopic density and lattice parameter were measured at room temperature on a sample after long anneals at 550°C. This temperature is the lowest temperature at which observable changes in the state of order take place. Below this temperature, kinetics are too slow to establish thermodynamic equilibrium. On the basis of the lattice parameter the so-called X-ray density ρ_x can be calculated by assuming occupancy of all lattice sites by atoms. If the lattice is not fully occupied by atoms, this quantity

is different from the 'real' macroscopic density ρ . Then vacancies 'blow up' the sample. It is not difficult to demonstrate that the vacancy fraction is given by:

$$c_v = \frac{\rho_x - \rho}{\rho} . \quad (16)$$

From such measurements it emerged that, after the annealing procedure at 550°C, the 50 at.% sample still contains 2.04% of vacancies. Apparently this is the vacancy content corresponding to 550°C. The mobility at lower temperature is too low to establish equilibrium.

The increase of vacancy content as a function of temperature can be found from a measurement of the length expansion and increase of the lattice parameter with temperature. The result of such measurements is given in Fig. 18. Below 550°C 'nothing' happens. i.e. the expansion of the sample length is equal to the expansion of the lattice parameter and is the result of anharmonicity of lattice vibrations. However, at a somewhat higher temperature both curves go apart after long periods of waiting (typically some tens of hours). Vacancies have become mobile and are able to diffuse into the sample from surfaces, grain boundaries and dislocations.

Fig. 18. Relative thermal expansion of lattice parameter and length of a stoichiometric CoGa sample.⁽⁴²⁾

Fig. 19. Vacancy fraction of stoichiometric CoGa as a function of temperature. Left-hand scale: relative to the number of sublattice sites. Right-hand scale: relative to the total number of atoms.⁽⁴²⁾

This gives an additional increase in length, whereas the increase of the lattice parameter is less than the extrapolated pure thermal expansion because of relaxation around the formed vacancies. The higher the temperature the faster the equilibrium is established. It is easy to show that the increase of the vacancy fraction is approximately given by (for full details see van Ommen *et al.*⁽⁴²⁾):

$$\Delta c_v(T) = 3 \left\{ \frac{\Delta L(T)}{L} - \frac{\Delta a(T)}{a} \right\}, \quad (17)$$

where L is the sample length and a is the lattice parameter. In this way the vacancy fraction is obtained as a function of temperature, taking into account the vacancy fraction that was already present in the sample annealed at 550°C. The vacancy fraction as a function of T in the 50 at.% sample is presented in Fig. 19. The amount of vacancies is huge compared to pure metals, where a typical vacancy fraction is only 0.0001–0.001 at the melting point. The reason is the special type of disorder. A two-dimensional schematic of this type of disorder is given in Fig. 20, where anti-site Co atoms combined with vacancies on the Co-sublattice are drawn.

Let us explain the occurrence of one anti-site Co atom combined with the formation of *two* vacancies. Let both sublattices contain N lattice sites in the completely ordered state (Fig. 20, left side). One Co atom is now transferred to the Ga sublattice. Then the Ga sublattice contains $N + 1$ sites, the Co sublattice N sites, among which one vacancy. However, in the B2 structure both sublattices should consist of an equal number of lattice sites. Therefore an additional vacant site is created on the Co sublattice, which leads to one anti-site Co atom combined with

Fig. 20. Two-dimensional schematic of triple-defect disorder. Left-hand figure: complete order. Right-hand figure: triple-defect disorder, i.e. 'black' atoms on the 'white' sublattice and vacancies on the 'black' sublattice.

the formation of two vacancies. A somewhat different way to visualise the situation is the initial formation of a double vacancy, one on the Co sublattice and one on the Ga sublattice, and a subsequent dissociation of the divacancy by a jump of a Co atom into the vacancy on the Ga sublattice.

It is also possible to quench a sample rapidly from high temperature in order to freeze-in the high temperature configuration. A typical quenching rate is $5 \cdot 10^4 \text{ Ks}^{-1}$ and for ensuring homogeneous cooling throughout the sample small powder particles are quenched. A measurement on such a sample reveals a decrease of the lattice parameter as a function of quenching temperature due to relaxation (Fig. 21)⁽⁴³⁾ and an increase of the magnetisation (Fig. 22).⁽⁴³⁾ That the magnetisation is increasing with disorder is explained as follows. In the completely ordered state (Fig. 20, left side) a Co atom is completely surrounded by Ga atoms and therefore loses its ferromagnetic character. In contrast, a Co atom on the 'wrong' sublattice is surrounded by nearest-neighbour Co atoms, in this way forming a small cluster of cobalt metal. Therefore, anti-site Co atoms bear a magnetic moment and behave as ferromagnetic centres. By means of these changed characteristics we have a tool in hand to monitor triple-defect disorder, if such a type of disorder were to be generated by milling. Then we expect a decrease of the lattice parameter and an increase of the magnetisation with milling time. It is interesting to note that in contrast to A15 compounds, where T_c decreases and the lattice parameter increases, in the present materials an increase in the magnetisation and a decrease in the lattice parameter is predicted.

Fig. 21. Lattice parameter of CoGa vs quenching temperature.⁽⁴³⁾

Fig. 22. Magnetisation of CoGa at 4.2 K in a field of 14 T vs quenching temperature.⁽⁴³⁾

2.5.3. Mechanically induced disorder in VIII–IIIA compounds

Equiatomic CoGa was milled for up to 32 h.⁽⁴⁴⁾ X-ray diffraction (Fig. 23) shows that during milling the weak superlattice reflections [100] and [210] disappear, but that the material remains in the b.c.c.-like structure. Figure 24 presents the increase of the magnetisation in a field of 14 T with milling time and Fig. 25 the decrease of the lattice parameter. From these figures it is clear that anti-site Co atoms and vacancies are formed as expected. From a comparison of the increase of the magnetisation and the decrease of the lattice parameter it is possible to find whether these defects are formed as real triple defects, i.e. in a ratio of 1:2. From measurements of the magnetisation in off-stoichiometric as-prepared Co-rich samples, in which the composition determines the number of anti-site atoms, it was found that the magnetic moment per anti-site atom in a field of 14 T is $1.9 \mu_B$. Through this knowledge we obtain from the magnetisation after 32 h of milling of CoGa (50 at.%) a fraction of about 4% of Co anti-site

Fig. 23. X-ray diffraction patterns of CoGa milled for various periods.⁽⁴⁴⁾

Fig. 24. Magnetisation of CoGa at 4.2 K in a field of 14 T as a function of milling period.⁽⁴⁴⁾

atoms, which should correspond to 8% of vacancies. The relation between the number of vacancies and the lattice parameter is known from experiments by Edelin⁽⁴⁵⁾ as:

$$a = a_0 \left\{ 1 + \frac{1}{3} (\Omega_v - 1) c_v + \frac{1}{3} (\Omega_{as} - 1) c_{as} \right\}, \quad (18)$$

where a_0 is the lattice parameter without defects, Ω_v the vacancy volume relative to the atomic volume ($=0.69$), Ω_{as} the volume of an anti-site atom relative to the atomic volume ($=0.89$) and where the c s are the fractions of the corresponding defects. When the increase of the vacancy fraction, derived from the magnetic measurements (8%), is substituted into this equation, we arrive at an expected decrease of the lattice parameter by 0.7%. This is in excellent agreement with the measured decrease (Fig. 25). This clearly proves that during ball milling triple defects are formed in CoGa.

To check these results on a similar compound CoAl was also milled.⁽⁴⁶⁾ An increase of the magnetisation and a decrease of the lattice parameter were also found. From the magnetisation a fraction of 1.9% of anti-site Co atoms was derived after milling for 30 h and, therefore, a fraction of 3.8% of vacancies is anticipated. An equation similar to eq. (18) leads to an expected change in the lattice parameter of -0.18% , which is in good agreement with the measured

Fig. 25. Relative change of the lattice parameter of CoGa as a function of milling period.⁽⁴⁴⁾

value. The fact that the decrease of the lattice parameter in CoAl is smaller than in CoGa can be understood from the consideration that Co and Al are closer in atomic size than Co and Ga.

Other compounds that exhibit triple-defect disorder at higher temperatures are NiGa, NiAl and probably PdIn. In NiAl no measurable degree of disorder could be detected by X-ray techniques even after long milling times.⁽⁴⁷⁾ Therefore, the behaviour of this compound could be similar to CoGa and CoAl.

The type of disorder in, for example, FeAl is not really known. Gialanella⁽⁴⁸⁾ milled a Fe(60 at.%)Al(40 at.%) alloy crystallising in the B2 structure. During milling the superlattice reflections disappeared, indicating disordering. However, in contrast to CoGa and CoAl, the lattice parameter *increased* with milling time. This strongly points in the direction of 'normal' anti-site disorder in this compound, which could mean that not all VIII–IIIA compounds crystallising in the B2 structure disorder in the same way. It is interesting to note the difference in phase diagram of CoGa and CoAl on the one hand and FeAl on the other hand. From the phase diagram it could be concluded that FeAl disorders rather easily to the α -Fe structure. Moreover, with a composition of 60 at.% Fe the studied compound is far from stoichiometry, which may also explain the difference with stoichiometric VIII–IIIA compounds.

2.6. Atomic Disorder in B8 Compounds

2.6.1. Introduction

It was shown in previous sections that by ball milling anti-site disorder is generated in the A15 structure and triple-defect disorder in a number of compounds with the B2 structure. The disordering was monitored in A15 compounds by following the degradation of the superconducting transition temperature and in B2 compounds by measuring magnetic properties and the change of the lattice parameter. The type of atomic disorder, obtained after milling, turned out to be similar to that generated by irradiation or at high temperature and is apparently characteristic of the respective compounds. In this section we present some recent results on ball milling of intermetallic compounds with the B8₂-hexagonal and with a strongly related orthorhombic structure. It will be shown that in these compounds even a third type of disorder is created by milling. The B8 structure is presented in Fig. 26. The large filled circles represent the lattice positions occupied by non-transition metal atoms, whereas the small open

Fig. 26. B8 structure.

and filled circles represent two different types of interstices: octahedral (I) and tetrahedral (II). Both positions can be occupied by transition metal atoms. The octahedral sites are always fully occupied, whereas the tetrahedral sites are filled depending on the x value in the formula $T_{1+x}Z$, where T stands for transition metal, Z for non-transition metal, and where $0 \leq x \leq 1$. If x is equal to zero, all tetrahedral sites are vacant ($B8_1$ or NiAs structure), whereas for x equal to unity all tetrahedral sites are occupied ($B8_2$ or Ni_2In structure). If $x > 0$ we call the compound $B8_2$ type. For compounds with formula $T_{1.5}Z$ (or T_3Z_2 , which is the same) half of the II sites are filled.

The magnetisation of $B8$ type compounds can be described by:

$$M = \frac{1}{1+x} (1 \cdot M_{T_I} \pm x \cdot M_{T_{II}}), \quad (19)$$

where M_{T_I} is the spin moment per T (transition metal) atom on I sites and $M_{T_{II}}$ is the spin moment per T atom on II sites. The factors 1 and x account for the occupancies of the respective sites. The plus sign on the right-hand side is valid for *ferro*-magnetic compounds, whereas the minus sign holds for *ferri*-magnetic compounds. This means that in ferro-magnetic systems the spin moment of transition metal atoms on I sites is parallel to that on II sites. In contrast, in ferri-magnetic systems the respective spin moments are antiparallel. Furthermore, it is known by neutron diffraction that in $B8_2$ -hexagonal Fe-Ge, Mn-Ge⁽⁴⁹⁾ and in closely related orthorhombic compounds⁽⁵⁰⁾ the magnetic moment of T_{II} atoms is always larger than that of T_I atoms. Numerical values are available for $B8_2$ -hexagonal $Fe_{1+x}Ge$, which is a ferromagnet. It was reported⁽⁵¹⁾ that when x increases from 0.5 to 0.85 the ferromagnetic moment increases from $1.46 \mu_B$ to $1.70 \mu_B$ per Fe atom and the Curie temperature from 430 K to 500 K. From this it is deduced that the moment of Fe atoms on I sites is equal to $0.8 \mu_B$ and on II sites to $2.8 \mu_B$. The underlying cause for the difference is that the interatomic distances and the neighbourhood of atoms on I sites are different from those on II sites. For clearness a schematic of an analogous two-dimensional structure is given in Fig. 27, in which both the different interstices are indicated and in which the magnetic moments are drawn as arrows for both ferro- and ferrimagnetism. From the above it is clear that measurements of changes of magnetic properties after ball milling provide a tool for monitoring changes in occupancies of the various sites.

2.6.2. Mechanically induced disorder in $B8_2$ compounds with composition $T_{1.5}Z$

In this section we restrict ourselves to the compounds Fe_3Ge_2 and Mn-Sn in the composition Mn_3Sn_2 . (In Section 3 we will see that the orthorhombic phases of Ni_3Sn_2 and Co_3Sn_2 disorder in the same way before transforming to the $B8_2$ structure. Both of the latter compounds crystallise in the so-called Ni_3Sn_2 structure, which is closely related to the $B8_2$ structure, only the atoms are shifted somewhat to form an orthorhombic structure. We will come to this later.) Although both Fe_3Ge_2 and Mn_3Sn_2 crystallise in the same $B8_2$ structure, there is a striking difference in their magnetic behaviour. Fe_3Ge_2 is a ferromagnet,⁽⁵¹⁾ corresponding to the upper part of Fig. 27, whereas Mn_3Sn_2 is a ferrimagnet,^(52,53) corresponding to the lower part of Fig. 27. X-ray diffraction patterns, taken after various periods of milling, show that, although all peaks decrease in intensity and broaden and some peaks even become invisible, the compounds remain in the same structure. The example of Mn_3Sn_2 is given in Fig. 28.^(54,55) After about 60 h of milling no further changes are observed. The results for Fe_3Ge_2 are essentially the same.^(55,56) In contrast, the changes in magnetisation as a function of milling time are opposite for both compounds. The magnetisation in ferromagnetic Fe_3Ge_2 *increases*, whereas it *decreases* in ferrimagnetic Mn_3Sn_2 . These results are presented in Fig. 29. The explanation is obvious.

Fig. 27. Two-dimensional schematic of the B8 structure. In a compound T_1Z_2 (T = transition metal, Z = non-transition element) the Z sublattice (filled circles) is occupied by Z atoms. There are two T sublattices. One T sublattice (filled squares) is fully occupied, the other sublattice (open squares) only half. T atoms on the fully occupied sublattice bear a smaller magnetic moment than those on the half-occupied sublattice. The upper figure gives the situation for ferromagnetic coupling, the lower figure for ferrimagnetic coupling (note the arrows).

Transition metal atoms are transferred during milling from the fully occupied T_I sites to empty T_{II} sites. We called this new type of disordering “redistribution of transition metal atoms over both interstices”. It is remarkable that, in contrast to the A15 compounds and the B2 compounds discussed before, the special type of disorder could not be frozen-in by quenching B8 compounds from high temperature. Apparently, ball milling is a unique technique for bringing these materials into this special disordered state. If we adopt eq. (19) for the present situation:

$$M = \frac{2}{3} \left\{ (1 - c)M_{T_I} \pm \left(\frac{1}{2} + c \right) M_{T_{II}} \right\}, \quad (20)$$

where c is the fraction of T atoms transferred, we deduce a maximum transfer of 5.3% of Fe atoms from I to II sites in Fe_3Ge_2 .⁽⁵⁶⁾ We can do so because the magnetic moments on both lattice sites are known. The fraction c as a function of milling time is shown in Fig. 30.

A number of further measurements were performed on both compounds.⁽⁵⁷⁾ All measured quantities saturate as a function of milling time: for Fe_3Ge_2 typically after 120 h and for Mn_3Sn_2 typically after 60 h. All quantities varied rapidly in the beginning and levelled-off for longer times. Using the Scherrer equation, after correction for strains, the final crystallite size turned out to be equal to 14 nm for Fe_3Ge_2 and 6 nm for Mn_3Sn_2 . The total heat released in DSC was 4 kJ (mole of atoms)⁻¹ for both compounds. In particular, in Mn_3Sn_2 two or even three different

Fig. 28. X-ray diffraction patterns of $\text{Mn}_{1.5}\text{Sn}$ after various periods of milling.⁽⁵⁴⁾

peaks could be distinguished. By comparison to X-ray patterns after the occurrence of a peak in DSC, these peaks could be identified with some confidence as being due to release of strain (and perhaps short-range re-ordering), long-range re-ordering and crystallite growth, respectively. One of the activation energies, measured by means of Kissinger plots, was nearly equal for both compounds, namely about 102 kJ mole^{-1} . This is about half the activation energy for self-diffusion of T atoms in B8 compounds, measured by radioactive tracers.⁽⁵⁸⁾ It could correspond to the 'easy' jumps from II sites to I sites in the diffusion process, which

Fig. 29. Magnetisation at 4.2 K and in a field of 21 T for $\text{Mn}_{1.5}\text{Sn}$ (filled squares and left-hand-side scale) and for $\text{Fe}_{1.5}\text{Ge}$ (open squares and right-hand-side scale).⁽⁵⁴⁾

Fig. 30. The fraction c of Fe atoms transferred from I to II sites in Fe_3Ge_2 versus milling period⁽⁵⁶⁾

are typically re-ordering jumps. The tracer-diffusion activation energy should then correspond to 'difficult' I to II jumps. Such arguments suggest a difference in energy between atoms on I and on II sites of about $100 \text{ kJ (mole of atoms)}^{-1}$. This high value would explain the undetectable content of thermal T atoms on II sites after quenching.

In both compounds the unit cell volume exhibited a final increase of about 1.2%. An increase of unit cell volume by atoms on 'wrong' sites seems plausible. Moreover, in the Mn–Sn compound the Curie temperature decreased during milling, which gives a deeper insight into the quantities that determine magnetic behaviour.⁽⁵⁷⁾ The expected increase of the Curie temperature in Fe_3Ge_2 could not be measured, because the Curie temperature is in the temperature range where the compound re-orders.

