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de Boer, F.R.; Zhao, Z.G.

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Systematics in the 4f–3d exchange interaction in intermetallic compounds

F.R. de Boer*, Z.G. Zhao

Van der Waals–Zeeman Laboratory, University of Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands

Abstract

The 4f–3d interaction in a large variety of intermetallic compounds based on a heavy rare-earth (R) and a transition metal (T = Fe, Co, Ni) has been derived from the magnetisation processes associated with the breaking up of the ferrimagnetic ground-state configuration in these compounds. The magnetisation measurements have been carried out at 4.2 K in fields up to 38 T in the High Field Facility at the University of Amsterdam on small single-crystalline particles that are free to rotate in the external field.

1. Introduction

Intermetallic compounds based on rare-earths (R) with their partially filled 4f shell and the late 3d transition (T) metals form a very important class of materials that find numerous applications in e.g. permanent magnets, magnetostrictive devices and magneto-optical recording, etc. In the R–T compounds with T = Fe, Co, the strongest interaction is the 3d–3d interaction which primarily determines the Curie temperature. The 4f–4f interaction is very weak and can be neglected. The 4f–3d interaction, although much weaker than the 3d–3d interaction, is of special importance since by this interaction the strongly anisotropic R-sublattice magnetisation is coupled to the much less anisotropic T-sublattice magnetisation.

The exchange interaction between the R and T magnetic moments is indirect: it consists of an intra-atomic, ferromagnetic interaction between the 4f and 5d spins and an interatomic interaction between the 5d and 3d spins. The latter interaction between electrons in a less than half-filled d band (5d) and electrons in a more than

half-filled d band (3d) is invariably found to be antiferromagnetic. Therefore, the resulting interaction between the 4f and 3d spins is also antiferromagnetic. In this way, it can be explained that the magnetic order is ferromagnetic in R–T compounds where R is a light rare-earth, so that in this category potential candidates for permanent-magnet applications can be found. On the other hand, the magnetic order is ferrimagnetic if R is a heavy rare-earth. Since the way in which the ferrimagnetic structure is affected by the applied field provides information about the strength of the 4f–3d coupling, the latter type of compounds is very well suited for fundamental magnetisation studies from which the strength of this interaction can be deduced.

Experimental information regarding the 4f–3d interaction can be obtained in various ways. If single crystals are available, the 4f–3d interaction can be derived by analysing the magnetic isotherms measured along the principal crystallographic directions. Another, much less reliable, method is to determine the 4f–3d interaction from the difference in Curie temperature of two isostructural R–T compounds in which R is magnetic and in which R is non-magnetic (Y, La, Lu). Information on the 4f–3d

*Corresponding author.

interaction can also be obtained from neutron-scattering and Mössbauer experiments.

Recently, Verhoef et al. [1, 2] have reported an elegant method to derive reliable quantitative information on the 4f–3d interaction from the high-field magnetisation of very fine powder particles. These particles, having a size of about 40 μm , are assumed to be small enough to be regarded as single crystalline and are free to rotate in the sample holder during the magnetisation process, so that they will be oriented by the applied field with their magnetic moment in the field direction. The validity of these assumptions made for the powder particles has been checked in arising occasions by performing experiments on single-crystalline spheres (diameter 3 mm) which were also free to be oriented by the external field [3].

In general, high magnetic fields are required to break up the ferrimagnetic ground-state configuration. Since 1969, an installation for quasi-stationary high magnetic fields is operational at the University of Amsterdam [4, 5]. In this installation, fields up to 40 T can be generated with a typical duration of 0.1 s and constant within 10^{-4} . The time during which the field can be kept constant is long compared with the typical time for the decay of eddy currents which may be induced in a metallic sample in the periods that the field is varied, so that the installation allows for accurate measurements on metallic specimens like the R–T compounds.

In the present paper, the systematic trends in the 4f–3d interaction derived by means of the free-powder method will be reviewed and new developments in the analysis of the free-powder magnetisation will be presented.

