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ELSEVIER

Invited Paper

High-magnetic-field studies of R–T intermetallics

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Abstract

A review is presented of high-field magnetization studies on 3d-rich rare-earth intermetallic compounds. The emphasis is on the evaluation of the intersublattice coupling of the rare-earth and 3d magnetic moments from magnetization studies on monocrystalline samples that are free to orient and reorient themselves in the applied magnetic field. As a first approach, a two-sublattice model is introduced with a dominant anisotropy for one of the sublattices. Several extensions of this model are also discussed. This model is found to be very well applicable to powdered samples prepared from polycrystalline ingots if the powder particles are sufficiently small to consider them as single-grain particles.

1. Introduction

Intermetallic compounds in which the magnetism of the rare-earth (R) ions with their partially filled localized 4f shell is combined with that of the itinerant 3d transition (T) metals form an important class of materials, both for fundamental studies in magnetism as well as from an applications point of view. The 4f and 3d electron spins are coupled by exchange interactions for which three different types are distinguished: T–T, R–T and R–R interactions. For the iron- and cobalt-rich RT compounds, the T–T interaction is the strongest interaction and primarily governs the Curie temperature. The R–R interaction is weak, although its effect contributes to a characteristic variation of the Curie temperature with the rare-earth element in an isostructural series. The R–T interaction, which is intermediate between the two former ones, plays an important role in the magnetism of RT compounds, since it couples the strongly anisotropic R-sublattice magnetization to the less anisotropic T-sublattice magnetization. In this way, some of the RT compounds exhibit large magnetic anisotropies even at room temperature, one of the prerequisites for potential application as permanent-magnet material.

The exchange coupling between the R and T electron spins is indirect: there is an intra-atomic, ferromagnetic exchange interaction between the 4f and 5d spins of the rare-earth ions and an interatomic interaction between the itinerant 5d and 3d spins. For electrons in a less than half-filled d band (the 5d electrons of the rare-earth ions) interacting with electrons in a more than half-filled d band

(3d electrons of the transition metal), the exchange interaction is, in general, found to lead to an antiparallel coupling between the 5d and 3d spins. Taking into account the coupling between the spin and orbital moments of the 4f electrons, it can be explained that the magnetic order is ferromagnetic (parallel R and T magnetic moments) in RT compounds with the light rare earths and ferrimagnetic with the heavy rare earths. The exchange interaction between the 3d and 4f electrons, J_{RT} , is usually represented by a molecular-field parameter, n_{RT} , by which the 4f and 3d sublattice magnetic moments are coupled. Values for this molecular field for the iron- or cobalt-rich RT compounds are typically of the order of 100 T and large magnetic fields are required in order to induce changes in the magnetic moment configuration of the two sublattices. To investigate the strength of the R–T interactions by magnetization measurements, ferrimagnetic compounds are best suited since noncollinear configurations can be induced by external fields irrespective of the presence of magnetic anisotropy. The magnetization curves along different crystallographic directions of the easy-plane, hexagonal compound $\text{Ho}_2\text{Co}_{17}$ provide a good example [1].

The analysis of magnetization curves of the RT compounds is a complex problem, even in the case where the experiments have been performed on monocrystalline samples along the different main crystallographic directions. In the simplest approach, in which a two-sublattice model is used, at least nine parameters have to be evaluated in case of a hexagonal crystallographic structure: five crystal-field parameters representing the rare-earth anisotropy, one anisotropy constant for the 3d sublattice, the sublattice moments of the two sublattices and the molecular field parameter n_{RT} . In reality, the problem is even more complex due to the inequivalent crystallographic sites of the R and T ions, to anisotropic terms in the exchange interac-

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tion, and to anisotropies of the magnetic moments. These complications force us not to restrict the analysis of the experimental data to one single compound, but to consider the trends in the evaluated parameters along the rare-earth series and for different transition metals. But more important, neutron-scattering data, Mössbauer and NMR experiments, thermomagnetic studies and electronic band-structure calculations should be compatible with this evaluation of parameters.