2.6.3. Mechanically induced disorder in $B8_2$ compounds with composition T_2Z and related orthorhombic phases

In the previous section we reported results on $B8$ compounds with one of the T sublattices half-occupied. We saw that ball milling introduces a redistribution of T atoms over both T sublattices (interstices). One could ask now what would happen in similar compounds, in which all interstices are occupied, i.e. $B8_2$ compounds with formula T_2Z (the so-called Ni_2In structure). In these compounds all T positions are occupied, so that a redistribution of atoms over the interstices is not possible. As a first example Co_2Ge was studied.⁽⁵⁹⁾ This compound crystallises at higher temperature in the $B8_2$ structure of the type Ni_2In ($\beta\text{-Co}_2\text{Ge}$) and at lower temperature in a closely related, but orthorhombic structure, the so-called Co_2Si structure ($\alpha\text{-Co}_2\text{Ge}$). We call $\alpha\text{-Co}_2\text{Ge}$ the low temperature phase (LTP) and $\beta\text{-Co}_2\text{Ge}$ the high temperature phase (HTP). We discuss here the early stages of milling and postpone the aspects of amorphisation to the second part of this review.

The HTP was prepared by quenching from above the phase transition temperature (cooling rate about $5 \cdot 10^4 \text{ K s}^{-1}$) and also by melt spinning (cooling rate about 10^7 K s^{-1}). It was verified that both methods of preparation result in the same compound with the same properties. After milling the HTP for 5.7 h, X-ray diffraction shows the same peaks as the as-prepared sample, albeit with reduced intensities. Apparently the crystal structure is preserved after such a short milling period. This is confirmed by DSC. The results are shown in Fig. 31. The HTP is a metastable phase and transforms to the LTP by an exothermic heat effect at 560 K.

Fig. 31. DSC scan of the as-prepared high temperature phase Co_2Ge and after a short milling time.⁽⁵⁹⁾

Subsequently, the LTP–HTP transition takes place at 670 K. This is manifest from the endothermic heat effect at this temperature. The scan for the 5.7 h milled sample exhibits the same features. Still the magnetisation (at 4.2 K and 21 T) almost doubles during this period, namely from $0.077 \mu_{\text{B}}/\text{Co}$ atom to $0.146 \mu_{\text{B}}/\text{Co}$ atom and the ferromagnetic Curie temperature, measured by means of Arrott plots, increases even more significantly, namely from 5 to 22.4 K. Apparently the Co–Co distances and the neighbourhood of Co atoms do change during milling. A natural explanation is that anti-site disorder is generated between Co atoms on interstices and Ge atoms on the Ge sublattice. Apparently ‘normal’ anti-site disorder is created in this B8_2 compound. This is in contrast to the compounds from the previous section. The reason must be the full occupancy of the T sublattice in the present compound, in contrast to the partially empty sublattice in compounds with the formula $T_{1.5}\text{Z}$. We already mentioned that Co_2Ge amorphises after longer milling periods, whereas Fe_3Ge_2 and Mn_3Sn_2 do not. This is once more an indication of the different behaviour of these seemingly similar types of compounds.

LTP Co_2Ge was also milled. Although the structure is orthorhombic, it is very similar to the high temperature phase. Compared to the HTP some extra peaks are visible in X-ray diffraction. Up until periods of milling of about 60 h the crystalline structure is still preserved and in DSC the transformation from LTP to HTP remains visible. However, changes in atomic order are manifest from changes in the magnetic behaviour. The magnetic moment increases from $0.113 \mu_{\text{B}}/\text{Co}$ atom for the as-prepared LTP to $0.218 \mu_{\text{B}}/\text{Co}$ atom (at 4.2 K and 21 T) after 60 h of milling. Thus in the LTP we observe also a doubling of the magnetic moment before amorphisation. The Curie temperature changes in this period from 46 to 84 K. Again an obvious explanation is mechanically induced anti-site disorder.

Co_2Si is the prototype of the orthorhombic structure of LTP Co_2Ge . In order to study the behaviour of this compound the material was milled for long periods.⁽⁶⁰⁾ Even for milling periods over 600 h, the magnetisation still increased and the material did not amorphise. The magnetisation (at 4.2 K and 21 T) increases from $0.06 \mu_{\text{B}}/\text{Co}$ atom for as-prepared material to $0.6 \mu_{\text{B}}/\text{Co}$ atom for milling periods of 629 h. X-ray diffraction patterns revealed the same crystalline structure throughout the processing. Obviously we are once more dealing with anti-site disorder in this compound.

So far we have not given too much attention to the results of DSC measurements in relation to the recovered X-ray patterns after DSC. However, Co_2Si offers a beautiful example of what

Fig. 32. Typical DSC scans of Co_2Si after milling for various periods.⁽⁶⁰⁾

is observed, sometimes less clearly, in other compounds. Thus, let us discuss the DSC results in more detail. Figure 32 presents DSC curves after various periods of milling. In particular, the curve labelled 120 h exhibits three clear peaks. Two of the peaks become particularly pronounced after 629 h of milling. Various badges of this sample were heated in DSC to different temperatures and subsequently quenched in the DSC as rapidly as possible. A combination of the DSC pattern and the X-ray patterns reveals the origin of the various heat effects. In Fig. 33 the X-ray patterns are presented. The bottom curve is the as-milled material. The curve labelled 510 K was taken after heating to 510 K, the end of the first exothermic peak near $2\theta = 45^\circ$. The first exothermic heat effect corresponds to defect annihilation and strain release. After heating to 650 K, extra diffraction peaks appear, such as the (101), (130), (420) and (312) lines. Although the crystallite size, derived with the aid of the Scherrer equation, seems also to increase somewhat (from 8 to 14 nm), the main effect is due to atomic re-ordering. Finally, after the third exothermic peak (X-ray pattern labelled 900 K), the average crystallite size has grown to about 50 nm, so that the third exothermic peak is seen to be due to crystallite growth.

The Scherrer equation was also used to evaluate crystallite size as a function of milling time. Figure 34 is typical for many intermetallics: a rapid decrease in the early stage of milling and a tendency to saturate on a nanometre-size scale after relatively short periods. As we saw, Co_2Si is an example of a material in which, even for very long milling periods, characteristics—such as high field magnetisation and total heat release in DSC—are still on the increase, whereas the crystallite size becomes constant during the long milling period. An obvious conclusion is that changes of crystallite size are *not* the main cause of the modification of the material. Rather this cause has to be sought in continuing atomic disordering.

Fig. 33. X-ray diffraction patterns of Co_2Si after milling for 629 h after heating to 510 K, 650 K and 900 K in the DSC and subsequent rapid quenching to room temperature.⁽⁶⁰⁾

2.7. Discussion

So far three different types of atomic disorder have been observed when intermetallic compounds are subjected to a continuous mechanical impact in a ball mill. Anti-site disorder of both components was found in the majority of compounds. In a number of compounds different types of disorder were generated. A characteristic of both these types of disorder is that one of the components remains on its own sublattice, in this way preserving the frame of the original crystal structure. This is found in a number of VIII–IIIA compounds with the B2

Fig. 34. The average crystallite size of Co_2Si as a function of milling time.⁽⁶⁰⁾

structure (triple-defect disorder) and in T_3Z_2 compounds with the $B8_2$ structure (redistribution of T atoms over available sublattice sites). In the next section it will be shown that the type of disorder has a profound influence on the behaviour of the compound for long milling times. Since both the amorphous state and the solid solution are inherently atomically disordered, the generation of anti-site disorder of both components is likely to be a prerequisite for transformations to those disordered states. Phase transformations are the subject of the next section.

A second point that needs attention is the evaluation of the long-range-order parameter from the intensity of superlattice reflections in X-ray diffraction, as applied by many authors. Are these results really unambiguous? In order to discuss this question let us inspect the case of CoZr. Two groups of investigators agree that in this material there is scarcely any decrease of relative intensities of superlattice lines, which would mean that the material remains essentially completely ordered^(24,25) before amorphisation takes place after longer milling times. However, it is observed⁽²⁵⁾ that in the early stage of milling the magnetisation increases by a factor of more than three! This, as discussed in Section 2.2.2, strongly points in the direction of atomic disorder as does the observed increase of the lattice parameter. Thus, although from intensities of superlattice reflections there does not seem to be disorder, disorder is certainly present in the compound after milling. A contrasting example is CoGa.⁽²³⁾ From Fig. 23 it is clear that after 32 h of milling the intensity of the superlattice lines has disappeared. However, measurements of the lattice parameter and magnetisation prove that the Ga atoms remain on their own sublattice, while only 4% of Co atoms have been substituted onto the Ga sublattice. The material is then definitely still in the ordered B2 structure. These two examples throw some doubt on the sensitivity of intensity of superlattice reflections for the evaluation of the precise degree of long-range order. Could these effects have anything to do with the nanocrystalline character of the material or could the crystallites exhibit preferential orientations in the powder particles? The reason is not clear.

A further interesting question is the relation between nanocrystallinity and physical properties. Figure 34 is typical for the development of nanocrystallinity during milling.⁽⁶⁰⁾ Nanocrystallinity clearly develops in the early stage of milling and the crystallite size saturates for longer milling periods. Still, in the example of Co_2Si (Section 2.6.3), heat content, measured by DSC, and magnetisation are increasing long after the crystallite size has saturated. Obviously the development of nanocrystallinity is *not* the main cause of changes of material properties during long milling. This is consistent with the implicit conclusion from Section 2 that the majority of changes in properties can be explained by changes in the bulk of the material (atomic disorder) rather than by special properties of atoms in grain boundaries. Admittedly, all starting materials discussed in Section 2 are intermetallic compounds with inherently a negative heat of mixing and are in the stage of milling, where the original crystal structure is still maintained. For example, in immiscible systems one component could segregate strongly in the grain boundaries, which could lead to drastic changes in properties.

Let us now proceed to the development of strain during milling. In this context Fig. 4 is interesting.⁽²³⁾ From this figure it is clear that initially strain develops together with nanocrystallinity, but then, after some 'critical' size, strain decreases. This suggests the absorption of dislocations by grain boundaries. A substantial part of the remaining strain is due to the mismatch of atoms on wrong sublattices.

A final remark concerns milling time, which is usually plotted as a physical parameter. It has to be emphasised that milling time is not a physical parameter. Firstly, it depends on the type of mill and milling intensity, but more importantly, it depends on the amount of material being milled. Usually small amounts of material are milled and after different milling periods

a substantial part is taken from the sample for characterisation. This introduces a discrepancy between milling time and real time. In the rare experiments where milling time is a real parameter, such as in the experiments on Nb₃Sn and Nb₃Au (Section 2.4.3), care was taken to start each milling period with the same amount of fresh powder.

3. PHASE TRANSFORMATIONS IN INTERMETALLIC COMPOUNDS INDUCED BY BALL MILLING

3.1. Amorphisation

Amorphisation of intermetallic compounds by ball milling was discovered in Gd–Co and Y–Co systems by Yermakov in the early 1980s.^(61,62) Since then a number of other intermetallic compounds have been found to exhibit such a phase transformation when subjected to heavy mechanical impact. Available experimental information has been reviewed^(14,63) (see also Section 3.7) and the reader is referred to these reviews for specific systems. In this section we would rather discuss under which conditions an intermetallic compound will amorphise. Evidently, when amorphising the compound attains a state of higher enthalpy than the starting compound. Johnson⁽⁹⁾ suggests a number of mechanisms by which energy may be stored during ball milling. In the first place enthalpy storage may take place in the form of atomic (chemical) disorder. In Section 2 of this paper we presented ample evidence for atomic disorder by means of mechanical milling. Certainly the enthalpy of the compound is raised by atomic disorder. As we suggest in Appendices A–C, this enthalpy has a chemical as well as an elastic component. Furthermore, elastic effects due to disordering are also responsible for at least a part of the observed strain and disordering leads also to a change in volume. In the second place it is known that, before amorphisation, the material becomes nanocrystalline, i.e. the crystallites in the powder particles are reduced to nanometre sizes. Therefore, part of the increase of the enthalpy will reside in the grain boundaries, which constitute an appreciable fraction of the material volume. Further enthalpy increase may be due to dislocations, vacancies and interstitials, although atomic disordering and grain boundary energy are generally considered as the main sources of enthalpy storage.⁽²⁴⁾ A criterion for amorphisation is that the total stored energy should exceed the energy difference between the compound and the amorphous state.^(9,24,64,65)

$$\Delta G_{\text{disorder}} + \Delta G_{\text{grain boundary}} > \Delta G_{\text{crystal-amorphous}} \quad (21)$$

A molecular dynamics study⁽⁶⁶⁾ suggested that the disordering enthalpy alone could be sufficient to drive the compound NiZr₂ to the amorphous state. On the other hand, Cho and Koch⁽²⁴⁾ did not observe a measurable decrease of the long-range-order parameter in B2 CoZr from superlattice reflections in X-ray diffraction, although after long milling periods amorphisation was observed. They suggested, that from this it could be concluded that the grain boundary energy alone could be high enough to overcome the energy needed for amorphisation in this system. In Zhou and Bakker⁽²⁵⁾ a similar conclusion concerning the X-ray intensities was made. However, as was shown in Section 2.2.2, the magnetisation as well as the lattice parameter increased in the early stage of milling, strongly pointing in the direction of anti-site disordering. When the amorphisation starts after 40 h of milling, the magnetisation decreases and reaches the value belonging to the amorphous structure. This decrease, and so the amorphisation, could be step-wise as is observed from Fig. 6 from Section 2.2.2. Besides, the magnetisation curves for 20 h of milling and 40 h of milling intersect (Fig. 35), which also points in the direction of a sudden structural change. Such a step-wise decrease of the l.r.o. parameter from a rather high value to zero value is not surprising in the light of the theoretical analysis of the order–disorder

Fig. 35. High field magnetisation curves of CoZr at 4.2 K after various periods of milling. The curve labelled 20 h + 1073 K is the magnetisation curve for a sample milled for 20 h and annealed at 1073 K showing that the original magnetisation is recovered to the original value (0 h). This means that no irreversible effects are encountered such as, for example, contamination by iron from the milling tools.⁽²⁵⁾

transformation in B2 compounds under the influence of ballistic action as performed by Bellon and Martin⁽³⁸⁾ (see also Appendix D). These authors find that, in contrast to the thermal order–disorder transition in equilibrium in B2 compounds, which is second-order, the transformation under ballistic action is first-order and so step-wise. Therefore, it could well be that, starting from a rather high value of the l.r.o. parameter, the l.r.o. parameter abruptly changes to zero value upon further milling. Then, as a result of disordering, the alloy could instantaneously self-organise in the amorphous structure. Of course, by the very process of milling the transformation is smeared out somewhat. Another interesting point is that, probably due to broadening and low intensity of X-ray lines, X-ray diffraction is less sensitive to atomic disorder than the magnetisation. Thus it is concluded on the basis of magnetisation measurements that CoZr certainly disorders to some degree before amorphisation and that usually both atomic disorder and grain boundary energy contribute to the stored energy in intermetallics.

From the above it is clear that knowledge of energy differences between the various states of an alloy are important. Although more sophisticated calculations on enthalpy differences between different states are imaginable, we will rely in the following on calculations based on Miedema's semi-empirical model.⁽⁶⁷⁾ Such calculations are simple and fast and have been performed for almost all alloy systems.^(68,69) Moreover, the agreement with experimental results is good and predictions are sometimes even surprisingly accurate. The underlying equations are presented in Appendix B. As a second guideline we will use an even simpler approach, based on information from the phase diagram. In order to make these ideas clear the compound CoZr will be treated as an example.

Figure 36 shows that this compound amorphises during ball milling.⁽²⁵⁾ The figure presents

Fig. 36. X-ray diffraction patterns of CoZr after various milling periods. The diffraction peaks of the crystalline compound are labelled.⁽²⁵⁾

the X-ray intensity as a function of diffraction angle for different milling periods. In the pattern of the crystalline phase all peaks can be identified as belonging to the crystalline intermetallic compound CoZr. These are labelled in the figure. The pattern corresponding to a milling period of 160 h is characteristic of amorphous material, in which atomic distances and atomic coordination are poorly defined, which leads to a broad first peak and a much lower broad second peak. The amorphous state is metastable and it exists only due to lack of mobility of the atoms at ambient temperature. When we heat the material, atoms become more mobile and eventually the alloy crystallises with release of heat. Now let us inspect the Co–Zr phase diagram Fig. 37.⁽⁷⁰⁾ From magnetic measurements it was found that atomic disorder is induced by milling. For the present compound it is not known whether thermal disorder also exists in equilibrium at higher temperatures as was demonstrated for the A15 compounds, for example (Section 2.4.2 of the present paper). Let us suppose that this is also the case for CoZr. Then for prolonged milling periods the compound attains degrees of disorder, corresponding to higher and higher temperatures in equilibrium. However, the temperature is not really raised much during milling,⁽¹⁴⁾ only the degree of disorder becomes similar to or maybe even higher than that in thermodynamic equilibrium at higher temperatures. Thus, during milling we in fact move from ambient temperature upwards in the phase diagram. Finally we cross the solid–liquid phase transition and the material would melt. Of course the temperature of the material is not the real melting temperature (because milling is performed at ambient temperature), but the degree of disordering corresponds to that at the melting temperature. The material cannot really melt, but adopts a liquid-like, i.e. amorphous, structure. Admittedly, this is a greatly oversimplified argument, but it will turn out to be useful in predicting which type of phase transformation occurs upon milling, if any.