2. Mean-field description of the magnetisation

In a mean-field description, the free energy of a compound consisting of two magnetic sublattices with magnetic moments M_R and M_T is represented by

$$E = E_R^{\text{an}}(\theta_R, \varphi_R) + E_T^{\text{an}}(\theta_T, \varphi_T) + n_{RT} \mathbf{M}_R \cdot \mathbf{M}_T - (\mathbf{M}_R + \mathbf{M}_T) \cdot \mathbf{B}. \quad (1)$$

The first two terms represent the anisotropy energies of the R and T sublattice, respectively, with θ_R and θ_T the polar angles and φ_R and φ_T the azimuthal angles of $\mathbf{M}_R$ and $\mathbf{M}_T$. The third term in Eq. (1) reflects the 4f–3d exchange interaction and contains the molecular-field coefficient n_{RT} and the angle α between $\mathbf{M}_R$ and $\mathbf{M}_T$. The last term in Eq. (2) represents the Zeeman energy in an external field B corrected for the demagnetising field.

The equilibrium directions of $\mathbf{M}_R$ and $\mathbf{M}_T$ can be determined by minimising the free energy with respect to the angles θ , ϕ and α . In general, due to the complexity of

the expressions for $E_R^{\text{an}}(\theta_R, \varphi_R)$ and $E_T^{\text{an}}(\theta_T, \varphi_T)$, this has to be done numerically. However, if the magnetisation is considered of a single crystal that is free to rotate into its minimum-energy direction in the external field, in some cases an analytical expression for the magnetisation may be obtained. Below, the field dependence of the free-powder magnetisation will be discussed for some particular cases of the R- and T-sublattice anisotropies.

3. Non-zero R-sublattice anisotropy and zero T-sublattice anisotropy

In R–T intermetallics, the R-sublattice anisotropy usually strongly dominates the T-sublattice anisotropy. Therefore, the approximation is justified that the T-sublattice anisotropy can be neglected. In this case, during the magnetisation process of a single crystal that can freely rotate in the external field, the R-sublattice magnetisation will be in its easy direction for all possible moment orientations of the two sublattices. In this simple case, no change in anisotropy energy is involved in the magnetisation process and Eq. (1) can be simplified to

$$E = n_{RT} M_R M_T \cos \alpha - B \sqrt{M_R^2 + M_T^2 + 2 M_R M_T \cos \alpha}. \quad (2)$$

The magnetisation curve (Fig. 1) is obtained by minimising the free energy in Eq. (2) with respect to α . At low fields, the moments of the two sublattices are perfectly antiparallel and the magnetisation is $M = |M_T - M_R|$. Above a first critical field, $B_{\text{cr},1} = n_{RT} |M_T - M_R|$, the sublattice moments start to rotate towards each other

Fig. 1. Field dependence of the magnetisation of a single crystal of a ferrimagnetic R–T compound free to rotate in the external field (from Ref. [6]). The magnetisation has been calculated in a mean-field description with a magnetic R sublattice with non-zero anisotropy and a T-sublattice with zero anisotropy.

Fig. 2. The coupling strength $-J_{\text{ErFe}}/k$ in Er-Fe compounds as a function of the reciprocal volume per formula unit ErFe_nM_m .

and the magnetisation is given by $B/M = n_{\text{RT}}$. Above a second critical field, $B_{\text{cr},2} = n_{\text{RT}}(M_{\text{T}} + M_{\text{R}})$, the forced ferromagnetic alignment of the two sublattice moments, corresponding to a magnetisation $M = M_{\text{T}} + M_{\text{R}}$, is reached.

