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Spin-Glass Behavior of Mechanically Milled Crystalline GdAl_2

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We report on the discovery of spin-glass behavior of a crystalline compound with a rather high content of the magnetic component, namely mechanically milled GdAl_2 (mm- GdAl_2). Both ac and dc magnetic susceptibility measurements show a single transition from the paramagnetic to the spin-glass state below 65 K (T_f), which is further confirmed by the observation of thermal irreversibility of the magnetization below T_f . Discovery of spin-glass behavior in mm- GdAl_2 is of significance since it not only represents a new class of spin-glass material but also demonstrates the use of mechanical milling as a novel technique to synthesize various new spin glasses.

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The discovery of spin glasses recently opened a new field of solid state physics [1-3]. This type of magnetic ordering is the third most frequently occurring type of magnetic ordering in solids after ferromagnetism and antiferromagnetism. The most important prerequisites for a spin glass are randomness in either the positions of the spins or the signs of the neighboring coupling (ferromagnetic or antiferromagnetic) and site or bond disorder. Both of these conditions can be achieved by either controlling the chemical composition of compounds and alloys or decrystallizing the materials. The former is attained by substituting into a pure metal or into one of the sublattices of a compound a magnetic species in place of a nonmagnetic one in dilute solution. Examples are $\text{Au}_{1-x}\text{Fe}_x$ and $\text{Cu}_{1-x}\text{Mn}_x$ solutions [1,4], and the compound $\text{La}_{1-x}\text{Gd}_x\text{Al}_2$ [5]. To decrystallize the compounds techniques such as rapid quenching and sputtering have been employed. However, the diluting method can only create spin glasses with rather low content of magnetic elements, usually in the range 0.1 to 10 at. % [1-5]. Although by quenching or sputtering techniques spin glasses with a magnetic element content as high as 70 at. % have been obtained, so far these have been in the amorphous state and have been composed of at least two transition metals and at least two nontransition elements in order to obtain the appropriate degrees of ferromagnetic and antiferromagnetic exchange. Amorphous $(\text{Fe}_x\text{Ni}_{1-x})_{79}\text{P}_{13}\text{B}_8$ and $(\text{Fe}_x\text{Ni}_{1-x})_{75}\text{P}_{16}\text{B}_6\text{Al}_3$ are typical examples [1]. Moreover, most of these materials exhibit multitransitions from the paramagnetic to the ferromagnetic and then to the spin-glass state (reentry behavior). Recently we succeeded in synthesizing a new spin-glass phase with a very high content of the magnetic element and containing two elements only, namely amorphous Co_2Ge . This material was obtained by mechanical milling of the crystalline compound in a high-energy ball mill [6]. This implies that ball milling could be a novel technique for synthesizing spin glasses.

In this Letter, we report on the discovery of spin-glass behavior in the crystalline compound GdAl_2 after high-energy ball milling. Mechanical milling results in atomic

(chemical) disorder but preserves the original crystalline structure. This crystalline disordered compound exhibits a single transition from the paramagnetic to the spin-glass state with a T_f of about 65 K. This means that mechanical milling can create a "pure" spin-glass state even in a crystalline compound with a magnetic element content as high as 33 at. %. Therefore, mechanical milling is a novel and unique nonequilibrium processing technique to synthesize unusual and so far unknown spin-glass materials with a high content of the magnetic element.

The starting compound GdAl_2 was obtained by arc melting of weighed amounts of pure Gd and Al in a purified argon atmosphere and by subsequently annealing at 800 °C for 2 d. Ball milling was carried out in a hardened steel vial under a vacuum of about 10^{-6} Torr. The ac susceptibility measurements were performed in self-constructed equipment (see Ref. [6] for details). The low dc-field magnetization was measured in a self-designed magnetometer. The sensitivity of the magnetometer is better than 10^{-5} A m². ac and dc magnetic measurements were performed on samples with fixed powder particles.

X-ray diffraction patterns showed that the starting compound GdAl_2 had the cubic MgCu_2 structure (C15, Laves phase) with space group $Fd\bar{3}m$ and magnetization measurements demonstrated that the compound is a ferromagnet at lower temperatures with a Curie temperature of about 175 K. This is in agreement with literature [7,8]. It indicates that our starting sample is of good quality. High-energy ball milling resulted in a broadening of all Bragg peaks and the disappearance of a few diffraction lines. These phenomena are quite usual after ball milling intermetallic compounds and are attributed to the introduction of atomic (chemical) disorder, internal stresses, and the refinement of crystallite size. The final crystallite size is found to be about 21 nm after correcting for the internal stress and instrumental broadening. The ferromagnetic transition of the compound became weaker by ball milling as illustrated in Fig. 1, where the temperature dependence of ac susceptibility of GdAl_2 after typical periods of milling is given. Both

FIG. 1. Temperature dependence of the ac susceptibility χ_{ac} of GdAl₂ after milling for typical periods in a field of 1.2 Oe and a frequency of 109 Hz.