As mentioned earlier, a better argument can, in principle, be obtained by a calculation based on Miedema's semi-empirical model (Appendix B). Curves for the enthalpy of the amorphous phase and for the crystalline solid solution of Zr in Co and Co in Zr, respectively, are given

Fig. 37. Phase diagram of the Co-Zr system from Massalski.⁽⁷⁰⁾

in Fig. 38. It is observed that for not too dilute compositions the curve for the amorphous state is always below that for the solid solution. Of course the enthalpy of the *compound* CoZr is lower than that of both forementioned states. The picture of what is happening during ball milling is now as follows. The enthalpy of CoZr is increased by disordering during ball milling. Thus in the enthalpy diagram we are moving upwards from the enthalpy value of the compound in the direction of the value of the amorphous state. As soon as the enthalpy is increased to, or above, the enthalpy of the amorphous state the compound amorphises. There also exist systems where the curve for the solid solution is below that of the amorphous state. In such a situation we first arrive at the curve for the solid solution and we expect the formation of the solid solution. In some cases the material amorphises subsequently from the solid solution. This could be the result of crystallite refinement of the crystalline solution supplying enough enthalpy to overcome the enthalpy difference between solid solution and amorphous state. In the following sections we apply the above arguments in order to predict and to understand experimental results.

Before that, however, attention will be given to an interesting phenomenon that was studied in a number of intermetallic compounds when amorphising during ball milling.^(71,72) In these papers it was argued that the topological structure of amorphous alloys can be well-approximated by a dense random packing of tetrahedral structural units, where the vertices are occupied by spherical atoms. Neutron total structure factors were measured on NiZr after various periods of milling and based on that the total radial distribution function

Fig. 38. Enthalpies of the amorphous phase (smooth curve) and solid solution (curve passing through zero for $x = 0$ and $x = 1$) for all compositions x of Co-Zr, calculated on the basis of the Miedema model (Appendix B).

was constructed (Fig. 39). The orthorhombic structure of crystalline NiZr can be conceived as being built up from octahedral as well as tetrahedral structural units. The Ni-Ni distances in an octahedral unit are mainly located around 4.2 Å and the corresponding Zr-Zr distances around 4.7 Å. These are the vertex to vertex distances characteristic of the octahedral structural unit. What is observed from Fig. 39 is that the second peak, located around 4.2 Å, decreases drastically with milling time, while the peak around 5 Å is broadened. This indicates the structural transition from octahedral units to tetrahedral units during the amorphisation process.

Fig. 39. Neutron total pair correlation functions of the compound NiZr for various milling periods.^(71,72)

So far we have been discussing the problem of amorphisation on the basis of energy differences between the amorphous and crystalline state. What exactly the mechanism of amorphisation is, is not completely clear. The above process of change of building units^(71,72) is one suggested mechanism; shear instability is another.⁽⁹⁾

3.2. Phase Transformations to the Solid Solution: The Au–Nb System

In this section we discuss transformations in the Au–Nb system as examples of transformations to the solid solution by milling. Let us apply the same arguments as in the previous section and so let us inspect the phase diagram of the Au–Nb system as given in Fig. 40.⁽⁷⁰⁾ When the phase field of the compound Nb_3Au is compared with that of the compound CoZr from the previous section, it is observed that at higher temperatures CoZr melts directly from the compound structure, whereas Nb_3Au transforms to the b.c.c. solid solution of Au in Nb before melting. In Section 2.4.3 it was demonstrated that ball milling introduces anti-site disorder in Nb_3Au , just as does high temperature. Ball milling brings the material into a more and more disordered state and these states correspond, if they were in thermal equilibrium, to higher and higher temperatures. So it is as if the temperature of the compound is increasing, although the real temperature of the material is not far from ambient temperature. In the phase diagram we virtually arrive in states belonging to increasing temperature and finally the A15 to b.c.c. transition point will be crossed. Based on these simplified arguments, we expect, in

Fig. 40. Phase diagram of the Au–Nb system from Massalski.⁽⁷⁰⁾

Fig. 41. Enthalpies of the amorphous phase (upper curve) and solid solution (lower curve) for all compositions x of Nb–Au, calculated on the basis of the Miedema model (Appendix B).

contrast to CoZr, no amorphisation for Nb₃Au, but a transformation to the b.c.c. solid solution. A somewhat more sophisticated estimate of the enthalpies involved, based on Miedema's semi-empirical model, is given in Fig. 41. It is observed that, in contrast to a similar diagram for Co–Zr (Fig. 38), for all compositions the enthalpy curve of the solid solution is below that of the amorphous state. The enthalpy of the as-prepared compound is lower than that of both curves drawn. Ball milling increases the enthalpy of the compound to higher values and if enough enthalpy can be stored the enthalpy curve corresponding to the solid solution will eventually be reached. This is another argument for expecting a transformation to the solid solution. The situation is similar for the compound Au₂Nb, the only difference being that, on the basis of the same arguments, a transition is expected from the structure of the compound to the f.c.c. solid solution of Nb in Au. Thus both compounds are expected to transform to the solid solution, but the solid solution to which both compounds transform is expected to exhibit a different structure. By inspection of Fig. 41 it is concluded that intermediate compositions should also transform to the solid solution.

Di *et al.*⁽⁷³⁾ milled various compositions of Nb–Au alloys. Some compositions were single phase, some were mixtures of two intermetallics, in agreement with the phase diagram (Fig. 40). X-ray diffraction patterns show most clearly the structural evolution during milling. Figure 42 presents the X-ray diffraction patterns of Nb₃Au (75 at.% Nb) for milling periods up to 60 h. The pattern of the as-prepared compound, labelled 0 h, is characteristic of the A15 (Cr₃Si) structure. All lines can be identified as corresponding to this structure. Lattice parameter (5.2057 Å) and superconducting transition temperature (11.2 K) are close to the literature values for the stoichiometric compound.^(74,75) From the figure it is observed that, after 10 h of milling, the A15 lines are broadened due to strain and refinement of crystallite size and that new lines appear. Analysis demonstrates that in this stage the sample contains a mixture of the original A15 structure and the disordered b.c.c. structure. Upon further milling the b.c.c. structure soon becomes dominant. Between 30 and 60 h of milling the diffraction pattern does not change any further and then the pattern is characteristic of the b.c.c. structure (with minor traces of A15 material). Thus the expected phase transformation has taken place, while there are no indications of amorphisation.

In order to check whether a compound on the other side of the phase diagram, i.e. an Au-rich compound, would transform to an f.c.c. solid solution as predicted, single-phase Au₂Nb (33 at.% Nb) was investigated. The compound has the AlB₂ structure. Again the lattice parameters

Fig. 42. X-ray diffraction patterns of Nb₇₅Au₂₅ (Nb₃Au) after various milling periods. The starting material has the A15 structure and becomes a b.c.c. solid solution after 60 h of milling.⁽⁷³⁾

of the compound were in agreement with those from the literature. The structural evolution during milling appears from the X-ray diffraction patterns, given in Fig. 43. As a matter of fact this compound transforms to the f.c.c. solid solution of Nb in Au as could already be predicted on the basis of the phase diagram. The preparation of a composition with 58 at. % Nb resulted in a mixture of mainly tetragonal Nb₃Au₂ with traces of Au₂Nb as expected on the basis of the phase diagram. The lattice parameters of both compounds were in close agreement with the literature values. From Fig. 44 it turns out that this composition transforms mainly to a b.c.c. solid solution, but one with traces of f.c.c. Remarkably, this composition is in the range, where

Fig. 43. X-ray diffraction patterns of Nb_{33.3}Au_{66.6} (Au₂Nb) after various milling periods. The starting material has the A1B₂ structure and becomes an f.c.c. solid solution after 40 h of milling.⁽⁷³⁾

Fig. 44. X-ray diffraction patterns of $\text{Nb}_{38}\text{Au}_{42}$ ($\text{Au}_3\text{Nb}_2 + \text{Au}_2\text{Nb}$) after various milling periods. The starting material is tetragonal $\text{Au}_3\text{Nb}_2 + \text{AlB}_2$ structure Au_2Nb and becomes an f.c.c.-b.c.c. two-phase solid solution after 40 h of milling.⁽⁷³⁾

a (small) two-phase field exists in the non-equilibrium phase diagram, generated by milling. Two more compositions were investigated, namely with 60 and 50 at.% of Nb. The 60 at.% compound mixture ($\text{Nb}_3\text{Au}_2 + \text{Nb}_3\text{Au}$) transformed to b.c.c. and the 50 at.% compound mixture ($\text{Nb}_3\text{Au}_2 + \text{Au}_2\text{Nb}$) to f.c.c.

Summarising: Nb-rich compositions transform to the b.c.c. solid solution down to a Nb concentration of about 58 at.%. Upon further decrease of the Nb content, compounds or mixtures of compounds transform to the f.c.c. solid solution. There is a small two-phase region of f.c.c. and b.c.c. around 58 at.% Nb. These investigations emphasise the use of the equilibrium phase diagram for the prediction of the structure of the metastable phases obtained by milling and moreover, the results are in good agreement with calculations by Miedema's model, i.e. for the Nb-Au system a solid solution rather than amorphisation is expected.

Lattice parameters were measured for the various f.c.c. and b.c.c. solid solutions and compared to the values found following Vegard's law. The agreement was within 0.5%, but all lattice parameters were somewhat smaller than those found following Vegard. This is a result of a contraction upon alloying described by Miedema.⁽⁶⁷⁾

The DSC traces usually exhibited two peaks. From X-ray diffraction, after heating in the DSC, it turned out that heating resulted in (a mixture of) the original compounds. Thus by heat treatment the original phases are completely restored and a considerable part of the heat evolved is due to the phase restoration. The total heat evolved was compared to the difference in enthalpy between the compound and the solid solution found following Miedema. The latter numbers followed the correct trend as a function of composition, but were overestimated by a factor of about 2 as we saw before for the heat effect of reordering in RuAl . Quantities such as the peak temperatures of the heat effects in DSC and the activation energies obtained by Kissinger plots followed the same trend as the melting temperatures in the phase diagram, which is not surprising, because these quantities have to do with atomic mobility. It is a well-known fact that the activation energy for diffusion roughly scales with melting temperature.

X-ray diffraction and DSC are normal techniques for the characterisation of structure and

Fig. 45. The maximal diagonal $D_{\max}$ of the powder particles as a function of milling time for two mixtures of intermetallic compounds of Nb and Au (50 and 58 at. % Nb).⁽⁷³⁾

transformations. Usually much less attention is given to the shape and size evolution of powder particles during milling of intermetallic compounds. The average particle shape and size were measured for two compositions by light microscopy using a computer controlled image analyser.⁽⁷³⁾ The results are given in Fig. 45 for the average particle size. It is observed that in the first stage the brittle intermetallics break to finer powder particles, but when the transformation starts to the most probably more ductile solid solution, the tendency reverses and the particle size increases apparently by cold welding. In the same periods the particles first tend to become more and more sphere-like and then reverse this tendency to become more flake-like. It is of course not surprising that all kinds of physical properties change after a phase transformation. Ball milling offers a simple technique to prepare such metastable phases with different and possibly favourable properties.

3.3. Phase Transformations in the Ni–V System

For further investigations the Ni–V system was chosen.⁽⁷⁶⁾ This system is similar to the Nb–Au system in that the primary and terminal phase fields are rather wide (see Fig. 46). Another similarity is that the primary phase is an f.c.c. solid solution of V in Ni, whereas the terminal phase is a b.c.c. solid solution of Ni in V. However, the phase diagram of Ni–V is somewhat more complex than that of the Nb–Au system. There is a rather wide phase field of a σ -phase. On the basis of the phase diagram, phase transformations can be expected by milling: in the Ni-rich compositions to an f.c.c. solid solution and in the V-rich compositions to the b.c.c. structure. What would happen to compositions in the σ -phase field is not immediately clear. Let us inspect our second criterion: the Miedema enthalpy diagram (Fig. 47). Here the solid-solution curve is below the amorphous curve at all points, except for compositions around the composition NiV_2 , where the enthalpy of the solid solution has a peak above the enthalpy of the amorphous state. The reason for this is the so-called structural term in the enthalpy of the solid solution (see Appendix B). Ni has the f.c.c. structure, whereas V has the b.c.c. structure and it is energetically unfavourable to solve V in the f.c.c. structure and on the other hand to solve Ni in the b.c.c. structure. Therefore there is a composition—in this system around the

Fig. 46. Phase diagram of the Ni-V system from Massalski.⁽⁷⁰⁾

composition NiV_2 —where the system ‘cannot decide’ whether it should crystallise in the f.c.c. or b.c.c. structure. This should also be related to the occurrence of the σ -phase in the equilibrium phase diagram. On the basis of this simplified argument, in principle, a similar effect could be expected for the Nb-Au system, but it can be demonstrated that when gold is involved as one

Fig. 47. Enthalpies of the amorphous phase (smooth curve) and solid solution (curve passing through zero for $x = 0$ and $x = 1$) for all compositions x of Ni-V, calculated on the basis of the Miedema model (Appendix B).

Fig. 48. The DO₂₂ structure of Ni₃V.

of the components the effect on the enthalpy is negligible.⁽⁶⁷⁾ These structural effects are only appreciable in transition metal–transition metal systems⁽⁶⁷⁾ except for systems containing Cu, Ag and Au. On the basis of the Miedema diagram for Ni–V one would expect phase transformations by ball milling to the solid solution for all compositions, except for compositions around NiV₂, where direct amorphisation is predicted. An intuitive and admittedly simplified argument could be: apparently at a certain composition the system ‘cannot decide’ whether the number of nearest neighbours of an atom should be twelve (f.c.c. structure) or eight (b.c.c. structure) and frustration could lead to amorphisation, where the effective number of nearest neighbours is between eight and twelve.

Considering the compounds in the Ni–V system, another aspect needs attention. The Ni-rich compounds Ni₃V and Ni₂V crystallise in structures that are directly derived from the f.c.c. structure, i.e. the atomic positions form an f.c.c. lattice and it is the atomic ordering that leads to the crystal structure of the compound. These are the DO₂₂ structure for Ni₃V (Fig. 48) and the MoPt₂ structure for Ni₂V (Fig. 49). The tetragonal unit cell of the DO₂₂ structure consists in fact of two f.c.c. unit cells, stacked along the *c*-axis. The relation of the tetragonal MoPt₂ structure to the f.c.c. unit cell becomes clear from the right-hand side figure in Fig. 49. This means that a phase transformation to a solid solution is mere disordering in both these compounds. In contrast NiV₃ is A15 type (Fig. 8) and a phase transformation of this compound to the b.c.c. structure implies a complex shifting of atoms at the phase transformation. The σ -phase has an even more complex arrangement of atoms. Thus the type of phase transformation to the solid solution is different for the Ni₃V and Ni₂V on the one hand and NiV₃ on the other hand. We will discuss aspects of a transformation as a result of mere

Fig. 49. The MoPt₂-type structure of Ni₂V.

Fig. 50. X-ray diffraction patterns of Ni_3V after various milling periods.⁽⁷⁶⁾

disordering, where the overall lattice positions still constitute an f.c.c. lattice, in more depth in the section on the L_{12} structure.

Let us inspect the X-ray patterns of Ni_3V for different milling times (Fig. 50). The as-prepared material (0 h) shows a pattern that is different from an f.c.c. pattern only in the split reflections at the higher diffraction angles. This split character disappears even after short milling periods of 5 h and the f.c.c. structure obtained does not change any further upon longer milling. The situation is very similar for Ni_2V (Fig. 51). Here, even after only 10 min of milling, clear changes towards the f.c.c. structure are visible and after 10 h the transformation is certainly complete. Thus these compounds easily transform to the f.c.c. solid solution and obviously the cause of the transformation is atomic disordering, which in these cases is identical to the phase transformation. NiV_3 , crystallising in the A15 structure, transforms to the b.c.c. structure as expected. The transformation is complete after 40 h of milling. The structural evolution of this compound is very similar to that of A15 Nb_3Au and therefore not shown. That the respective compositions transform to the f.c.c. and b.c.c. structures can be understood also from the so-called structural energy term used in Miedema's model (see Appendix B).

Also interesting are the structural changes of the σ -phase with composition NiV_2 (Fig. 52). The X-ray pattern of the as-prepared compound, labelled 0 h, shows a huge number of diffraction lines, reflecting the complex structure of this phase. Upon milling the intensity of the lines decreases, while the lines broaden and become more difficult to separate. However, the pattern is still a σ -phase pattern without any sign of a transformation to a b.c.c. solid solution. For very long milling times the pattern is still changing until eventually, after a milling period as long as 240 h, the pattern becomes stable. The pattern is then characteristic of an amorphous structure. The amorphisation was corroborated by TEM observations. Prior to milling, separate crystals could be identified, whereas no crystallites could be found after 240 h of milling. The electron diffraction pattern confirmed the X-ray diffraction results. An

Fig. 51. X-ray diffraction patterns of Ni_2V after various milling periods.⁽⁷⁶⁾

amorphous halo was detected after 240 h of milling. In the DSC scan of the amorphous product an exothermic crystallisation peak followed by a peak due to crystallite growth was found with heat contents of 3.4 and 0.17 kJ (mole of atoms)⁻¹, respectively.

Fig. 52. X-ray diffraction patterns of NiV_2 after various milling periods.⁽⁷⁶⁾

For the other compounds exothermic heat effects were also observed in DSC. It is interesting to note that the heat content of Ni_2V after 10 min of milling is much lower than after 10 h of milling. This could indicate that after 10 min of milling the structural change is still incomplete. Moreover, during milling periods longer than 10 min, energy may be stored in the material in the form of defects other than atomic disorder only, such as grain boundaries and strains. Finally, milling times needed for the various compounds to attain their final states seem to correlate with the enthalpy differences between initial and final state as obtained by applying Miedema's model.