Recently, an elegant method has been developed [2] to derive information on the R–T interaction which, in a first approximation, is not disturbed by other terms in the free energy. This method has first been applied to a monocrystalline sphere (diameter 3 mm) of the compound $\text{Ho}_2\text{Co}_{17}$. In the high-field magnetization experiments, this sphere was free to rotate in the sample holder. Around 20 T, the magnetization curve at 4.2 K was found to exhibit a kink which could be understood as a change from the ferrimagnetic to a canted moment configuration. For magnetic fields above the kinkfield, the magnetization of $\text{Ho}_2\text{Co}_{17}$ is found to be strictly linear in field according to the relation:

$$M = B/n_{\text{RT}}. \quad (1)$$

Powdering the polycrystalline material to a particle size below 30 μm , leads to almost the same result for the magnetization curve. This implies that the powder particles can be considered as a collection of monocrystalline samples. Subsequently, a large number of RT compounds have been studied using this technique, yielding important information on the variation of the parameter n_{RT} with the rare-earth element, with the concentration of 3d elements, with the molar volume, etc. A few aspects of this method are reviewed in this paper.

2. Mean-field description of the magnetization

In a mean-field description, the free energy of a RT compound consisting of two magnetic sublattices with sublattice magnetic moments M_{R} and M_{T} can be represented by:

$$E = E_{\text{a}}^{\text{R}}(\theta_{\text{R}}, \phi_{\text{R}}) + E_{\text{a}}^{\text{T}}(\theta_{\text{T}}, \phi_{\text{T}}) + n_{\text{RT}} M_{\text{R}} \cdot M_{\text{T}} - (M_{\text{R}} + M_{\text{T}}) \cdot B. \quad (2)$$

The first two terms represent the anisotropy energies of the R and T sublattices, respectively. The third term describes the 3d–4f exchange interaction and contains the molecular-field coefficient, n_{RT} , and the angle, α , between the directions of M_{R} and M_{T} . The last term represents the Zeeman energy in an external field corrected for the demagnetizing field. The equilibrium positions of M_{R} and M_{T} can be obtained by minimizing Eq. (2) with respect to the angles θ , ξ and ϕ , which has to be carried out numerically due to the complexity of Eq. (2). The analysis is somewhat simplified by taking the parameters of the 3d

sublattice from an isostructural compound with a non-magnetic rare-earth partner and by only considering the ground-state multiplet for the rare-earth ion.

3. The ‘free-sample’ method and a two-sublattice model

At low temperatures, the R-sublattice anisotropy strongly dominates the T-sublattice anisotropy in the majority of RT compounds. As a first approximation, therefore, we neglect the T-sublattice anisotropy in Eq. (2). As a second approximation we give the sample the freedom to find for any field value its orientation with the lowest energy with respect to the direction of the applied magnetic field, i.e. the direction for which M_{R} is along its preferred direction. With these two assumptions, Eq. (2) reduces to:

$$E = n_{\text{RT}} M_{\text{R}} M_{\text{T}} \cos \alpha - MB, \quad (3)$$

with the resulting magnetization M given by:

$$M = [M_{\text{R}}^2 + M_{\text{T}}^2 + 2M_{\text{R}}M_{\text{T}} \cos \alpha]^{1/2}. \quad (4)$$

The equilibrium directions of M_{R} and M_{T} can now be obtained by minimizing Eq. (3) with respect to α for any field value. Above a first critical field, $B_1^{\text{crit}} = n_{\text{RT}} |M_{\text{T}} - M_{\text{R}}|$, the magnetization can be represented by Eq. (1) up to the second critical field, $B_2^{\text{crit}} = n_{\text{RT}} |M_{\text{T}} + M_{\text{R}}|$, above which the forced ferromagnetic alignment is achieved. A textbook example of this type of magnetization process is the compound $\text{DyCo}_{12}\text{B}_6$, in which the full range of phenomena is observable in magnetic fields up to 40 T; see Fig. 1 [3]. For many other compounds, the second critical field is far above the accessible field range for magnetization measurements. Even the first critical field is not always accessible but here we have the possibility to reduce $|M_{\text{T}} - M_{\text{R}}|$ by appropriate substitutions with, for instance, non-magnetic elements. A prototype for this behaviour is the series $\text{Ho}_2\text{Fe}_{17-x}\text{Al}_x$ [4].