the Curie temperature T_C and the transition intensity decrease upon milling, indicating the introduction of defects and the reduction of ferromagnetic phase. After 475 h of milling the T_C is decreased by about 10 K and after 600 h of milling the ferromagnetic transition disappeared completely. On the other hand, starting from 60 h of milling, another anomaly at a quite different temperature, namely at about 45 K, is detected, indicating the formation of a new magnetic phase. The peak temperature and intensity increase with milling time, indicating the homogenization and the increase of the amount of this new magnetic phase. After 600 h of milling the material completely transforms to this new magnetic phase. The transition temperature tends to become constant with a value of 65 K after milling for 1000 h or longer. This new magnetic phase turns out to be a new spin-glass phase but not a ferromagnet. Even after 1210 h of milling, the material could still be identified as crystalline with the MgCu₂ structure. No evidence for amorphization was obtained and the half-widths of both main peaks were $\Delta 2\theta = 1^\circ$, which is small compared to a typical half-width for amorphous alloys of $\Delta 2\theta = 9^\circ$. (The more detailed structural and magnetic changes will be presented elsewhere [9].) All samples milled for 1000 h and longer exhibit the same behavior. Therefore, in the following we will present the characteristic results obtained for a typical sample milled for 1000 h. We will refer to this material as mm-GdAl₂ (mechanically milled GdAl₂).

One of the characteristic features of a spin glass is the occurrence of sharp cusps in the ac and dc susceptibilities and their special sensitivity to the external field. Figure 2 gives the temperature dependence of the ac susceptibility χ_{ac} (the real part) of mm-GdAl₂ in different ac fields measured at a frequency of 109 Hz. The values are normalized by the applied fields. It is clear from

FIG. 2. Temperature dependence of the ac susceptibility χ_{ac} of mm-GdAl₂ at different amplitudes of the external ac field. A frequency of 109 Hz was used.

this figure that a sharp cusp at about 65 K (the freezing temperature T_f) is observed when the external field is low, e.g., 0.1 Oe. This cusp loses its sharpness and becomes a rounded maximum by an increase of the external field. Both peak intensity and 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 physical picture will be the following. 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 should be observed. Such a process can be approximately described by the Curie-Weiss law. When T approaches T_f , the various spin components begin to interact with each other over a longer range and the system seeks its ground state configuration for the particular distribution of spins. This means a favorable set of random alignment axes into which the spins or clusters can lock. So, a more rapid increase in susceptibility and magnetization is expected. At $T \approx T_f$ all spins or clusters freeze cooperatively in those random directions and the growth of clusters stops. Upon further cooling below T_f , since the thermal movement is small it becomes more difficult for the frozen spins or clusters to rotate. This leads to a lower response to an external field and so a decreasing susceptibility. 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 since 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 relaxation to a new metastable state [1]. Thus, the true equilibrium suscep-

FIG. 3. M/B vs T curves of mm-GdAl₂ in various dc magnetic fields after zero-field cooling (open symbols) and field cooling (filled circles).

tibility is given by $\chi(T) = \lim_{B \rightarrow 0} M(T)/B$ where T is gradually varied. The observation of a sharp cusp and its sensitivity to the external field in mm-GdAl₂ proves that the material exhibits a typical spin-glass behavior similar to that observed by Cannella and Mydosh in the prototype spin-glass AuFe [1,4]. Moreover, a pronounced anomaly in the imaginary part of the ac susceptibility is also observed around T_f . The appearance of the imaginary component means that relaxation processes are indeed affecting the measurement and by decoupling the spins from each other they cause the energy absorption.

Furthermore, the results of the ac susceptibility measurements are confirmed by low dc field magnetization measurements. The M/B vs T curves of mm-GdAl₂ in different external dc fields [after zero-field cooling (ZFC) (open symbols) and field cooling (FC) (filled circles)] are given in Fig. 3. After cooling the sample to 4.2 K in zero field (ZFC) and in an external field (FC) the measurement was successively made during heating. The M/B gives the initial dc susceptibility, χ_{dc} , when the applied fields are small so that magnetization is proportional to susceptibility. Now we note just the ZFC curves (open symbols). When applying a field of 40 Oe a sharp maximum is observed like in the ac susceptibility. This maximum becomes a rounded transition and it shifts to lower temperature with increasing field. The value of M/B also decreases with increasing field. These observations fully confirm the results of the ac susceptibility measurements.