The molecular-field coefficient n_{RT} is related to the exchange-coupling constant J_{RT} , appearing in the interaction Hamiltonian $H_{\text{exch}} = -\sum 2J_{\text{RT}}\mathbf{S}_{\text{R}}\cdot\mathbf{S}_{\text{T}}$, by

$$J_{\text{RT}} = -\frac{g_{\text{R}}}{g_{\text{R}} - 1} \frac{N_{\text{T}}\mu_{\text{B}}^2}{Z_{\text{RT}}} n_{\text{RT}}, \quad (3)$$

with g_{R} the Landé factor, N_{T} the number of T atoms per formula unit and Z_{RT} the number of nearest T neighbours of an R atom.

The complete magnetisation process is not frequently observed, because the second critical field $B_{\text{cr},2}$ is usually much higher than the experimentally accessible fields. Only occasionally, e.g. for $\text{DyCo}_{12}\text{B}_6$ [7], the whole bending process is observed below 40 T. In practice, even the first critical field $B_{\text{cr},1}$ exceeds in most cases the available external fields. However, $B_{\text{cr},1} (= n_{\text{RT}}|M_{\text{T}} - M_{\text{R}}|)$ can be reduced and be brought into the accessible field window by appropriate substitutions of non-magnetic ions on the sublattice with the largest magnetic moment. The experimental results obtained in recent years by means of the free-powder method on practically all known R-T systems and the derived values for the R-T coupling strength J_{RT} are reviewed in detail elsewhere [8]. One main result is the general observation of a systematic decrease of $|J_{\text{RT}}|$ with increasing atomic number Z of the R element in a given R-T series, which was first reported by Belorizky et al. [9] and explained in terms of an increasing 4f–5d distance and therefore decreasing 4f–5d interaction with increasing Z . Another important result is that for each T element $|J_{\text{RT}}|$ decreases with

increasing T concentration of the R-T compound. In Fig. 2, the coupling strength $-J_{\text{ErFe}}/k$ in Er-Fe compounds is plotted as a function of the reciprocal volume per formula unit normalised to one Er atom, i.e. ErFe_nM_m . The correlation in Fig. 2 shows that $|J_{\text{ErFe}}|$ increases with decreasing volume per unit ErFe_nM_m , which may be understood since the 5d–3d hybridisation increases in the same sense.

4. Non-zero T-sublattice anisotropy

In practical cases, the T-sublattice anisotropy turns out not always to be negligible. The influence of the T-sublattice anisotropy on the magnetisation can be derived [10] in analytical form taking into account only the second-order anisotropy terms. In this case, the free energy can be represented by

$$E = K_{\text{T}}^{\text{R}} \sin^2 \theta + K_{\text{T}}^{\text{T}} \sin^2 (\theta + \alpha) + n_{\text{RT}} M_{\text{R}} M_{\text{T}} \cos \alpha - B \sqrt{M_{\text{R}}^2 + M_{\text{T}}^2 + 2M_{\text{R}} M_{\text{T}} \cos \alpha}. \quad (4)$$

Here, θ is the angle between M_{R} and the c axis with a special sign convention [10], and α is the angle between M_{R} and M_{T} . The equilibrium directions of M_{R} and M_{T} can be determined by minimising the free energy with respect to θ and α .

If the R and the T sublattice both possess easy-plane anisotropy, i.e. $K_{\text{T}}^{\text{R}} < 0$ and $K_{\text{T}}^{\text{T}} < 0$, M_{R} and M_{T} will both remain in the basal plane during the entire magnetisation process. In the absence of magnetic anisotropy within the basal plane, M_{R} and M_{T} can freely rotate in this plane and one will observe the simple magnetisation shown in Fig. 1.