In conclusion: ball milling induces phase transformations to f.c.c. and b.c.c. solid solutions in most compositions of the Ni–V system. Ni-rich compositions transform to f.c.c. and V-rich compositions to b.c.c. These transformations could already be expected, similar to the Nb–Au system, on the basis of the phase diagram. However, between both systems there is one big difference and that is the amorphisation of NiV_2 , whereas all Nb–Au alloys attained the solid solution. Remarkably, this difference in behaviour of both systems is completely in agreement with predictions based on Miedema's model.

3.4. Phase Transformations in Compounds with the $B8_2$ Structure and Related Orthorhombic Structure

In previous sections phase transformations to either the solid solution with simple f.c.c. or b.c.c. crystal structures or to the amorphous state were described. Predictions of the type of transformation were made on the basis of the phase diagram. In order to investigate whether transformations from the one complex crystal structure to another complex crystal structure could also be generated by mechanical milling the compounds Ni_3Sn_2 and Co_3Sn_2 were investigated.^(57,77,78) The phase diagram of Ni–Sn is given in Fig. 53. From the phase diagram it is observed that Ni_3Sn_2 crystallises in two different structures depending on temperature. The high temperature phase (HTP) has the $B8_2$ structure. The low temperature phase (LTP) crystallises in an orthorhombic structure (space group Pnma), which is obtained from the $B8_2$ structure by a slight shift of the atoms. In this structure, similar to the $B8$ structure, the Ni atoms occupy two different positions, which we call T_I and T_{II} positions. The T_I positions are fully occupied, whereas the T_{II} positions are only half-occupied. The X-ray diffraction patterns of both structures are given in Fig. 54, labelled '0 h' for the low temperature phase and 'HTP' for the high temperature phase, respectively. The HTP was obtained by rapid quenching of a powdered sample from 800°C into water in a special quenching device.⁽³²⁾ Co_3Sn_2 exhibits the same phases. Results of milling are presented in Fig. 54. The intensity of a number of reflections decrease with increasing milling time and eventually disappear. These are the reflections resulting from the orthorhombic LTP structure. Besides, the remaining peaks become broader and broader upon milling. After 40 h of milling, the peaks originating from orthorhombic Ni_3Sn_2 have disappeared and instead the pattern has become characteristic of a hexagonal structure. Apparently the compound has completely transformed to the HTP and even after prolonged milling periods the material remains in this structure without any tendency to amorphisation. Through Fig. 54 a comparison of the milled material to the quenched material is possible and both materials reveal the same reflections, although the peaks of the milled sample are much broader and the peaks at $2\theta = 43.7^\circ$ and 44.5° cannot be separated. The crystallite size after 40 h of milling is estimated by the Scherrer equation as 7 nm.

Figure 55 shows the magnetisation as a function of milling period. In the LTP the magnetisation increases as a result of transfer of Ni atoms from I to II sites in a similar way, as discussed before, to the $B8_2$ compounds Fe_3Ge_2 and Mn_3Sn_2 (Section 2.6.2). At the

Fig. 53. Phase diagram of the Ni-Sn system from Massalski.⁽⁷⁰⁾

transformation, which by inspection of the X-ray pattern turns out to occur after 32 h of milling, the magnetisation jumps and then becomes constant. The abrupt increase in the magnetisation at the transformation is not surprising, because the magnetisation of quenched HTP material (full circle in Fig. 55) is higher than the LTP magnetisation. However, in milled material it is much higher than in the quenched sample. Apparently the atoms that were transferred from I to II sites in the LTP remain in these positions after the transformation, in this way causing the extra high value of the magnetisation. Results for Co_3Sn_2 are very similar. In this compound the transformation takes place in a shorter period (between 3 and 12 h of milling), which is reflected by a jump in the magnetisation (Fig. 56). The total increase of the magnetisation amounts to a factor of about ten as in the case of Ni_3Sn_2 . The Curie temperature scarcely changes.

The DSC results obtained for Co_3Sn_2 are interesting. These are presented in Fig. 57.⁽⁷⁹⁾ The curve, labelled 0 h, represents a DSC scan for the as-prepared LTP. An endothermic heat effect corresponding to the LTP-HTP transition is observed. The curve, labelled 1073 K, is the DSC scan for the quenched HTP. An exothermic effect is found at 650 K. The HTP is metastable at room temperature, but by lack of atomic mobility is not able to transform to the LTP. However, with increasing temperature atomic mobility increases and at 650 K the material is able to overcome an energy barrier and transforms to the LTP as it should. At higher temperature again the LTP-HTP transformation is observed. The curve, labelled 48 h, is for milled and transformed material. The behaviour is similar to the HTP curve. Clearly the LTP-HTP transformation can be identified, demonstrating that the as-milled sample is in the

Fig. 54. X-ray diffraction patterns of Ni_3Sn_2 after various milling periods.⁽⁷⁷⁾ The pattern of the low temperature phase is labelled '0 h', the pattern of the high temperature phase is labelled 'HTP'.

HTP. It is not surprising that this endothermic effect occurs at a somewhat different temperature than in the quenched HTP, because the occupancies of the transition metal sublattices are different in both materials. Furthermore, it turns out that the heat, consumed in the LTP–HTP transition, decreases with milling time and becomes constant after about 12 h of milling. It is remarkable is that states, corresponding to the HTP obtained by milling (high magnetisation), could not be obtained by rapid quenching. Ball milling seems to be a unique technique for obtaining the somewhat disordered HTP, characterised by the high value of the magnetisation.

Co_2Ge resembles both of the compounds discussed above. It has an orthorhombic LTP and a hexagonal B8_2 HTP above 625°C . A major difference between the 3-2 compounds, such as Co_3Sn_2 , and this 2-1 compound Co_2Ge is that all transition metal sublattice sites are occupied

Fig. 55. Magnetisation of Ni_3Sn_2 at 4.2 K and in a field of 21 T.⁽⁷⁷⁾ The filled circle represents the magnetisation of the quenched HTP.

Fig. 56. Magnetisation of Co_3Sn_2 at 4.2 K and in a field of 21 T.⁽⁷⁸⁾ The filled circle represents the magnetisation of the quenched HTP.

in the latter compound in order to obtain the stoichiometric composition. A transfer of T metal atoms to a half-occupied second sublattice is here obviously not possible. Still this compound was chosen to investigate whether the LTP–HTP transformation could be induced mechanically.⁽⁸⁰⁾ Figure 58 represent the structural changes, induced by ball milling, as monitored by X-ray diffraction. In the first stage many peaks disappear, indicating anti-site disordering between the Co and Ge sublattices. The magnetisation measured at 4.2 K in a field of 21 T continuously increases with milling time up to 60 h of milling as a result of disordering and becomes almost constant after 80 h, when from X-ray diffraction it is clear that amorphisation starts. The same applies to the Curie temperature. Milling for longer periods

Fig. 57. DSC scans of the as-prepared low and high temperature phase of Co_3Sn_2 , labelled 0 min and 1073 K, respectively. The curve labelled 48 h is the DSC scan of an originally LTP sample milled for 48 h. The latter sample exhibits the characteristics of the HTP, demonstrating the phase transformation after milling.⁽⁷⁹⁾

Fig. 58. X-ray diffraction patterns of the LTP of Co_2Ge after various milling periods.⁽⁸⁰⁾ The pattern labelled 'HTP' is that of the quenched HTP.

does not change the X-ray pattern, which remains characteristic of amorphous material. For comparison the pattern of the quenched HTP is given. Clearly ball milling does not induce a LTP–HTP transformation in this material. Rather a LTP–amorphous transformation is induced. As already discussed in Section 2.7 the prerequisite for amorphisation, namely the creation of anti-site disorder of both components, seems to be fulfilled in the present case. The milling was prolonged for very long periods. From about 80 h on, no observable changes occur in the X-ray pattern. Still there are changes in the material as is clear from the measurements of the a.c. susceptibility as presented in Fig. 59. This is once more an indication that a measurement of magnetic properties is a more sensitive monitoring tool than measurements by other techniques. The magnetic state, that was introduced by ball milling, is very interesting and will be discussed in a further section separately.

In DSC an endothermic peak at 680 K, corresponding to the LTP–HTP transition, is detected in the as-prepared sample. The heat content of this peak decreases with increasing milling time in the early stage of milling. After 10 h of milling an exothermic peak develops at 550 K. The heat content increases with milling time and the peak broadens. It corresponds to the re-ordering process as could be checked by X-ray diffraction after DSC. After 40 h of milling a second exothermic peak appears at lower temperature (430 K), which becomes more and more pronounced for longer milling periods. This peak is due to crystallisation of amorphous material as was found from X-ray diffraction after the occurrence of the peak in DSC and fast quenching. Here we are clearly dealing with a polymorphous transformation. First the material crystallises to the disordered structure, which at higher temperature orders to the intermetallic compound.

From the above it is clear that LTP Co_2Ge cannot be driven to the HTP by milling. In contrast to Ni_3Sn_2 and Co_3Sn_2 , it transforms to the amorphous state. In the latter compounds energy is stored in the form of transfer of atoms to the half-occupied transition metal sublattice. Since in Co_2Ge both Co sublattices are fully occupied, this possibility is absent. Apparently anti-site

Fig. 59. Temperature dependence of the real part of the a.c. susceptibility χ' of the LTP of Co_2Ge after various periods of milling (external field 0.6 Oe, frequency 109 Hz). The susceptibility for the quenched HTP is also given.⁽⁸⁰⁾

disorder is generated, whereby both atomic species substitute on the other sublattice. Finally this leads to amorphisation and on this basis it is tempting to argue that the generation of anti-site disorder is a prerequisite for amorphisation as it is for the transformation to a solid solution.

The HTP of Co_2Ge was obtained by melt-spinning, by which no amorphisation was achieved. Ball milling of the HTP also resulted in amorphisation. Other features were also very similar to the LTP. The milling times needed were much shorter.⁽⁸⁰⁾

Fig. 60. The L₁₂ or Cu₃Au structure.

3.5. Mechanically Induced Disorder and Phase Transformations in L₁₂ Compounds

The L₁₂ or Cu₃Au structure is given in Fig. 60. It has already been mentioned in Section 2.3 that in compounds with this structure atomic disordering is identical to the phase transformation from the L₁₂ to the f.c.c. solid solution. This is the reason why atomic disorder and phase transformation are not treated separately here, but together in one and the same section. (The situation is actually identical to the relation of the disordered B2 to the b.c.c. structure, but for the B2 structure it was more feasible to separate atomic disorder from the phase transformation.) The first ball milling experiment on L₁₂ structure compounds was performed by Koch *et al.*^(81,82) on Ni₃Al. Ball milling was carried out in an Invicta Vibrator Mixer/Mill (Model BX920/2) in argon atmosphere. The milling process was followed by X-ray diffraction, transmission electron microscopy (TEM) and differential scanning calorimetry (DSC). It was shown that the long-range-order parameter η , derived from X-ray diffraction measurements with the aid of eq. (2), decreases monotonously with milling time (see Fig. 61). This means an increase of anti-site disorder in Ni₃Al with increasing milling time. This was confirmed by selected area diffraction in the TEM, where superlattice reflections completely disappeared after 5 h of milling. The atomic reordering process was evidenced by DSC analysis. Later, Gialanella *et al.*⁽⁸³⁾ also studied the behaviour of Ni₃Al upon ball milling. They measured the lattice parameter during milling. The relative change of the lattice parameter as a function of milling time is plotted in Fig. 62. From this figure it is clear that ball milling of Ni₃Al results in a volume expansion. This is expected for anti-site disordering, where atoms do not fit on the 'wrong' sublattice. Moreover, it is in agreement with an abrupt change of the lattice

Fig. 61. Long-range-order parameter η as a function of milling time for Ni₃Al.⁽⁸²⁾

Fig. 62. The relative change of the lattice parameter as a function of milling time for Ni_3Al .⁽⁸³⁾

parameter as observed in Cu_3Au during the order–disorder transition in equilibrium at the transition temperature.⁽⁸⁴⁾ Furthermore, the relative increase found in Ni_3Al (a value⁽⁸³⁾ of $\Delta a/a_0$ of about 0.8%) is not far from the value (0.9%) obtained by using Vegard's law. A recent study on ball milling of Ni_3Al ⁽⁸⁵⁾ was undertaken with emphasis on magnetic measurements for monitoring structural changes. The long-range-order parameter turned out to behave identically to the one measured by Jang and Koch,⁽⁸²⁾ represented by Fig. 61. Even the extrapolated milling period, where η becomes zero, was about 5–6 h in this study, very similar to Jang and Koch's study.⁽⁸²⁾ The measured magnetisation as a function of milling time is given in Fig. 63. Both the magnetisation and the l.r.o. parameter η decrease monotonously with milling time, indicating anti-site disordering in Ni_3Al during ball milling. However, it is interesting to note that, when the value of η becomes zero after about 5–6 h, the magnetisation still continuously decreases upon further milling. The magnetisation tends to become constant after as long as 20 h of milling, so well after the disappearance of the l.r.o. parameter. The lattice parameter turned out to increase upon milling. The change of the lattice parameter is similar to that of the magnetisation, i.e. long after the disappearance of η , it still varies (cf. Fig. 62). These observations strongly suggest that structural changes take place even after the disappearance of η . It could be that then existing short-range order is destroyed, that the

Fig. 63. The magnetisation of Ni_3Al at 4.2 K and 21 T as a function of milling period.⁽⁸⁵⁾

measured intensities of superlattice reflections are not completely decisive for the evaluation of atomic order as discussed in Section 2.7, or that the material separates into two phases with different composition (f.c.c. solid solution and some amorphous). Of course, there could be a different explanation for the decrease of the magnetisation between 6 and 40 h of milling, namely that it would be due to refinement of the crystallites, whereby a substantial fraction of atoms could reside in grain boundaries. However, this seems improbable as discussed by Zhou *et al.*⁽⁸⁵⁾ because the average crystallite size already tends to become constant after about 10 h of milling with a final size of about 25 nm. This value is much larger than the limit for the reduction of magnetisation due to grain boundary atoms, which is usually 4–6 nm. Therefore, nanocrystallinity does not seem to explain the decreasing magnetisation. The situation becomes even more complicated by information based on a study by extended X-ray absorption fine-structure (EXAFS) of Ni₃Al by Nasu *et al.*⁽⁸⁶⁾ In agreement with X-ray data these authors showed that both the Ni–Ni and Ni–Al atomic distances increase slightly with milling time. A more important result is that in the early stage of milling the Ni–Ni coordination decreased (from 8 to 7), while the Ni–Al coordination increased. This is a peculiar result, because one would expect the opposite during disordering: in the ordered state the Ni–Ni coordination is by definition a minimum, whereas the Ni–Al coordination is a maximum. Then, in a later stage, the Ni–Ni coordination increased as expected during disordering, while the Ni–Al coordination increased. However, the Ni–Ni coordination increased even up to a value of 11 (instead of 9 in a random alloy). The explanation is given in terms of the segregation of Al atoms in grain boundaries, a diffusion process which could cost some (milling) time. However, recent magnetisation measurements⁽⁸⁵⁾ show a decrease of the high field magnetisation as a function of milling time. If the interior of the grains were almost pure Ni, then an increase of magnetisation would certainly be expected, the more so because the crystallite sizes in this material are not exceptionally small (20–25 nm). The results seem to be contradictory. The conclusion is somewhat disappointing. Although Ni₃Al is one of the most studied systems and although different techniques were applied, the behaviour of the system during milling is not understood and even information from different experimental sources seems not to be in agreement.

The kinetics of re-ordering of mechanically disordered Ni₃Al and Ni₃Al + Fe were extensively studied by Baro *et al.*^(87,88) and Yavari.⁽⁸⁹⁾ These results are somewhat outside the scope of the present paper and the reader is referred to the original papers.

Milling of the L1₂ compound Ni₃Si also results in a decrease of the l.r.o. parameter to zero value^(24,90) and a decrease of the magnetisation at 4.2 K,⁽⁹⁰⁾ indicating anti-site disordering. In this compound the more detailed information about the processes of structural changes is obtained from DSC analysis. Typical DSC traces are given in Fig. 64. The exothermic peak resulting from atomic reordering is clearly observed (peak I). With increasing milling time this peak becomes more and more pronounced. After 40 h of milling a shoulder at the right-hand side of peak I is visible and it becomes a clear peak (peak II) after 60 h of milling. After 100 h of milling, the intensity of peak I decreases rapidly without change of peak temperature. In contrast, the intensity of peak II increases abruptly between 40 and 100 h of milling and the peak temperature shifts to higher temperature. Even after 220 h of milling the reordering peak I is still visible. X-ray diffraction patterns, taken at a temperature higher than the peak II temperature, show that peak II results from the phase restoration from the nanocrystalline disordered f.c.c. solid solution to the more or less disordered L1₂ structure. This will be discussed further in this section. The magnetic signal of Ni₃Si is too weak to draw definite conclusions for long milling periods, where η is zero. In contrast to L1₂ Ni-based compounds, the magnetisation at 4.2 K in the Fe-based compound Fe₃Ge, is increased by milling in the early

Fig. 64. DSC scans of Ni_3Si after various periods of milling.⁽⁹⁰⁾

stage of the process.⁽⁹¹⁾ This is due to the introduction of anti-site disorder in the L1_2 -f.c.c. lattice, which leads to an increase in the number of nearest Fe neighbours of an Fe atom.

From the above it is clear that anti-site disorder is introduced in L1_2 compounds by mechanical milling in a high energy ball mill. Anti-site disorder in Ni-based L1_2 compounds leads to a decrease of magnetisation at 4.2 K, whereas in L1_2 Fe compounds it results in an increase. This certainly has to do with a difference in magnetic character of Fe (and Co) on the one hand and Ni on the other hand.