Fig. 1. High-field magnetization curve at 4.2 K of powdered $\text{DyCo}_{12}\text{B}_6$, reflecting the collinear ferrimagnetic, the canted and the forced ferromagnetic moment configurations. The circles represent measurements at constant (for 100 ms) field values; the dotted line corresponds to a measurement in a field decreasing linearly with time at a rate of 50 T/s [3].

4. The 4f–3d exchange interaction

In order to give a more elementary discussion of the interaction between the rare-earth and transition-metal sublattice magnetizations, it is useful to transform the molecular field coefficient n_{RT} into the exchange interaction parameter, J_{RT} , entering in the exchange interaction Hamiltonian $H_{\text{exch}} = -2\sum J_{RT} \mathbf{S}_R \cdot \mathbf{S}_T$. Considering nearest-neighbour interactions only and taking the exchange parameter to be isotropic, the following relation can be deduced:

$$J_{RT} = \gamma_R n_{RT} N_T \mu_B^2 / Z_{RT}, \quad (5)$$

where $\gamma_R = g_R(g_R - 1)$ with g_R the Landé factor, N_T is the number of T atoms per unit of mass and Z_{RT} is the number of T nearest neighbours of a rare-earth atom. The above two assumptions that are behind Eq. (5) have little effect on the variation of the parameter J_{RT} with the rare-earth elements within an isostructural series like the R_2T_{17} compounds. Nevertheless, there is some advantage in not performing the analysis in terms of J_{RT} but, instead, to use the parameter $\gamma_R n_{RT}$ which is directly proportional to J_{RT} and which already takes into account that the nature of the coupling between the R and T sublattices is a spin–spin interaction. A comparison between series with different R/T ratios, like the R_2T_{17} and the $R_2Fe_{14}B$ series, for instance, is less straightforward in that case. A major result of the systematic studies is a decrease in J_{RT} with increasing atomic number of the R element, which was first reported by Belorizky et al. [5] and explained in terms of the lanthanide contraction and the concomitant increase in the 4f–5d distance, which reduces the 4f–5d interaction and consequently the 4f–3d coupling with increasing atomic number of the rare-earth element. Another evident result is the decrease in J_{RT} with increasing concentration of the T element. This decrease is attributed to the decreasing hybridization of the 3d- and 5d-electron states. A similar effect is found for the variation of J_{RT} with the 3d elements where the values for the nickel compounds reveal systematically lower values than those for the iron and cobalt compounds. A third phenomenon that is well documented is the volume dependence of the exchange parameter J_{RT} . In a plot of J_{RT} for a series of Er compounds as a function of the reciprocal volume per formula unit, normalized to one Er atom, a linear dependence between J_{RT} and V^{-1} is deduced with $\partial \ln J_{RT} / \partial \ln V \approx -1$ [6].

5. 3d anisotropy effects on the ‘free-powder’ magnetization curves

The assumption of zero anisotropy for the T sublattice is not always realistic. Especially for the Er compounds, the competition between the Er and T anisotropy can even cause the easy direction of the magnetization to be along the preferential direction of the T sublattice magnetization

instead of along that of the Er sublattice. An example is the compound Er_2Fe_{17} , which shows easy-plane behaviour due to a dominant iron anisotropy even at the lowest temperatures. The effect of a nonzero 3d anisotropy on the ‘free-powder’ magnetization curves has been discussed by Hong et al. and Zhao et al. [7]. Restricting the discussion to the first anisotropy constants of the R and T sublattices, K_1^R and K_1^T , respectively, modified expressions for the two critical fields in the free-powder magnetization curves are found:

$$B_{1,2}^{\text{crit}} = (n_{RT} \pm \Delta) |M_R \mp M_T|, \quad (6)$$

where Δ is given by:

$$\Delta = 2K_1^R K_1^T / [M_R M_T |K_1^R + K_1^T|]. \quad (7)$$

The linear field dependence of Eq. (1) is now replaced by a more complex expression which results in a convex curve for $K_1^R K_1^T > 0$ and a concave one for $K_1^R K_1^T < 0$, both of which intersect the linear curve obtained for $K_1^T = 0$. For easy-plane compounds for which the moment rotations in the free-powder experiments take place in the easy plane, a modulation of the linear magnetization curve is observed in specific cases due to a competition between the R and T in-plane anisotropies. In principle, the value for Δ can be used to further evaluate the anisotropy constants.