If at least one of the sublattices has easy-axis anisotropy, i.e. if $K_{\text{T}}^{\text{R}} > 0$ and/or $K_{\text{T}}^{\text{T}} > 0$, the following field dependence of the magnetisation in the bending process is found [10]:

$$\frac{B}{M} = n_{\text{RT}} - \frac{2K_{\text{T}}^{\text{R}} K_{\text{T}}^{\text{T}} \cos \alpha}{M_{\text{R}} M_{\text{T}} |K|}, \quad (5)$$

with

$$K = [(K_{\text{T}}^{\text{R}})^2 + (K_{\text{T}}^{\text{T}})^2 + 2K_{\text{T}}^{\text{R}} K_{\text{T}}^{\text{T}} \cos 2\alpha]^{1/2}.$$

From Eq. (5) it can be seen that the simple linear behaviour in the bending process as shown in Eq. (5) is regained if K_{T}^{R} or K_{T}^{T} is zero. The correction term in Eq. (5) vanishes for $\alpha = \pi/2$. For this value of α , the magnetisation curve crosses the straight line $B/M = n_{\text{RT}}$.

In Figs. 3(a) and (b), the magnetisation curves to be expected for the case (a) $K_{\text{T}}^{\text{R}} K_{\text{T}}^{\text{T}} > 0$ (i.e. $K_{\text{T}}^{\text{R}} > 0$ and $K_{\text{T}}^{\text{T}} > 0$) and for the case (b) $K_{\text{T}}^{\text{R}} K_{\text{T}}^{\text{T}} < 0$ are schematically

Fig. 3. Schematic representation of the magnetisation curves of a free ferrimagnetic single crystal with (a) $K_1^R K_1^T > 0$ and (b) $K_1^R K_1^T < 0$.

represented. The two critical fields are given [10] by

$$B_{cr,1,2} = \left(n_{RT} \pm \frac{2K_1^R K_1^T}{M_R M_T |K_1^R + K_1^T|} \right) |M_R \mp M_T|. \quad (6)$$

This expression reflects that if both sublattices possess easy-axis anisotropy, i.e. $K_1^R K_1^T > 0$, which is favourable both for the parallel and the antiparallel orientation of the two sublattice moments, indeed $B_{cr,1}$ will increase and $B_{cr,2}$ will decrease. Calculations show that for larger values of the anisotropy constants jumps may occur in the bending process [10].

The free-powder magnetisation of $\text{ErCo}_{10}\text{Mo}_2$ at 4.2 K presents an example of a magnetisation process that corresponds to the case $K_1^R K_1^T < 0$ [11]. In this compound, the Er sublattice has easy-plane anisotropy, whereas the Co-sublattice anisotropy is of easy-axis type. The Er and the Co sublattice have approximately equal moments so that the bending process, that eventually leads to ferromagnetic alignment, starts already in low fields. The result of the fitting procedure is shown in Fig. 4, where also the calculated field dependencies of the moment orientations of the Er and the Co sublattice are shown. At about 60 T, the two sublattice moments are predicted to become parallel. In the bending process, the Er-sublattice moment oscillates around its easy direction.

5. Higher-order anisotropy

In some R–T compounds with strong T-sublattice anisotropy, more complex behaviour of the free-powder

Fig. 4. (a) Calculated free-powder magnetisation (solid line) and experimental free-powder magnetisation at 4.2 K (dots) of $\text{ErCo}_{10}\text{Mo}_2$. (b) Calculated field dependence of the orientations of the Er- and Co-sublattice moments (from Ref. [11]).

magnetisation can be expected. As examples, the free-powder magnetisations of compounds of the systems $\text{Er}_{2-x}\text{Y}_x\text{Co}_7\text{B}_3$ and $\text{Er}_{3-x}\text{Y}_x\text{Co}_{11}\text{B}_4$ are shown in Figs. 5 and 6, respectively. One can see that there are several magnetic transitions in these systems, which may be expected since the Co-sublattice anisotropy is extremely large in these systems. This is manifested by the fields of about 20 T at 4.2 K in both $\text{Y}_2\text{Co}_7\text{B}_3$ and $\text{Y}_3\text{Co}_{11}\text{B}_4$ [12]. If the anisotropy is taken into account up to sixth order, the free-energy expression reads as

$$\begin{aligned} E = & K_1^R \sin^2 \theta_R + K_2^R \sin^4 \theta_R + K_3^R \sin^6 \theta_R \\ & + K_1^T \sin^2 \theta_T + K_2^T \sin^4 \theta_T + K_3^T \sin^6 \theta_T \\ & + n_{RT} M_R M_T \cos \alpha - B \sqrt{M_R^2 + M_T^2 + 2M_R M_T \cos \alpha}. \end{aligned} \quad (7)$$