Now we proceed in more detail to the phase transformations in L1_2 compounds. The phase transformation from the L1_2 to the f.c.c. structure is in fact completed when the η value becomes zero. In fact, in a first-order transformation the l.r.o. parameter should change abruptly at the phase transformation. This is not observed experimentally (Fig. 61). The reason could be that the measured η value is an average of different local η values in the material. It was shown in Jang and Koch⁽⁸²⁾ that the first traces of an amorphous phase in disordered Ni_3Al were observed well after the disappearance of superlattice reflections ($\eta = 0$). It was concluded that the extra energy, needed for the partial amorphisation of Ni_3Al , stems from the nanocrystallite grain boundaries. The formation of a small fraction of amorphous material during mechanical milling of Ni_3Al was also observed by Benameur and Yavari.⁽⁹²⁾ These authors explain the result by the existence of a two-phase region in the non-equilibrium phase diagram, corresponding to the common tangent to the free energy curve of the f.c.c. solid solution and of the undercooled liquid (amorphous phase). This would imply the coexistence of two phases with different compositions, the f.c.c. phase being somewhat poorer in Al. It would explain the fact that a long milling period is needed to attain the final state after the l.r.o. parameter has become zero, because the necessary diffusion process takes time. However, it is difficult to understand why the magnetisation would decrease. As already mentioned the results on Ni_3Al are somewhat puzzling. It was also reported by these authors⁽⁹²⁾ that a larger amorphous fraction than in Ni_3Al was observed in Ni_3Ge and that full amorphisation was found in Zr_3Al .

In Ni_3Si , even after prolonged periods of milling, the disordered f.c.c. solid solution did not

Fig. 65. X-ray diffraction patterns for Ni_3Si for milling longer than 40 h. Filled circle: (111) peak of L_{12} ; filled triangle: (111) peak of f.c.c. solid solution; filled square: WC contamination.⁽⁹⁰⁾

transform to the amorphous state.^(24,90) As already mentioned, the L_{12} -f.c.c. transformation is a first-order transition, during which the l.r.o. parameter should change abruptly from a non-zero to a zero value. From the intensities of superlattice reflections such a jump was not observed in Ni_3Al , nor was it in Ni_3Si . However, when they coexist, the difference between both phases is clear. This is observed from Fig. 65. From 60 h milling on, the f.c.c. phase develops and after 220 h of milling both phases clearly coexist. The (111) peak of (somewhat disordered) L_{12} is indicated by a filled circle, the (111) peak by a filled triangle. (Unfortunately there is some contamination by WC from the bottom, indicated by a filled square.) These results clearly show a step-wise change of the lattice parameter at the transformation, corresponding to a volume change of 5.6%. Moreover, as described above (see Fig. 64), the heat effects for atomic re-ordering and the phase restoration occur at quite different temperatures, which also indicates a sudden change of the η parameter (from zero to a value much higher than zero during phase restoration). The milled sample was also heated in a diffractometer with a position sensitive detector. Figure 66 shows that the (111) peak of f.c.c. is disappearing at higher temperature, whereas the (111) peak of the L_{12} phase is growing. This all makes clear that the L_{12} -f.c.c. transition is not mere disordering, but a real phase transformation.

An even clearer phase transformation was observed in Fe_3Ge .⁽⁹¹⁾ It turned out that after long periods of milling a phase transformation occurred not to the f.c.c. solid solution, but to the b.c.c. solid solution of Ge in α -iron. The X-ray diffraction patterns after typical periods of milling are shown in Fig. 67. After 130 h of milling a clear b.c.c. pattern is obtained. The magnetic measurements, presented in Fig. 68, are interesting. First, in the period of 2 h of milling the L_{12} structure disorders. In the completely ordered structure an Fe atom has 8 Fe neighbours, an average of 9 in the disordered structure, and after the phase transformation (130 h of milling) to disordered b.c.c. an average of 6. Apparently the number of nearest-Fe neighbours determines the magnetisation. Let us inspect the value of the magnetisation at 14 T, the highest field used. M increases in the early stage, when the number of Fe-nearest

Fig. 66. X-ray diffraction patterns for Ni_3Si , milled for 220 h and measured at different temperatures for 2 min. Filled circle: (111) peak of L_{12} ; filled triangle: (111) peak of f.c.c. solid solution; filled square: WC contamination.⁽⁹⁰⁾

neighbours increases from 8 to 9. Subsequently, it decreases in the period from 2 to 130 h of milling, when the number of nearest-Fe neighbours decreases from 9 to 6. Can magnetism be that simple, that the number of nearest neighbours is proportional to the magnetisation, i.e.

Fig. 67. X-ray diffraction patterns for Fe_3Ge , milled for various periods.⁽⁹¹⁾

Fig. 68. Magnetisation curves for Fe_3Ge , milled for various periods.⁽⁹¹⁾

$$\Delta M(\text{L}_{12} - \text{f.c.c.}) \equiv M(8 \text{ Fe neighbours}) - M(9 \text{ Fe neighbours}) = 0.5$$

$$\times \Delta M(\text{b.c.c.} - \text{L}_{12}) \equiv 0.5 \times \{M(6 \text{ Fe neighbours}) - M(8 \text{ Fe neighbours})\} \quad (22)$$

Amazingly, for the magnetisation at 14 T, eq. (22) is fulfilled almost exactly!

In order to find some systematics in the type of phase transformation let us first compare the different compounds on the basis of phase diagrams. The alloys Ni_3Al , Ni_3Ge , Ni_3Si and Fe_3Ge exhibit a range of existence, whereas Zr_3Al is a line compound. This indicates that the formation of anti-site disorder is easier in the Ni and Fe compounds than in the Zr compound, which could be used as an argument that Zr_3Al would not easily form a solid solution. None of the compounds transforms in equilibrium at high temperature to a solid solution. Inspecting the enthalpy curves, obtained by the Miedema model, we would expect that all five compounds would transform to the solid solution. However, for Ni_3Al and Ni_3Ge the enthalpy curve for the amorphous phase crosses the enthalpy curve for the solid solution not far from the 75–25% composition, which could indicate some tendency towards the formation of amorphous material. The same does not apply to Ni_3Si and Fe_3Ge . The enthalpy differences between the amorphous and solid solution are as follows: Ni_3Ge : $0.50 \text{ kJ (mole of atoms)}^{-1}$; Ni_3Al : $1 \text{ kJ (mole of atoms)}^{-1}$; Fe_3Ge : $2 \text{ kJ (mole of atoms)}^{-1}$; and Ni_3Si : $4 \text{ kJ (mole of atoms)}^{-1}$. On the basis of these numbers it is not surprising that Ni_3Ge contains a higher fraction of amorphous phase than Ni_3Al and that Fe_3Ge and Ni_3Si just transform to the solid solution. On the basis of Miedema's model the full amorphisation of Zr_3Al cannot be understood. Probably more realistic free energy curves for this system are given in Benameur and Yavari.⁽⁹²⁾

3.6. Phase Transformations in σ -Phases

The σ -phase has a very complex crystal structure with thirty atoms at five different sites in one unit cell. Figure 69 shows the unit cell of this structure. For easy identification of the atoms in different planes the c -axis is not drawn on scale. The structure may be conceived as being produced by starting with hexagonal close packed layers in the planes $z = 0$ and $z = c/2$. Certain atoms are then displaced parallel to the c -axis from the close packed layers to the planes $z = c/4$ and $z = 3c/4$ (atoms at sites E). The planes $z = 0$ and $z = c/2$ are called 'main layers' and the planes $z = c/4$ and $z = 3c/4$ are called 'subsidiary layers'.⁽⁹³⁾ The positions and coordinates of different sites are summarised in Table 1. Often the σ -phase is located in the

Fig. 69. Crystal structure of the σ -phase (a), the (100) plane of the b.c.c. structure (b) and the base plane of the σ -structure, where the black circles are empty sites (c).

equilibrium phase diagram 'below' the b.c.c. solid solution. This indicates that this complex tetragonal structure is related to the b.c.c. structure. Figure 69(b) shows the (110) plane of the b.c.c. structure. The drawn lines form a rhombus. The diagonal lines are the [100] and [011] crystal directions, respectively. If the four atoms, represented by black filled circles, move out of this plane to form a sub-plane, four vacancies are left in this plane. Then by relaxation this plane is compressed along the diagonals. If such a compression makes the two diagonals equal in length, the rhombus becomes a square. This situation is drawn in Fig. 69(c). Figure 69(c) represents the $z = 0$ plane of the σ -phase, if the atoms indicated by black filled circles are missing. In the σ -structure these atoms are shifted in the z direction over a distance $z = c/4$ and form the plane $z = c/4$ parallel to the plane $z = 0$. Figure 69(c) also shows five different types of sites. From Fig. 69(a) it can be found that the (110) plane of the b.c.c. lattice transforms to the base plane of the σ -lattice. The (220) b.c.c. plane corresponds to the $z = c/2$ plane with

Table 1. Number of Sites and Occupancies in the σ -Phase of a Compound LR , Where L is a Metal Left of Mn in the Periodic Table (e.g. V, Cr and Mo) and R is a Metal Right of Mn (e.g. Fe, Co and Ni), while Mn is Considered to Belong to Both Groups

	Site A	Site B	Site C	Site D	Site E
Number in $Z = 0$ plane	1	2	4	4	0
Number in $Z = c/4$ plane	0	0	0	0	4
Number in $Z = c/2$ plane	1	2	4	4	0
Number in $Z = 3c/4$ plane	0	0	0	0	4
Total number of sites	2	4	8	8	8
Coordination of site	12	15	14	12	14
Occupancy in σ - LR	R	L	R and L	R	R and L

four atoms, shifted over a distance of $z = c/4$, to form the $z = 3c/4$ subsidiary layers of the σ -structure. The σ -phase has a tetragonal structure and belongs to the space group $P4_2/mnm$. Table 1 also presents the atomic occupancies of the five sites. From the above analysis we can conclude that the complex σ -phase is an ordered and partially distorted b.c.c. structure. Obviously the free energy of the σ -compound is lower than that of the b.c.c. phase.

Figure 70 shows the X-ray diffraction patterns after milling σ -CrFe (53.5 at.% Fe) for different periods.^(94,95) The X-ray pattern of the starting material is characteristic of the σ -phase with six sharp lines between $2\theta = 40$ – 50° . With increasing milling time the intensities of the σ -phase diffraction peaks show a fast decrease, whereas the peaks of the b.c.c. structure appear. After 10 h of milling, only b.c.c. peaks are visible. The material remains in the b.c.c. structure after a prolonged milling period, but the peaks clearly broaden due to the reduction of the

Fig. 70. X-ray diffraction patterns of σ -FeCr after various milling periods. The curve labelled HTP is for the quenched high temperature solid solution.⁽⁹⁴⁾

Fig. 71. Saturation magnetisation at 4.2 K and 21 T of σ -FeCr as a function of milling time. The magnetisation of quenched b.c.c. FeCr is indicated by HTP.⁽⁹⁴⁾

crystallite size. For comparison Fig. 70 also includes the pattern of a quenched sample (labelled HTP). This is also in the b.c.c. structure, but the peaks are much narrower than those of the ball milled sample, revealing much bigger crystallites. The crystallite size, calculated from the broadening of the X-ray peaks, shows a decrease with milling time and finally arrives at nanometre level (about 7 nm). Figure 71 shows the saturation magnetisation M at 4.2 K and 21 T as a function of milling time. There is an increase in M up to 10 h of milling, which corresponds to the transformation from the σ -phase with a lower magnetisation (the value indicated at $t = 0$ h) to the b.c.c. phase with a higher magnetisation (the value indicated at $t = 0$ by HTP). The magnetisation of the transformed milled sample is lower than that of the quenched material. For longer milling periods the magnetisation decreases. Such a decrease could be due to a further refinement of nanocrystallites.

The compound σ -FeV (50 at.% Fe) transforms also to the b.c.c. solid solution during ball milling. This was observed by X-ray diffraction⁽⁹⁵⁾ as well as by neutron diffraction.⁽⁹⁶⁾ The magnetic behaviour of this compound is very similar to σ -CrFe.⁽⁹⁵⁾ DSC was used for thermal analysis.⁽⁹⁵⁾ The DSC trace of the 120 h milled FeV sample exhibits two exothermic peaks. X-ray diffraction was used to check the meaning of these peaks and it was found that the first peak is a mixture of the heat effect of grain growth and recovery of atomic disorder, whereas the second peak corresponds to the phase restoration from the metastable b.c.c. structure to the σ -phase structure.

X-ray spectra of σ -NiV (33.3 at.% Ni), taken at different milling times,⁽⁹⁵⁾ show that the intensity of most peaks of the σ -phase decreases and finally disappears, whereas with increasing milling time the peaks between $2\theta = 40\text{--}50^\circ$ first start to overlap and eventually form a broad peak after 240 h of milling. From TEM observations the difference between the starting material and the final product is evident. Prior to milling separate crystals can be identified, whereas after 240 h of milling no crystalline material is found and the final product shows amorphous rings in the electron diffraction pattern. This confirms that σ -NiV transforms to the amorphous phase after prolonged milling. In DSC measurements, an exothermic crystallisation peak is found for the 240 h milled sample. The crystallisation heat is 3.43

$\text{kJ (mole of atoms)}^{-1}$. In the DSC scan a second exothermic peak at 928 K with a heat content of $0.17 \text{ kJ (mole of atoms)}^{-1}$ was observed. This may be due to grain growth. Also for the composition 40 at.% Ni amorphisation was reported.⁽⁷²⁾ By neutron diffraction similar phenomena were observed in this material as reported for NiZr in Section 3.1. The compound $\sigma\text{-CoV}$ (50 at.% Co) is also an example of an amorphising material as observed from X-ray diffraction and DSC.⁽⁹⁷⁾ The magnetisation increases with milling time and tends to become constant after 80 h of milling.

X-ray diffraction patterns of $\sigma\text{-CoCr}$ (41 at.% Co) were taken at various milling times. With increasing milling time, the peaks of the σ -phase are broadening and overlapping. Finally it is no longer possible to identify them separately. The pattern for the sample after 240 h of milling is somewhat similar to that of amorphous NiV, but with two broad peaks instead of one. To investigate a possible amorphisation, the sample after 240 h of milling was examined by TEM. The electron diffraction pattern shows that the material is still crystalline, but the average crystallite size, revealed by the dark field image, is only 5 nm.⁽⁹⁵⁾ From the X-ray diffraction pattern it can be observed that the positions of the two broad peaks are the same as in the original σ -phase. In contrast, the X-ray spectrum of the b.c.c. structure should have three peaks in this range of angle. Apparently this compound does not show any transformation to a different structure—it remains in the σ -phase structure—but becomes nanocrystalline.

In conclusion we can state that three types of metastable phases are induced during mechanical milling of the binary σ -phase, formed by alloying Fe, Co or Ni with V or Cr. The compounds $\sigma\text{-CrFe}$ and $\sigma\text{-FeV}$ transform to the b.c.c. solid solution, and the compounds $\sigma\text{-NiV}$ and $\sigma\text{-CoV}$ become amorphous. In contrast, $\sigma\text{-CoCr}$ remains in the σ -phase, but the material becomes nanocrystalline. Apparently the crystal structure of the starting phase is not determining at all for the type of transformation, if any. Differences between the enthalpy of the amorphous state and the solid solutions, as calculated by Miedema's model, are small and not very decisive. In a number of cases a rather sharp maximum in the enthalpy curve of the solid solution crosses the enthalpy curve of the amorphous state near 50 at.%. Small changes in the positions of both curves would give rise to an opposite prediction of the phase transformation than expected. Successful here are the predictions on basis of phase diagrams. At higher temperature there are transitions to the solid solutions for FeCr and FeV, but not for CoV and NiV.

3.7. Prediction of Phase Transformations in Intermetallic Compounds Induced by Milling

If an intermetallic compound undergoes a phase transformation during ball milling, it may transform to a solid solution of the one component in the other component, to the amorphous state or to a different (complex) crystal structure. Without claiming that the list of compounds and their transformations, as presented in Table 2, is complete, the behaviour of a large number of compounds is given.

Let us first inspect in Table 2 the A15 compounds (for the meaning of the different columns see the table caption). So far five A15 compounds have been studied. In two of these the type of atomic (chemical) disorder was investigated in-depth and assessed as anti-site disorder of both components. This makes this type of disorder also probable in the other three compounds. Among the five A15 compounds four transform to the b.c.c. solid solution, whereas one compound becomes amorphous. It is evident that for all compounds the ordered A15 structure is no longer preserved and that the transformed structure is atomically disordered. As discussed in Section 2.7, this is an argument to believe that anti-site disorder is a prerequisite for either a transformation to the solid solution or to the amorphous state. Furthermore, a

transformation to the solid solution is expected if the enthalpy of the amorphous state, as estimated by Loeff *et al.*⁽⁶⁸⁾ and Yang and Bakker,⁽⁶⁹⁾ is higher than that of the solid solution. This applies to all A15 compounds listed. However, it was pointed out in Section 3.1 that atomic disorder is not the only source of enthalpy increase during milling. During the process the crystallite size is also refined to nanometre size and the grain boundary energy can amount most probably to a few kJ (mole of atoms)⁻¹. Therefore the increase of the free enthalpy after milling is given by eq. (21) as the sum of the increase due to atomic disorder and grain boundary energy. It could well be that in Nb₃Sn the grain boundary energy is high enough to overcome the small enthalpy difference ($\Delta H(a - ss) = 1$ kJ (mole of atoms)⁻¹) between the solid solution and the amorphous state. Furthermore, it is remarkable that from the equilibrium phase diagram it is found that Nb₃Sn melts directly, whereas V₃Ga and Nb₃Au transform to the solid solution at higher temperature before melting (see sixth column of Table 2). This could also be an argument to believe that V₃Ga and Nb₃Au would rather form a solid solution, whereas Nb₃Sn would prefer a liquid-like (amorphous) state upon milling.