6. Extensions to three-sublattice models

It has been noted that in some RT compounds in which the R atoms occupy different crystallographic sites, the magnetic structure of the rare-earth sublattice is not collinear due to different preferential orientations of the rare-earth moments at the different crystallographic sites. Here, the different anisotropies of the two sites are in competition with the 3d–4f exchange that favours a collinear structure of rare-earth and 3d moments. In fact, different anisotropy contributions can also be distinguished for the different 3d sites in, for instance, the 2:17 and 2:14:B compounds, but in these cases the 3d–3d exchange is strong enough to enforce a collinear structure of the 3d sublattice. An applied magnetic field now has the additional effect that the canting between the Er moments will change, resulting in a nonzero differential susceptibility below the first critical field B_1^{crit} :

$$M_{\text{Er}} = M_{\text{Er,I}} \cos \varepsilon_I + M_{\text{Er,II}} \cos \varepsilon_{II}, \quad (8)$$

with

$$\varepsilon_{I,II} = \varepsilon_{I,II}(n_{RT}, E_a^{\text{Er,I}}, E_a^{\text{Er,II}}, B). \quad (9)$$

This type of behaviour is evident for Er_2Fe_{17} [10]. Other easy-plane compounds like Ho_2Co_{17} and Dy_2Co_{17} do not reveal this phenomenon and it is apparently also absent in the easy-axis system Er_2Co_{17} . In ‘free-powder’ magnetization measurements it is hard to obtain reliable quantitative experimental information on the field dependence of this canting angle from the differential susceptibility since

multigrain particles will also contribute to a nonzero susceptibility. Nevertheless, experiments on $\text{Er}_2\text{Fe}_{14-x}\text{Mn}_x\text{B}$, with x -values of 0, 1, 2 and 3, have yielded magnetization curves that very much resemble the calculated curves for a three-sublattice model in which $n_{\text{R,T}}$ and the in-plane anisotropy of the two Er sublattices are taken independent of x [8]. In fact, the magnetization curves of $\text{Er}_2\text{Fe}_{14-x}\text{Mn}_x\text{B}$ suggest that with Mn substitution the resulting 3d moment is reduced and the molecular coupling constant n_{RT} remains virtually unchanged. The reduction of the 3d moment is thought to be due to an antiparallel moment configuration between the iron and manganese moments. The fact that n_{RT} remains constant implies that the intersublattice coupling for Mn is the same as for Fe. In connection with the application of the free-powder technique to rare-earth manganese compounds, a description of a three-sublattice model has recently been provided by Colpa and Brabers [9], who considered two types of exchange interaction: J_{RMn} and J_{MnMn} . High-field free-powder magnetization measurements on RMn_6Ge_6 compounds show antiferromagnetic interactions within the Mn sublattice for the compound YMn_6Ge_6 with a metamagnetic transition around 20 T [10]. Due to the strong R–3d exchange interactions (exchange fields are of the order of 100 T), a collinear ferrimagnetic configuration is found for the RMn_6Ge_6 compounds with $\text{R} = \text{Gd, Tb and Dy}$ with the dominant manganese sublattice moment antiparallel to the rare-earth moment. The results for the exchange parameter J_{RMn} are in line with those for J_{RFe} and J_{RCO} .

7. Summary and conclusions

A review is presented of high-field magnetization studies on 3d-rich rare-earth intermetallics. The emphasis is on the experimental determination of the intersublattice coupling of the rare-earth and 3d magnetic sublattices, especially by the ‘free-powder’ technique. The systematic variation of this parameter with the rare-earth and 3d partner,

as well as with the concentration of the 3d element in the intermetallic, has been addressed. The free-powder technique has been discussed in its most simple approximation in which the anisotropy of one of the two magnetic sublattices is dominant and the anisotropy of the second sublattice, in most cases the 3d sublattice, is neglected. Extensions of the model to a nonzero 3d anisotropy and to a system consisting of three magnetic sublattices that takes into account the multiplicity of the crystallographic sites have also been reviewed.

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