We have fitted the magnetisation curves of the two Er-rich compounds in the systems $\text{Er}_{2-x}\text{Y}_x\text{Co}_7\text{B}_3$ and $\text{Er}_{3-x}\text{Y}_x\text{Co}_{11}\text{B}_4$. The fitting results are shown in Figs. 5 and 6 and give an average $-J_{\text{ErCo}}/k$ value of 9.9 ± 1.0 K for $\text{Er}_{0.5}\text{Y}_{1.5}\text{Co}_7\text{B}_3$ and $\text{Er}_{0.6}\text{Y}_{1.4}\text{Co}_7\text{B}_3$ and 8.3 ± 1.0 K

Fig. 5. Free-powder magnetisation at 4.2 K of $\text{Er}_{2-x}\text{Y}_x\text{Co}_7\text{B}_3$ compounds. The solid lines are calculated magnetisation curves.

Fig. 6. Free-powder magnetisation at 4.2 K of $\text{Er}_{3-x}\text{Y}_x\text{Co}_{11}\text{B}_4$ compounds. The solid lines are calculated magnetisation curves.

for $\text{ErY}_2\text{Co}_{11}\text{B}_4$ and $\text{Er}_{1.1}\text{Y}_{1.9}\text{Co}_{11}\text{B}_4$. Although the calculated magnetisation curves reflect the presence of the magnetic transitions in a satisfactory way, the overall quality of the fits is very poor, which is reflected in the large error bar in the values of $-J_{\text{ErCo}}/k$. Since in these compounds the Er atoms occupy inequivalent crystallographic sites, it is very likely that for these systems a description of the magnetisation process in terms of more than two magnetic sublattices is needed.

6. Systematics of the exchange interaction in Er–Co compounds

The extensions of the analysis of the free-powder magnetisation to the cases presented in Sections 4 and 5 enable us to determine values for J_{ErCo} also for systems with a more complex magnetisation behaviour for which n_{RT} cannot simply be derived from a linear magnetisation in the region where canting of the two magnetic-sublattice moments occurs. The J_{ErCo} values estimated in Section 5 for the compounds $\text{Er}_2\text{Co}_7\text{B}_3$ and $\text{Er}_3\text{Co}_{11}\text{B}_4$ are compared in Fig. 7 with J_{ErCo} values for other Er–Co intermetallics summarised in Ref. [8]. In Fig. 7, the coupling strength $-J_{\text{ErCo}}/k$ is plotted as a function of the reciprocal volume per formula unit normalised to one Er atom, i.e. ErCo_nM_m . It is seen that the values derived in the present paper for the

Fig. 7. The coupling strength $-J_{\text{ErCo}}/k$ in Er–Co compounds as a function of the reciprocal volume per formula unit ErCo_nM_m .

compounds $\text{Er}_2\text{Co}_7\text{B}_3$ and $\text{Er}_3\text{Co}_{11}\text{B}_4$ obey the general trend of the other Er–Co compounds reported in Ref. [8] that $|J_{\text{ErCo}}|$ increases with this decreasing volume per unit ErCo_nM_m .

7. Conclusions

The magnetic-coupling strength between antiferromagnetically coupled sublattices can in a very simple

way be determined from the free-powder magnetisation of single-crystalline particles if the anisotropy of the transition-metal sublattice can be neglected. It is shown for some specific cases in which the anisotropy of the transition-metal sublattice cannot be neglected, that by taking into account the anisotropies of both sublattices the magnetisation can properly be analysed, providing information regarding the magnetic-coupling strength as well as the anisotropy constants.

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