Another characteristic feature of spin glasses is the irreversibility at temperatures below T_f . For mm-GdAl₂, this is illustrated in Fig. 3 by the two M/B vs T curves measured in a field of 220 Oe (circles) after ZFC and FC. The features at T_f are remarkable. The FC magnetization (filled circles) decreases gradually with increasing temperature but to a great extent independent of

FIG. 4. Field dependence of the magnetization of mm-GdAl₂ after zero-field cooling and field cooling measured at 5.0 K.

time: When we stopped and waited at a given temperature ($T < T_f$), the magnetization remained unchanged. Moreover, field cooling followed by field warming showed reversibility; i.e., when we cycled the temperature back and forth (with $B = \text{const}$) the FC magnetization traced the same path. In contrast, the ZFC magnetization (open circles) is zero until the field is applied. In the presence of an external field, the magnetization 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 down again, there was first the reversible "paramagnetic" regime above T_f and then during further cooling the magnetization became the reversible M_{FC} . So, the dc field, when applied below T_f , creates a metastable and irreversible state in mm-GdAl₂. In Fig. 4 the magnetization curves of mm-GdAl₂ at 5.0 K after ZFC and FC in a field of 1 T are given. A remanence of about $0.5 \mu_B/\text{Gd atom}$ is clearly observed in the FC sample, whereas there is no remanence in the ZFC sample within the experimental accuracy. The two curves coincide at a field of about 0.6 T. The high-field (from 1 to 3 T) susceptibility is about $4.4 \times 10^{-6} \text{ m}^3/\text{mole Gd}$. This value is much higher than that in the ferromagnetic GdAl₂ compound.

Altogether the results shown above prove that mm-GdAl₂ undergoes a single paramagnetic to spin-glass transition with a freezing temperature of about 65 K upon cooling from room temperature to lower temperatures. The freezing temperature is shifted to lower temperature with increasing magnetic field. Thus the T_f vs B_{ext} phase diagram is established and displayed in Fig. 5. It is obvious that the decrease of T_f is faster in the low field region and is slower in fields higher than about 200 Oe. This again emphasizes the peculiar sensitivity of T_f to low fields in mm-GdAl₂. As mentioned above the ordered intermetallic compound GdAl₂ is ferromagnetic at lower temperatures with a T_C of about 175 K and the

FIG. 5. The T_f vs B_{ext} phase diagram for mm-GdAl₂ (SG, spin-glass region; PM, paramagnetic region). The open circles denote the peak temperatures in ac susceptibility and the filled circles represent the data points from dc magnetization measurements.

T_C value of this ferromagnet is decreased by milling by about 10 K just before the disappearance of this phase. During the intermediate stage of milling, the coexistence of the ferromagnetic phase and the spin-glass phase is found (see Fig. 1), which strongly suggests that atomic (chemical) disorder in the GdAl₂ lattice induces a real magnetic phase transition from a ferromagnet (with a Bragg-Williams long-range order parameter $S_1 \leq 1$) to a spin glass (with a $S_2 < S_1$). The ordering temperature of the spin-glass phase is 110 K lower than that of the original ferromagnetic phase. It is also known that an amorphous Gd_{0.37}Al_{0.63} film obtained by sputtering, whose composition is not far from GdAl₂, shows spin-glass behavior with a T_f of about 16 K (α -GdAl₂) [10]. However, mm-GdAl₂ has a completely different magnetic-ordering temperature ($T_f=65$ K), which means that mm-GdAl₂ represents a new class of spin-glass materials because it is neither a dilute solution nor amorphous. It is a crystalline intermediate phase, but atomically (chemically) disordered and so metastable. With a grain size of about 21 nm the great majority of atoms are bulk atoms, so that the observed phenomena are bulk phenomena and the contribution of grain-boundary atoms is very small. The iron contamination and oxygen content of the samples by the milling tools must be low, because all properties including magnetic properties were completely restored after annealing the samples milled for 1000 and 1210 h to the original phase. Apparently, ball milling is a unique technique to create this spin-glass phase in GdAl₂. It is also interesting to note that the value of T_f of mm-GdAl₂ is higher than that of α -GdAl₂. This could mean that the cluster sizes in mm-GdAl₂ are on the average larger than those in α -GdAl₂. This is further reflected in the value of the paramagnetic Curie temperature, which is about 30 K in α -GdAl₂ [10] and about 84 K in mm-GdAl₂. (This value was obtained by extrapolating χ^{-1} against T using

the high-field magnetic susceptibility data in the temperature range from 100 K to room temperature.) The paramagnetic Curie temperature represents a sum of all the exchange interactions for a completely random alloy. So, ferromagnetic exchanges are more probable in mm-GdAl₂ than in α -GdAl₂.

In conclusion, the crystalline intermetallic compound GdAl₂ exhibits, after mechanical milling in a high-energy ball mill, a single transition from the paramagnetic to the spin-glass state below 65 K. The spin-glass transition temperature is lowered with increasing external field. Discovery of spin-glass behavior in mechanically milled GdAl₂ which remains a crystalline compound is of significance since it not only represents a new class of spin-glass material but also demonstrates the use of mechanical milling as a novel technique to synthesize various new spin glasses. In the alloy systems containing a rather large amount of magnetic element mechanical milling is even a unique technique to synthesize spin-glass phases. Remarkably such a seemingly crude and rough technique as ball milling can induce such a subtle magnetic state as the spin-glass state. Another advantage of synthesizing spin-glass materials by mechanical 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 a small amount of thin ribbons or thin films are obtained.

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