The next two compounds in the table, NiZr and CoZr, transform to the amorphous state in agreement with large negative $\Delta H(a - ss)$ values. Subsequently a number of group VIII-group IIIA compounds with the B2 structure are listed. CoGa, CoAl and NiAl are known to exhibit triple-defect disorder, in which the frame of the structure is preserved, because the IIIA atoms remain on their own sublattice (Section 2.5). It is reasonable to assess that this prohibits a phase transformation to any inherently disordered structure, such as a solid solution or the amorphous state. The precise type of disorder in RuAl (a VIII-IIIa compound!) is not

Table 2. Compounds and their Transformations

Compound	Crystal structure	Type of disorder	Transformation	$\Delta H(a - ss)$ kJ (mole) ⁻¹	Phase diagram	Ref.
Nb ₃ Al	A15	?	ss:b.c.c.	+8	?	(98)
V ₃ Ga	A15	?	ss:b.c.c.	+2	ss > T _c	(99)
Nb ₃ Sn	A15	anti-site	amorphous	< +1 >	liq.	(39)(100)
Nb ₃ Au	A15	anti-site	ss:b.c.c.	+8	ss > T _c	(40)(73)
NiV ₃	A15	?	ss:b.c.c.	+6	?	(76)
NiZr	B ₁	?	amorphous	-20	liq.	(72)(101)
CoZr	B2	anti-site	amorphous	-22	liq.	(24)(25)
CoGa	B2	triple-defect	none	irrelevant	irrelevant	(44)
CoAl	B2	triple-defect	none	irrelevant	irrelevant	(46)
NiAl	B2	triple-defect	none	irrelevant	irrelevant	(47)
RuAl	B2	triple- defect?	none	irrelevant?	irrelevant?	(23)
Fe ₃ Ge ₂	B8 ₂	red.int.	none	irrelevant	irrelevant	(57)
Mn ₃ Sn ₂	B8 ₂	red.int.	none	irrelevant	irrelevant	(57)
Ni ₃ Sn ₂	orthorhombic	red.int.	LTP-HTP	irrelevant	LTP-HTP	(77)
Co ₃ Sn ₂	orthorhombic	red.int.	LTP-HTP	irrelevant	LTP-HTP	(78)
Co ₂ Ge	Co ₂ Si	anti-site	amorphous	-1	LTP-HTP-liq.	(80)
Co ₂ Ge	Ni ₂ In	anti-site	amorphous	-1	HTP-liq.	(80)
Nb _{0.61} -Au _{0.48}	A15 + tetrag.	?	ss:b.c.c.	+7	ss > T _c	(73)
Nb _{0.58} -Au _{0.42}	AlB ₂ + tetrag.	?	ss:b.c.c./f.c.c.	+7	ss > T _c	(73)
Nb _{0.5} -Au _{0.5}	AlB ₂ + tetrag.	?	ss:f.c.c.	+6	ss > T _c	(73)
NbAu ₂	AlB ₂	?	ss:f.c.c.	+4	ss > T _c	(73)
Ni ₃ V	DO ₂₂	?	ss:f.c.c.	+10	ss > T _c	(76)
Ni ₂ V	MoPt ₂	?	ss:f.c.c.	+9	ss > T _c	(76)
NiV ₂	σ -phase	?	amorphous	-2	σ - σ' -liq.	(76)
Ni ₄ V ₆	σ -phase	?	amorphous	< +2 >	σ - σ' -liq.	(72)
CoV	σ -phase	disorder	amorphous	0	liq.	(97)
Cr _{0.53} Fe _{0.47}	σ -phase	disorder	ss:b.c.c.	+2	ss > T _c	(94)
FeV	σ -phase	?	ss:b.c.c.	< -1 >	ss > T _c	(72)(102)

Continued

Table 2.—Continued

Compound	Crystal structure	Type of disorder	Transformation	$\Delta H(a - ss)$ kJ (mole) ⁻¹	Phase diagram	Ref.
Co _{0.41} —Cr _{0.59}	σ -phase	?	none	< +2 >	σ - δ -liq.	(102)
Ni ₃ Sn	DO ₁₉	?	amorphous	-21	LTP-HTP-liq.	(103)
LaAu	B27	?	amorphous	-13	LTP-HTP-liq.	(104)
Ni ₃ Al	L1 ₂	anti-site	ss:f.c.c. + a	+1	?	(81,82,83)
Ni ₃ Si	L1 ₂	anti-site	ss:f.c.c.	+4	?	(24)(90)
Ni ₃ Ge	L1 ₂	?	ss:f.c.c. + a	+0.5	?	(72) (92)
Fe ₃ Ge	L1 ₂	anti-site	ss:b.c.c.	+2	?	(91)
Zr ₃ Al	L1 ₂	?	amorphous	< +3 >	?	(105)
NiTi ₂	E9 ₃	?	amorphous	< +3.5 >	?	(106)
TiAl ₃	DO ₂₂	anti-site	ss:f.c.c.	+4	?	(107)
Ti _{0.51} Al _{0.49}	DO ₁₉ /L1 ₂	anti-site	ss:hcp	+5	?	(107)
Ti ₃ Si ₃	D8 ₈	?	amorphous	< +5 >	liq.	(107)
TiSi ₂	C54	?	C54-C49	irrelevant	irrelevant	(107)
Ni _{0.45} Nb _{0.55}	W ₆ Fe ₇	?	amorphous	-5	?	(108)
YCo ₂	Cu ₂ Mg	?	amorphous	-24	?	(15) (61)
YCo ₃	CeNi ₃	?	amorphous	-12	?	(15) (61)
Y ₂ Co ₇	Co ₇ Er ₂	?	amorphous	-21	?	(15) (61)
YCo ₅	Co ₃ Y	?	amorphous	-12	?	(15) (61)
Y ₂ Co ₁₇	Ni ₁₇ Th ₂	?	amorphous	-1	?	(15) (61)
GdAl ₂	Cu ₂ Mg	?	none	< -7 >	liq.	(109)

The first column gives the compound and its composition. The second column gives the crystal structure either following 'Strukturberichte' or in terms of a prototype structure or by a different common name. The third column gives the type of disorder: a question mark means that the type of disorder has not been investigated; 'anti-site' means anti-site disorder of both components; 'triple-defect' means triple-defect disorder; 'red. int.' means redistribution of interstitials; 'disorder' means that disorder is mentioned in the paper, but that the type of disorder is not specified. The fourth column gives the type of transformation: 'amorphous' means transformation to the amorphous state; 'ss' means transformation to the solid solution and then the crystal structure of the solid solution is specified; 'none' means no transformation; LTP-HTP means a transformation from the low temperature phase in the phase diagram to the high temperature phase and C54-C49 means also a crystalline-to-crystalline transformation. The fifth column gives $\Delta H(a-ss) = H(\text{amorphous}) - H(\text{solid solution})$ in kJ/(mole of atoms). If negative, the material should amorphise, if positive it should transform to the solid solution, unless the type of disorder is not anti-site disorder. Then this column contains the term 'irrelevant'. The < > sign is used to indicate cases, which are not in agreement with the prediction. Information on the type of transformation from the phase diagram is given in the sixth column. A question mark means either that the information is not available or not clear, e.g. in cases where the compound is formed peritectically; 'liq.' means that the compound melts directly from its crystal structure, which could point in the direction of amorphisation; ss > T_c means the formation of a solid solution above a critical temperature, which could point in the direction of the formation of a solid solution. The other indications are self-explaining. The seventh column gives the reference.

known. Disorder in the material was examined by intensity changes of superlattice reflections and a final value of the long-range-order parameter η of 0.7 was inferred (Section 2.2). If the type of disorder were to be triple-defect disorder, the meaning of such a value of η is not clear, the more so because in CoGa with only 4% of vacancies—and so 2% of anti-structure Co atoms—the superlattice reflections are no longer visible (Section 2.5). Apparently the relation between the η value and triple-defect disorder is not obvious. Also in the compounds Fe₃Ge₂, Mn₃Sn₂, Ni₃Sn₂ and Co₃Sn₂ with B8-like structures the hexagonal frame, formed by the non-transition atoms, is preserved during milling (Section 2.6). In both the VIII-IIIa compounds and in these latter compounds the preservation of the original structure by the non-transition atoms, remaining on their own sublattice, prohibits any transformation to a disordered structure, such as the solid solution or the amorphous state.

In contrast, both the low temperature phase (LTP) and high temperature phase (HTP) of the B8-like compound Co₂Ge transform to the amorphous state, as expected following Miedema's model.^(68,69) The reason for this is a great difference in atomic arrangement between

this compound and the 3-2 compounds. In the 3-2 compounds part of the sublattice sites of the transition metal sublattices are empty and during milling transition metal atoms are partly redistributed over the available sublattice sites. This is not possible in Co_2Ge with full occupancy of all sublattice sites. Therefore, the only choice for disorder in Co_2Ge seems anti-site disorder of both components, which leads subsequently to a transformation to the amorphous state. This emphasises once more the importance of anti-site disorder of both components for a transformation to a completely disordered structure (amorphous or solid solution).

In the Nb–Au and Ni–V systems all compounds, apart from the composition Ni_4V_6 , behave as expected. Possibly the positive value of 2 kJ (mole of atoms)^{–1} for the latter compound, whose composition is not far from NiV_2 (amorphous as expected!), can be overcome by grain boundary energy.

Similar arguments as discussed for the compounds so far apply to the further compounds in the table. It is interesting to note that the type of transformation is not determined by the original structure of the compound. This is clear from the results on σ -phases. Most transform to amorphous states, two to the solid solution and one does not transform at all. As mentioned in Section 3.7, in a number of cases there is a rather sharp maximum in the enthalpy curve of the solid solution and there the enthalpy of the solid solution becomes higher than the enthalpy of the amorphous state. Small changes or shifts of the curves would lead to the opposite prediction. This may be the reason that the prediction for the phase transformation in these σ -phases is not correct in relatively many cases. In the case of σ -phases the better prediction is based on the information from the phase diagram.

Intuitively one would expect that atomic disorder in L1_2 compounds is identical to the phase transformation to f.c.c., because of the close relationship of the L1_2 structure to the f.c.c. structure. In fact disordered L1_2 is f.c.c. However, this is not completely true, because the L1_2 to f.c.c. transformation is a first-order transformation accompanied by an abrupt change in the lattice parameter.⁽⁹⁰⁾ The occurrence of a real phase transformation is once more illustrated by Fe_3Ge , which does not transform to f.c.c., but to the b.c.c. α -iron structure.

Finally, three scarce cases of transformations from a complex crystal structure to another complex structure are found in the table. LTP Ni_3Sn_2 and Co_3Sn_2 transform to the HTP structure, while TiSi_2 transforms from the C54 to the C49 structure.

In conclusion we can state that anti-site disorder of both components is a prerequisite for a transformation to a structure without atomic (chemical) long-range order (solid solution or amorphous). Calculations, based on Miedema's semi-empirical model, are useful in predicting phase transformations, if anti-site disorder is induced. In Table 1, 48 compounds are considered. Only in eight cases does the Miedema prediction fail. However, in half of these compounds $\Delta H(\text{a} - \text{ss})$ is only slightly positive (1 to 2 kJ (mole of atoms)^{–1}), so that the grain boundary energy can drive the transformation to amorphous. The general conclusion is that, knowing the type of atomic disorder, we can predict with the aid of Miedema's model the type of phase transformation (amorphous or solid solution) with a probability of about 90%.

3.8. Discussion

The phase transformations, described in Section 3, are all phase transformations far from equilibrium. Therefore, the terms 'entropy' and 'free energy' were avoided as much as possible, because under the circumstances these thermodynamical functions lose their meaning. Rather the kinetic path has to be followed (see Bellon and Martin⁽³⁸⁾ and Appendix D). Conclusions, based on common tangents to free energy curves, may lose their meaning. Still the enthalpy (energy) of the system, frequently used in this review, may have a meaning if we assume this

quantity to be temperature independent in first-order and determined by the arrangement of the atoms in the solid.

There is a question as to whether during all stages of milling homogeneous material is obtained. In scarce cases this is suggested. Clear examples are Nb_3Sn and Nb_3Au for not too short milling periods (Section 2.4.3). A single superconducting transition temperature is here an indication for homogeneous, but still changing, material. Admittedly, this occurs in a milling stage before any transformation. However, in by far the majority of cases during the milling process, and when this process leads to a phase transformation, X-ray diffraction shows a mixture of the original phase and transformed material. A further question is then whether this mixed character is due to the milling process itself, in which not all powder particles are attacked by the ball(s) simultaneously, or whether this has a more fundamental reason. Sometimes, as in the case of some L_{12} compounds, even the end product is a mixture of two phases, solid solution and amorphous. Could it be that both phases have different compositions and that therefore it costs time (diffusion process) before the final state is attained, even long after the l.r.o. parameter has become equal to zero? In $\text{Nb}_{0.58}\text{Au}_{0.42}$ (Section 3.2), after the transformation to the b.c.c. solid solution, traces of an f.c.c. solid solution develop, so that in this system we are also dealing with a mixed final state. There are also contrasting examples. Milling of Co_2Ge (Section 3.4) yields amorphous material after 80 h of milling and no observable changes occur in X-ray diffraction for longer milling times. In contrast, during these longer milling times, the atomic arrangement is certainly still changing. This is clear from a substantial sharpening of the a.c. susceptibility peak. Apparently the material becomes, even after complete amorphisation, more and more homogeneous. If a material is crystalline after milling, we are in fact always dealing with a two-phase product, namely bulk material and material in grain boundaries. It is imaginable that both these phases also differ in composition.

In some cases the magnetisation of magnetic compounds passes through a maximum as a function of milling time. The reason is clear in, for example, CoZr , which first disorders and then transforms to the amorphous state with a low magnetisation (Section 3.1). The explanation for $\sigma\text{-FeCr}$ and $\sigma\text{-FeV}$ (Section 3.6) is different. The decrease of M occurs after the phase transformation to the b.c.c. solid solution. Because of changed mechanical properties further refinement of crystallites could take place, which could lead to a lower magnetisation. Still, a priori, it cannot be excluded that changes in the atomic arrangement in the bulk of the material could play a role.

There are examples where the magnetisation of ball milled transformed material is higher than of the same quenched phase. Ball milled and transformed Ni_3Sn_2 and Co_3Sn_2 are examples. The reason is a special type of disorder in the ball milled samples (Section 3.4). In contrast, transformed FeCr and FeV exhibit a somewhat lower magnetisation than the same quenched b.c.c. phase (Section 3.6). Here nanocrystallinity may play a role.

A further question is: Would mechanical milling (MM) always yield the same end product as mechanical alloying (MA) of the same composition? The answer to this question is not obvious. Let us inspect, for example Fig. 38, the results of enthalpy calculations for the solid solution and the amorphous state of the Co–Zr system. In MA we start from the reference state of just mixed elemental powders, i.e. zero enthalpy. Gaining enthalpy by MA lowers the enthalpy of the system and the first curve that is encountered is the enthalpy curve of the solid solution. In contrast, starting from a compound, the enthalpy is increased and the first curve that is crossed is the curve for the amorphous state. Thus it is imaginable that MA would lead to a solid solution, whereas MM would lead to the amorphous state. Also, based on the non-equilibrium character, i.e. non-linearity of the process, it is imaginable that different

starting states could give different end products (see Appendix D). In spite of these considerations, MA and MM seem to yield the same end products so far.

Considering MM and MA, it could seem somewhat artificial to use pre-alloyed material and MM instead of starting from elemental powders, which are alloyed by the MA process 'by itself'. Of course a fundamental reason for applying MM is to study which changes occur in the material during milling. But there may also be an advantage from a practical point of view. Elemental powders are much more expensive than elemental bulk material, so that pre-alloying and subsequent milling (MM) may be even more economical for obtaining a special metastable end product than applying MA.

4. NEW MATERIALS SYNTHESISED BY MECHANICAL MILLING

4.1. Introduction

From the previous sections it is clear that mechanical milling of an intermetallic compound in a high energy ball mill results in atomic disorder. The disordered materials may remain in the same crystal structure. However, in many cases disorder leads to a catastrophe and causes a transformation to a different structure. These can be the amorphous structure, the simple crystal structure of the solid solution or, in scarce cases, the complex crystal structure of a high temperature phase. If the material is crystalline it always becomes nanocrystalline. The final metastable state, attained after milling, is always different from the starting material and therefore properties can be quite different from the equilibrium stable phases. Sometimes the materials obtained by ball milling even have very special properties because of the special atomic arrangement. The special properties of *amorphous materials* are widely known and treated in many textbooks, *nanocrystalline materials produced by mechanical attrition* were extensively reviewed by Koch,⁽¹¹⁰⁾ special properties of *atomically disordered crystalline materials* are evident from the many examples given in this paper and in a review by Cahn.⁽¹¹¹⁾ Thus there is no need to give a review of these aspects in the present paper. Rather novel and very special spin-glass materials, obtained by milling, are reported. This is a further example of the potentials of the ball milling technique.

4.2. Novel Spin-Glass Materials by Ball Milling of Intermetallic Compounds

In order to prove that very subtle physical properties can be induced by the seemingly rough and crude technique of ball milling and that in fact ball milling creates very subtle states in materials, attention is given in this section to novel spin-glasses, prepared by milling. Spin-glasses were discovered in the 1970s. This discovery opened a new field of solid-state physics.^(112,113,114) A spin-glass is defined as a random, mixed-interacting, magnetic system, characterised by a random, yet cooperative freezing of spins at a well-defined temperature T_i , below which a highly irreversible, metastable frozen state occurs *without the usual long-range spatial magnetic order*. A schematic picture of a random-site spin-glass is given in Fig. 72. The magnetic impurities bearing a moment or localised spin (designated by arrows) are randomly distributed throughout the non-magnetic host metal lattice. An example is Fe atoms in the crystal lattice of Au. The schematic in Fig. 73 illustrates an amorphous spin-glass, in which a periodic lattice is absent and where the ratio of magnetic to non-magnetic sites is an integer. For simplicity a one-to-one ratio was chosen in this figure. Such a positional (or bond) randomness creates an 'impurity' spin-distance distribution, which is essential for a spin-glass. Spin-glass behaviour is not scarce. As a 'magnetic-order' phenomenon it occupies the third

Fig. 72. Schematic picture of a site-random spin-glass.⁽¹¹²⁾

place after ferromagnetism and antiferromagnetism. From the previous explanation it is clear that the most important prerequisites for a spin-glass are randomness, in either position of the spins or the signs of the neighbouring coupling (ferro- or antiferromagnetic), and site- or bond-disorder. Both of these conditions can be achieved by either controlling the chemical compositions of compounds and alloys, or de-crystallising the compounds. The former is attained by diluting into one of the sublattices a magnetic species in a place of a non-magnetic one. Examples are crystalline $\text{Au}_{1-x}\text{Fe}_x$ and $\text{Cu}_{1-x}\text{Mn}_x$ solutions^(112,113,114,115) and the $\text{La}_{1-x}\text{Gd}_x\text{Al}_2$ compound,⁽¹¹⁶⁾ where magnetic Gd is substituted for non-magnetic La. The diluting method can only create a spin-glass with a rather low content of magnetic elements, usually in the range 0.1–10 at.%.^(112,113,114,115,116) For de-crystallisation to obtain amorphous spin-glasses, techniques such as rapid quenching and sputtering are employed. By quenching or sputtering spin-glasses with a magnetic element content even greater than 50 at.% were obtained. However, these are in the amorphous state and are composed of at least two transition metals and of at least two non-transition elements in order to establish the appropriate degrees of ferromagnetic and antiferromagnetic exchange. Examples are amorphous $(\text{Fe}_x\text{Ni}_{1-x})_{75}\text{P}_{13}\text{B}_8$ and amorphous $(\text{Fe}_x\text{Ni}_{1-x})_{75}\text{P}_{16}\text{B}_6\text{Al}_3$.⁽¹¹²⁾ Moreover, most of these exhibit multi-transitions from the paramagnetic to the ferromagnetic and then to the spin-glass state (re-entry behaviour).

Mechanical milling is now known to also create atomic disorder in crystalline compounds as amorphisity. Therefore, it would not be too surprising if mechanical milling could create spin-glass conditions in solids. And indeed it was discovered recently^(80,109,117,118) that mechanical milling can be used as a technique to synthesise various novel spin-glass materials. Two binary

Fig. 73. Schematic diagram of an amorphous (bond-random) spin-glass.⁽¹¹²⁾

spin-glass alloys, namely amorphous Co_2Ge and atomically disordered crystalline GdAl_2 , were obtained by milling. These are special, because amorphous Co_2Ge contains a large amount of the magnetic component (> 50 at.%) and as an amorphous spin-glass only two constituents, while disordered crystalline GdAl_2 contains a much higher concentration of the magnetic component than so far known for crystalline alloys. The spin-glass state of these materials cannot be obtained by traditional rapid solidification techniques. The main results are summarised in the following.

Amorphous Co_2Ge was obtained by mechanical milling of the crystalline compound. Crystalline Co_2Ge turned out to be a ferromagnet at lower temperature, whereas amorphous Co_2Ge appeared to be a spin-glass phase.^(80,117) Figure 74 gives the temperature dependence of the a.c. magnetic susceptibility of amorphous Co_2Ge in different applied fields at a frequency of 109 Hz. A sharp asymmetric cusp at 41 K is observed, when the field is low. This cusp loses its sharpness and becomes a rounded maximum as a result of an increase in the external field. Both the peak intensity and the peak temperature decrease with increasing field. Generally speaking, during cooling of a spin-glass from $T \gg T_f$ to $T \ll T_f$, the following changes take place. First, as the temperature is lowered from $T \gg T_f$, many of the randomly positioned and freely rotating spins build themselves into locally correlated clusters or domains, which can then rotate as a whole. The size and number of various magnetic clusters will increase with decreasing temperature and thus a gradual increase in susceptibility is observed. Such a process can be approximately described by the Curie–Weiss law. As $T \rightarrow T_f$, the various spin components begin to interact with each other over longer distances and the system seeks its ground-state configuration for the particular distribution of spins. This means a favourable set of random alignment axes into which the spins or clusters can lock. So, a more rapid increase in susceptibility and magnetisation is expected. At $T \approx T_f$ all spins or clusters freeze cooperatively in those random directions and the growth of clusters stops. Since the thermal mobility is small,

Fig. 74. Temperature dependence of the a.c. susceptibility χ_{ac} of amorphous Co_2Ge in different external a.c. fields. A frequency of 109 Hz was used.⁽¹¹⁷⁾

upon further cooling to below T_f , the frozen spins or clusters become more difficult to rotate. This leads to a weaker response to a magnetic field. Therefore a decrease in susceptibility is observed upon further cooling. For $T \ll T_f$ various types of excitations manifest themselves within the frozen spin matrix. The sharp cusp can be observed only in low fields, because the true spin-glass equilibrium is obtained only in the limit of zero external field. A sudden change in B or T will result in a long time-scale ($\log t$) relaxation to a new metastable state.⁽¹¹²⁾ Thus, the true equilibrium susceptibility is given by:

$$\chi(T) = \lim_{B \rightarrow 0} \{M(T)/B\}, \quad (23)$$

where T is gradually varied. The observation of the sharp cusp and its sensitivity to external field in amorphous Co_2Ge proves that the material shows the typical spin-glass behaviour, similar to prototype spin-glass alloys, e.g. AuFe .^(112,115) Moreover, a pronounced anomaly in the imaginary part χ'' of the a.c. susceptibility is also observed around T_f . The appearance of this imaginary component means that relaxation processes are indeed affecting the measurement. Decoupling of the spins from each other causes energy absorption.

Low d.c. field magnetisation measurements confirmed the a.c. susceptibility measurements. Figure 75 shows the M/B_a vs T curves of amorphous Co_2Ge in different external d.c. fields. After cooling the sample to 4.2 K in zero field (ZFC) the measurements were made during heating. M/B_a gives the initial d.c. susceptibility $\chi_{d.c.}$ when the applied fields are small, so that the magnetisation is proportional to susceptibility. A sharp maximum, similar to that in the a.c. susceptibility, is evident when measuring in a field of 25 Oe. With increasing field this maximum becomes a rounded transition and shifts to lower temperature. The value of the M/B_a also decreases with increasing field. These observations fully confirm the results of the a.c. susceptibility measurements.

Irreversibility at temperatures below T_f is a characteristic of spin-glasses. The magnetic behaviour differs, depending on whether the material is cooled down with or without field. This

Fig. 75. M/B_a vs T curves of amorphous Co_2Ge in various d.c. magnetic fields after zero-field cooling (ZFC).⁽¹¹⁷⁾

is illustrated by Fig. 76. Here the M vs T curves of amorphous Co_2Ge after zero field cooling (ZFC) and field cooling (FC) in a field of 50 Oe are given. This figure nicely illustrates the difference in temperature behaviour between FC and ZFC samples. The features at T_f are remarkable. The FC magnetisation decreases gradually with increasing temperature, but is virtually independent of time: during an arrest at a given temperature ($T < T_f$), the magnetisation remains unchanged. Furthermore, the process of FC, followed by field warming, is reversible. When we cycled the temperature back and forth (with $B = \text{constant}$), the FC magnetisation traced the same path. In contrast, the ZFC magnetisation is zero until the field

Fig. 76. Temperature dependence of the magnetisation of amorphous Co_2Ge after zero-field cooling (ZFC) and field cooling (FC), measured in a field of 50 Oe.⁽¹¹⁷⁾

is applied. In the presence of an external field the magnetisation increases with increasing temperature until T_f , where the two curves coincide. These traces are irreversible. This means that M_{ZFC} is always drifting upwards. When we continued to increase the temperature above T_f and then cooled the sample back down, first above T_f , the reversible 'paramagnetic' regime was observed, and subsequently by further cooling the magnetisation became the reversible M_{FC} . Thus, the d.c. field, when applied below T_f , creates a metastable and irreversible state in amorphous Co_2Ge . The magnetisation curves at 4.4 K of amorphous Co_2Ge after cooling in zero-field (ZFC) and in a field of 1 T (FC) were also measured. There is a remanence of about $0.09 \mu_B/\text{Co}$ atom in the FC sample. No remanence is observed after zero field cooling. Using the Sherrington–Kirkpatrick theory, the spin-glass order parameter was derived.⁽¹¹⁷⁾ It turned out that this spin-glass phase can be well-described by the Sherrington–Kirkpatrick mean-field theory.

Ferromagnetic GdAl_2 (with a T_c of about 170 K) transforms also to the spin-glass phase by mechanical milling.^(109,118) This was proved by similar experiments as performed for amorphous Co_2Ge . However, there is a big difference. Of course, in the first place Gd is, in contrast to Co, a 4f metal, but more importantly, GdAl_2 did not become amorphous by milling. From X-ray diffraction patterns⁽¹¹⁸⁾ it became clear that during ball milling GdAl_2 remains in the original cubic MgCu_2 structure, but becomes atomically disordered and reaches an average crystallite size of about 21 nm. Figure 77 gives the temperature dependence of the a.c. magnetic susceptibility of GdAl_2 after milling for typical periods. It clearly demonstrates a transition from the ferromagnetic to a new magnetic phase. Simultaneously, the Curie temperature of the ferromagnet decreases slightly until the disappearance of the ferromagnetism after 600 h of milling, where the material completely transforms to the new magnetic phase. This new magnetic phase is a spin-glass phase as was demonstrated by measurements also used for amorphous Co_2Ge . The T_f vs B_{ext} phase diagram could be established for this material and is displayed in Fig. 78. It is obvious that the decrease of T_f is faster in the low field region and

Fig. 77. Temperature dependence of the a.c. susceptibility χ_{ac} of GdAl_2 in a field of 1.2 Oe after milling for typical periods. A frequency of 109 Hz was used.⁽¹⁰⁹⁾

Fig. 78. The T_f vs B_{ext} phase diagram for milled $GdAl_2$. SG: spin-glass region; PM: paramagnetic region. The open circles denote the peak temperatures in the a.c. susceptibility and the filled circles represent the data points from the d.c. magnetisation measurements.⁽¹⁰⁹⁾

is slower in fields higher than about 200 Oe. This again emphasises the peculiar sensitivity of T_f to low fields. As mentioned above, the ordered intermetallic compound $GdAl_2$ is a ferromagnet at lower temperatures with a Curie temperature of about 170 K. It is known that amorphous $Gd_{0.37}Al_{0.63}$ film, prepared by sputtering, shows spin-glass behaviour with a T_f of about 16 K.⁽¹¹⁹⁾ This composition is not far from the composition of $GdAl_2$ for ball milling. However, the amorphous film has a completely different magnetic ordering temperature, which means that ball milled $GdAl_2$ represents a new class of spin-glass materials, because it is neither a dilute solution nor amorphous. It is an atomically disordered intermediate phase.

Discovery of spin-glass behaviour in these materials is of significance because they do not only represent new classes of spin-glass materials, but this discovery also demonstrates the use of mechanical milling as a novel technique to synthesise very special materials. Mechanical milling is even a unique technique for the synthesis of spin-glass phases in binary amorphous systems with the magnetic component as the majority element and in crystalline phases with an unusually large content of the magnetic element. Besides, ball milling is a simple and easily controllable technique. Another advantage of synthesising spin-glass materials by milling is the possibility of producing large quantities of powder, which might be compacted to obtain bulk material for studies of physical properties. This is in contrast to materials obtained by traditional rapid solidification, whereby only thin ribbons or thin films are obtained.

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APPENDIX A. ESTIMATE OF THE DISORDERING ENTHALPY IN COMPLETELY ORDERED COMPOUNDS

A fast and simple way to estimate enthalpy effects in alloys is by the application of Miedema's semi-empirical model.⁽⁶⁷⁾ Recently the model was applied to the problem of disordering in completely ordered alloys.⁽¹²⁰⁾ Let us consider anti-site disorder. Then, in terms of Miedema's model, there are two contributions to the total enthalpy. In the first place there is a chemical contribution, because in the disordering reaction the atom is transferred from a site, where it was mainly in contact with dissimilar atoms, to a site, where it is mainly in contact with similar atoms. The second contribution is an elastic contribution. The atom is brought from a position, in which it did fit completely, to a hole of different size in the other sublattice. This will give rise to an elastic mismatch energy. Therefore the total enthalpy change, when an atom is brought to the 'wrong' sublattice (for example an A atom to the β sublattice) can be written as:

$$\Delta H(A \text{ on } \beta) = \Delta H^{\text{chemical}}(A \text{ on } \beta) + \Delta H^{\text{elastic}}(A \text{ on } \beta). \quad (\text{A1})$$

First we estimate the chemical enthalpy change by using Miedema's model for calculating heats of formation of intermetallic compounds. Following this model the heat of formation of an intermetallic compound, composed of A atoms and B atoms, is per mole of A atoms:

$$\Delta H^{\text{formation}} = f_B^A \Delta H^{\text{interface}}(A \text{ in } B), \quad (\text{A2})$$

where $\Delta H^{\text{interface}}(A \text{ in } B)$ is the chemical, i.e. electronic enthalpy effect of solving one mole of A in an excess of B (infinitely dilute solution). Following Miedema, these chemical enthalpy effects take place at the contact area of the A atom and its surrounding B atoms. The latter quantity is characterised by f_B^A , the degree to which A atoms are in contact with B atoms. In infinite dilution obviously $f_B^A = 1$. Values for $\Delta H^{\text{interface}}(A \text{ in } B)$ for many alloy systems are tabulated in Miedema's book.⁽⁶⁷⁾ In an intermetallic compound the A atoms are not completely surrounded by B atoms, but partially by A atoms as well, and so $f_B^A < 1$. On empirical grounds Miedema estimates the degree to which A atoms are in contact with B atoms in any intermetallic compound as:

$$f_B^A = c_B^A \{1 + 8(c_A^A c_B^A)^2\}, \quad (\text{A3})$$

where c_B^s is the surface fraction of B in the compound defined as:

$$c_B^s = \frac{c_B V_B^{2/3}}{c_A V_A^{2/3} + c_B V_B^{2/3}}, \quad (\text{A4})$$

and a similar definition for c_A^s . Here c_A and c_B are the overall fractions of A and B , respectively, and the molar volume is denoted by V , $V^{2/3}$ being a measure of the atomic surface of the respective components. For further details the reader is referred to De Boer *et al.*⁽⁶⁷⁾

From the above concept $\Delta H^{\text{chemical}}$ (A on β) can be estimated. We proceed as follows. On the α -sublattice the A atom was in contact with a B atom to a degree f_B^A . On a β -position the A atom is surrounded by B atoms to a degree that is equal to the degree for the B atom, which occupied this position before: f_B^B . Obviously $f_B^B = 1 - f_A^B$. Therefore the amount of chemical enthalpy, that corresponds to the displacement of an A atom to the 'wrong' sublattice, is per mole of displaced A atoms:

$$\Delta H^{\text{chemical}}(A \text{ on } \beta) = - (f_B^A - 1 + f_A^B) \Delta H^{\text{interface}}(A \text{ in } B), \quad (\text{A5})$$

and a similar equation for displaced B atoms. For the displacement of one mole of $A + B$ atoms we obtain:

$$\begin{aligned} \Delta H^{\text{chemical}}(A \text{ on } \beta, B \text{ on } \alpha) \\ = - \frac{1}{2} \left(f_B^A - 1 + f_A^B \right) \{ \Delta H^{\text{interface}}(A \text{ in } B) + \Delta H^{\text{interface}}(B \text{ in } A) \}. \end{aligned} \quad (\text{A6})$$

The values of the f factors can be found from eq. (A3). The values of the interfacial enthalpies are tabulated in de Boer *et al.*⁽⁶⁷⁾

As already mentioned, there is a second contribution. A atoms do fit on the sublattice, but do *not* fit on the β -sublattice. When we try to accommodate, for example, a big A atom into a small β -hole, the A atom will be compressed, while the lattice accommodates itself to the new situation by shear. If we accept elastic continuum theory on an atomic level, we can use Eshelby's result:⁽¹²¹⁾

$$\Delta H^{\text{elastic}}(A \text{ on } \beta) = \frac{2K_A G_{AB} (V_A - W_B)^2}{4G_{AB} V_A + 3K_A W_B}, \quad (\text{A7})$$

where K_A is the bulk modulus of metal A , G_{AB} is the shear modulus of the compound, V_A is the molar volume of A and W_B the molar volume of a hole on the β sublattice. In simple cases $W_B = V_B$ is a good approximation. A similar equation holds for B atoms on the sublattice. The problem has been handled in more detail by Beke *et al.*⁽⁶⁴⁾ Since scarcely any values are known for G_{AB} , an estimate from Beke *et al.*^(64,65) can be used:

$$G_{AB} = 1.25 \cdot (c_A G_A + c_B G_B), \quad (\text{A8})$$

where G_A and G_B are the shear moduli of the pure components. Values of the bulk and shear moduli of pure elements are found in Gschneider.⁽¹²²⁾ By the equations given above we are able to estimate the chemical and elastic contributions to the disordering enthalpy in completely ordered compounds in order to get at least an idea of the relative importance of both contributions.

APPENDIX B. ESTIMATE OF THE ENTHALPY OF THE COMPOUND, THE SOLID SOLUTION AND THE AMORPHOUS STATE

By Miedema's semi-empirical model estimates can be made of the enthalpies that are important in the process of phase transformation of the compound to the solid solution or to the amorphous state. The formation enthalpy of the compound is given by eq. (A1) and values for this quantity for systems, in which at least one of the components is a transition metal, have been tabulated.⁽⁶⁷⁾ The formation enthalpy of the solid solution consists of three terms:^(68,69)

$$\Delta H^{\text{ss}} = \Delta H^{\text{chemical}} + \Delta H^{\text{elastic}} + \Delta H^{\text{structural}}. \quad (\text{B1})$$

Since the solid solution is considered to be a random alloy, the degree to which, for example, an A atom is surrounded by B atoms, is given by c_B^s and thus this quantity is to be substituted in eq. (A1) to obtain the chemical contribution to the enthalpy. However, in the semi-empirical model $c_B^s \Delta H^{\text{interface}}(A \text{ in } B)$ is not necessarily equal to $c_A^s \Delta H^{\text{interface}}(B \text{ in } A)$, and therefore in Loeff *et al.*⁽⁶⁸⁾ and Yang and Bakker⁽⁶⁹⁾ the average is taken of both quantities. This leads per mole of atoms to:

$$\Delta H^{\text{chemical}} = c_A c_B \{ c_B^s \Delta H^{\text{interface}}(A \text{ in } B) + c_A^s \Delta H^{\text{interface}}(B \text{ in } A) \}. \quad (\text{B2})$$

The second term to be considered is the mismatch term. For the completely ordered compound the mismatch term was given by eq. (A7) for the transfer of an A atom to the β -sublattice and a similar equation for the transfer of a B atom to the α -sublattice. For the solid solution an equation of the type of eq. (B2) is preferred:

$$\Delta H^{\text{elastic}} = c_A c_B \{ c_B \Delta H^{\text{elastic}}(A \text{ in } B) + c_A \Delta H^{\text{elastic}}(B \text{ in } A) \}, \quad (\text{B3})$$

where:

$$\Delta H^{\text{elastic}}(A \text{ in } B) = \frac{2K_A G_B (W_A - W_B)^2}{4G_B W_A + 3K_A W_B}, \quad (\text{B4})$$

where K_A is the bulk modulus of pure A and G_B is the shear modulus of pure B . W_A and W_B are the corrected volumes for A and B atoms, respectively.⁽⁶⁷⁾ A similar equation holds for $\Delta H^{\text{elastic}}(B \text{ in } A)$.

There is a third term in eq. (B1), the so-called structural term, which is different from zero only for transition metal-transition metal alloys, where both transition metals have partly filled d -shells. It has to do with the preference of certain transition metals to crystallise in the f.c.c./h.c.p. structure or in the b.c.c. structure. Figure 79 shows⁽⁶⁸⁾ the empirical curves of the lattice stability E^{str} of the b.c.c., f.c.c. and h.c.p. crystal structures as a function of the number of valence electrons of the metal. Assuming that in solid solutions atoms form a common d -band, the lattice stability of the solution will have the same functional dependence on the average number of valence electrons per atom $\langle z \rangle$. For example, for 25 at. %–75 at. %, Ni–V holds $\langle z \rangle = 6.25$. The lowest structural energy belonging to this $\langle z \rangle$ value is that of the b.c.c. phase and as a matter of fact we saw in Section 3.3 that NiV_3 crystallises in the b.c.c. structure after ball milling for long enough periods. To evaluate $\Delta H^{\text{structural}}$ from the value found from Fig. 79 we have to subtract as the reference state the weighted average of the structural energies of the pure metals. Now all three (or two) contributions to the enthalpy of the solid solution can be obtained.

In amorphous alloys the structural and elastic contributions are negligible, because there is no crystal structure and the atoms can arrange themselves in such a way that mismatch is avoided. There is however, besides the chemical term in the formation enthalpy (which is taken

Fig. 79. Lattice stabilities as a function of the number of valence electrons for the three main types of crystal structures: b.c.c. (solid curve); f.c.c. (dashed curve); and h.c.p. (dotted curve).⁽⁶⁸⁾

as identical to that in the solid solution), a second term. The second term reflects the topological disorder in the amorphous state and is estimated by Miedema⁽⁶⁸⁾ as $3.5 \langle T_m \rangle$, where $\langle T_m \rangle$ is the average melting temperature. The result is:

$$\Delta H^{\text{amorphous}} = \Delta H^{\text{chemical}} + 3.5 \langle T_m \rangle. \quad (\text{B5})$$

On the basis of eqs (B1) and (B5) diagrams for almost all alloy systems as a function of composition have been constructed as well for the solid solution as for the amorphous state.^(68,69) These have been collected in an atlas. The enthalpy of many compounds is found in de Boer *et al.*⁽⁶⁷⁾ Neither the amorphous state nor the solid solution are likely to be completely random. Most probably there will always be some short-range order, which in particular could affect the value for the chemical terms in both eq. (B1) and eq. (B5). Since in both equations the chemical term is present, the difference in the enthalpy of the amorphous state and the solid solution is scarcely influenced. What could be influenced is the difference in enthalpy of both disordered states with that of the ordered compound. From the scarce examples there seems to be such a tendency.

APPENDIX C. ESTIMATE OF THE ENTHALPY OF PARTLY ORDERED B2 AND L1₂ STRUCTURES

In this report we have encountered a number of times compounds that were partly ordered. In Appendix A disordering in a completely ordered compound was treated, and in Appendix B the enthalpy of the fully disordered compound (solid solution) was estimated. How can we estimate the enthalpy of *partly* disordered B2 and L1₂ structures? For such a compound the occupancy of the neighbouring positions is no longer that of complete order and the equations, given in Appendix A, will not provide a reasonable estimate. Let us for this case adopt the Bragg-Williams approximation of the Ising model for the B2 structure. The results are also valid for the L1₂ structure.⁽²¹⁾ Using the Ising model, for the 'chemical' enthalpy holds:

$$\Delta H(\eta) - \Delta H(1) = \{\Delta H(0) - \Delta H(1)\}(1 - \eta^2), \quad (\text{C1})$$

where all enthalpies are relative to just a macroscopic mixture of the pure components and where η is the long-range-order parameter. $\Delta H(1)$ is the enthalpy of the compound. Estimates of this quantity are tabulated in de Boer *et al.*⁽⁶⁷⁾ The enthalpy $\Delta H(0)$ is the chemical enthalpy of the solid solution, which can be estimated following eq. (B2). For the mismatch enthalpies a similar equation holds,^(64,65) where the mismatch enthalpy of the compound is zero and where the mismatch enthalpy of the solid solution is estimated by eq. (B3). The structural term is absent, because here we are considering only disordering (no real phase transformations) in b.c.c. and f.c.c. type compounds. Summarising: eq. (C1) can be used to estimate the enthalpy difference between the completely ordered compound ($\eta = 1$) and a state with long-range-order parameter η . Equation (C1) was used in Section 2.2.2 to estimate the enthalpy of somewhat disordered RuAl with $\eta = 0.7$, assuming anti-site disorder. (As we discussed in Section 3.8, this type of disorder is not obvious in this VIII–IIIA compound.)

A final remark concerns units. Note that the equations in Appendix A are given *per mole of pairs of disordered atoms*, whereas in Appendix B and C the quantities are given, as usual, *per mole of atoms in the solid*.

APPENDIX D. ORDER–DISORDER INCLUDING BALLISTIC ATOM–ATOM EXCHANGES, A NON-LINEAR PROBLEM

As mentioned before, there are relatively few intermetallic compounds that exhibit an order–disorder transition at a certain temperature in equilibrium. However, disordering is also important, because many intermetallic compounds exhibit a small degree of disorder at higher temperatures and this disorder influences physical properties. Therefore the heat treatment of the alloy (rapidly cooled, slowly cooled or ageing at a certain temperature) may be of influence on properties. By continuous mechanical impact in a high energy ball mill or by irradiation with heavy particles it is possible to disorder materials to even much higher degrees and thus to influence physical properties even more profoundly. Eventually the disorder may drive a phase transformation. The exact mechanism of this disordering by mechanical action is not yet known. But general features of the process can be described by so-called *ballistic atomic jumps*, the number of which depends on the milling intensity. Bellon and Martin⁽³⁸⁾ investigated the problem and emphasised the non-linear character of the process. Only the relatively simple deterministic treatment will be presented here, in a somewhat modified form. Such a treatment is intended to give an impression of the rather unusual and unexpected phenomena that could occur. For more sophisticated treatments the reader is referred to Bellon and Martin⁽³⁸⁾ and, for example, Bellon *et al.*⁽¹²³⁾

Let us again consider a 50%–50% alloy, crystallising in the B2 structure (Fig. 2). We apply the Ising model, which means interaction energies between nearest neighbours only. These interaction energies are denoted by v_{AA} between two neighbouring *A* atoms, v_{BB} between two neighbouring *B* atoms and v_{AB} for a neighbouring *AB* pair. Furthermore, let us assume a direct exchange of *A* and *B* atoms. This is not a realistic mechanism, but leads to the correct stationary state (see the discussion in Section 2.4.3). We apply the Bragg–Williams approximation. This means that, for example, the probability of finding next to an *A* atom on the α -sublattice a *B* atom on the β -sublattice is given only by the occupancy of this sublattice by *B* atoms, c_B^β .⁽²¹⁾ Then we write the change of the number of *A* atoms on the sublattice (N_A^α) per unit time as:

$$\frac{dN_A^\alpha}{dt} = -N_A^\alpha z c_B^\beta \Gamma_{AB}^\alpha + N_A^\beta z c_B^\alpha \Gamma_{AB}^\beta - N_A^\alpha z c_B^\beta \Gamma_b + N_A^\beta z c_B^\alpha \Gamma_b. \quad (D1)$$

Here Γ_{AB}^{ab} is the *thermal* exchange frequency of an A – B pair with A on the α -sublattice and B on the β -sublattice etc. The coordination z is equal to 8. For the meaning of the other quantities see Section 2.4.3. In contrast to the thermal exchange frequencies, the ballistic exchange frequency Γ_b is independent of temperature and dependent on the intensity of ballistic action. In the Bragg–Williams approximation the order–disorder temperature T_c is given by:⁽²¹⁾

$$kT_c = - \frac{zv}{2}, \quad (D2)$$

where k is Boltzmann's constant and v the so-called ordering energy:

$$v = v_{AB} - \frac{v_{AA} + v_{BB}}{2}. \quad (D3)$$

It can be shown⁽³⁸⁾ that eq. (D1) can be written in terms of the long-range-order parameter η , defined by eq. (1), as:

$$\begin{aligned} \frac{1}{2} \frac{d\eta}{dt} = \{ & - \frac{z}{4} (1 + \eta)^2 \exp\left(- \frac{2T_c}{T} \eta\right) + \frac{z}{4} (1 - \eta)^2 \exp\left(+ \frac{2T_c}{T} \eta\right) \} v \\ & \exp\left(- \frac{Q}{kT}\right) + \Gamma_b \{ - \frac{z}{4} (1 + \eta)^2 + \frac{z}{4} (1 - \eta)^2 \}, \end{aligned} \quad (D4)$$

where v is the attempt frequency of the exchange and Q has to do with the potential barrier to overcome and contains all quantities independent of η . After some algebra and substituting the dimensionless quantities:

$$t' = 4t v \exp\left(\frac{-Q}{kT}\right), \quad (D5)$$

and

$$\gamma = \frac{\Gamma_b}{v \exp\left(\frac{-Q}{kT}\right)}, \quad (D6)$$

we obtain ($z = 8$):

$$\frac{d\eta}{dt'} = - (1 + \eta)^2 \exp\left(- \frac{2T_c}{T} \eta\right) + (1 - \eta)^2 \exp\left(+ \frac{2T_c}{T} \eta\right) - 4\gamma\eta. \quad (D7)$$

Let us first consider the first term on the right-hand side only. This is the equation for $d\eta/dt'$ without ballistic jumps:

$$\frac{d\eta}{dt'} (\text{no ballistic jumps}) = - (1 + \eta)^2 \exp\left(- \frac{2T_c}{T} \eta\right) + (1 - \eta)^2 \exp\left(+ \frac{2T_c}{T} \eta\right). \quad (D8)$$

Fig. 80. Curve corresponding to the left-hand side of eq. (D8) without ballistic exchanges for $T_c/T = 6$ and straight lines, representing $+4\gamma\eta$ for three different γ values. The difference between the curve and the straight line gives values for the right-hand side of eq. (D7) and thus for $d\eta/dt'$. For $\gamma = \gamma_2$ the points of intersection are indicated by P , Q and R and the corresponding η values by P ($\eta = 0$), Q' and R' . At the bottom of the figure the sign of $d\eta$ for a positive time step is indicated as well as the direction in which the system moves to a stationary state.

The right-hand side of eq. (D8) is drawn as a function of η in Fig. 80 for a certain value of T/T_c ($=6$) as the curved line. For high values of T/T_c (e.g. 6) this function is equal to 0 for $\eta \approx 1$. This means that the stationary state, i.e. the state in which $\frac{d\eta}{dt'} = 0$, corresponds to (nearly) complete order. Since we are dealing here with only thermal exchanges, this stationary state is also the equilibrium state at this temperature. For higher temperatures the line will intersect the η -axis at a value less than unity. For example, for $T/T_c = 1.5$ the equilibrium state will correspond to $\eta = 0.89$. This is obviously the equilibrium value of η for this temperature. However, the value of the function is also equal to 0 at $\eta = 0$. As can be shown this is an unphysical (unstable) solution.

Let us now consider the case where we do not allow for *thermal* jumps ($T = 0$), but only for *ballistic* jumps. Equation (D7) then becomes:

$$\frac{d\eta}{dt'} = -4\gamma\eta. \quad (D9)$$

The solution is:

$$\eta = \eta_0 \exp(-4\gamma t'), \quad (D10)$$

where η_0 is the starting value ($t' = 0$) of η . From eq. (D10) it is clear that the system will evolve to complete disorder for $t' \rightarrow \infty$.

Now we consider the complete eq. (D7). Figure 80 shows, besides a plot of the first term in the right-hand side of this equation (curve) also straight lines corresponding to $+4\gamma\eta$ for various milling intensities γ . Three different straight lines for three different intensities γ_1, γ_2 and γ_3 of the ballistic action are given. The $+4\gamma_1\eta$ line for the highest intensity intersects the curve only at $\eta = 0$ (point P). It is clear that the stationary state ($d\eta/dt' = 0$) is the state corresponding to $\eta = 0$, i.e. complete disorder. Note that we can no longer speak about thermodynamic equilibrium, because the state of the system is no longer determined by thermodynamics. The $+4\gamma_2\eta$ line intersects the curve at the points P , Q and R . Which points are stable, which are unstable?

Let us inspect the situation on the right-hand side of point $\eta = R'$. For values of $\eta > R'$ the function $d\eta/dt'$ (difference of the curve and the straight line) is negative. This means that a small time step dt' gives a negative value of $d\eta$. Since $\eta(t' + dt') = \eta(t') + d\eta$, the value of η will decrease with time and the system will move towards the value $\eta = R'$. For values of $\eta < R'$ the function is positive. This means that a small time step dt' gives a positive value of $d\eta$. Since $\eta(t' + dt') = \eta(t') + d\eta$, the value of η will increase with time and the system will move also towards the value of $\eta = R'$, but from the other direction. Therefore $\eta = R'$ is a stable point. Similar arguments show that $\eta = 0$ (P) is a stable point. Thus the system exhibits two stable solutions for η . The situation is different for $\eta = Q'$. Right to Q' the function $d\eta/dt'$ is positive, which means $d\eta$ is positive, thus $\eta(t' + dt') = \eta(t') + d\eta$ is increasing with time. The system moves away from $\eta = Q'$. This applies also to the left-hand side of $\eta = Q'$. From this it is clear that $\eta = Q'$ is an *unstable* solution. The sign of $d\eta$ is indicated at the bottom of Fig. 80 by arrows. The instability of Q is once more illustrated by a numerical example: For $\gamma = 100$ and $T/T_c = 6$ the function $d\eta/dt' = 0$ for $\eta = 0.6216820778$. Starting from a value of $\eta = 0.6216820779$, small time steps drive the system towards a stationary ordered state with $\eta = 0.9254$, whereas starting from $\eta = 0.6216820777$ small time steps drive the system to the completely disordered state $\eta = 0$. This is an example of *bifurcation*, the system can go two ways, which is characteristic of non-linear behaviour. Whether in real nature both states can be established is still an open question.

Let us proceed now to the third straight line (γ_3) in the figure. Suppose that starting from intensity γ_2 we increase the milling intensity until intensity γ_3 as indicated in the figure. This gives the tangent of the curve at a value $\eta = \eta_i$. An infinitesimal increase of γ at this point gives a sudden change in η from η_i to 0! By this we conclude that the phase transformation, which was, without ballistic action, a *second-order transition* has now become a *first-order transition*.

From the above considerations it is obvious that temperature is not the only quantity determining the final state of the system. In fact thermodynamics is no longer adequate to handle the problem. The stationary state is obtained by examining the *kinetic path* of the system. The above is an example of *phase transformations far from equilibrium* and has all features of a *non-linear* problem.

Finally we make a Taylor expansion to the first order of the right-hand side of eq. (D7) around $\eta = 0$. The result is:

$$\frac{d\eta}{dt'} = 4 \cdot \left(-1 + \frac{T_c}{T} - \gamma \right) \eta. \quad (D11)$$

If the coefficient of η is negative, the system will evolve from a small positive value of η to 0 and so $\eta = 0$ is a stable solution. This coefficient is in the theory of non-linearity called the *Lyapunov exponent*. Thus $\eta = 0$ is (one of the) stable points if:

$$4 \cdot \left(-1 + \frac{T_c}{T} - \gamma \right) < 0, \quad (D12)$$

which means that the disordered state can be stable for temperatures above:

$$T_c' = \frac{T_c}{1 + \gamma}. \quad (D13)$$

For lower temperatures $\eta = 0$ becomes unstable. Of course, we find the old critical temperature back when $\gamma = 0$.