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The magnetization process in free single-crystalline particles of rare-earth–transition-metal compounds¹

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Abstract

The high-field magnetization of small single crystalline particles of ferrimagnetic rare-earth (R)–3d-transition-metal (T) compounds that are free to rotate in an external field provides direct quantitative information regarding the strength of the 3d–4f interaction. Calculations of the influence of the magnetocrystalline anisotropy of the R and T sublattices on the magnetization process are reviewed and compared with experimental results obtained in the Amsterdam High Field Installation.

1. Introduction

Intermetallic compounds in which the magnetism of the rare-earth (R) ions with their partially filled 4f shells is combined with that of a 3d transition (T) metal form a very important class of materials, both for fundamental studies in magnetism as well as from the point of view of applications. The strongest interaction in RT compounds is the T–T interaction which primarily determines the Curie temperature. The R–R interaction is extremely weak and can be neglected. The R–T interaction, although modest in strength compared with the T–T interaction, plays a very important role in the magnetism of this class of compounds, as it couples the strongly anisotropic R-sublattice magnetization to the much less anisotropic T-sublattice magnetization. In this way, the magnetization of R–T compounds can be strongly

anisotropic which, in the case of uniaxial anisotropy, fulfils one of the prerequisites for potential applications of a compound as permanent-magnet material.

The magnetic coupling between the R and T moments is indirect: there is an intra-atomic, ferromagnetic exchange interaction between the 4f and 5d spins, and an inter-atomic interaction between the 5d and 3d spins. For electrons in a less than half-filled d band (the 5d electrons) interacting with electrons in a more than half-filled d band (the 3d electrons), this latter interaction is generally found to be antiferromagnetic, so that 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 and ferrimagnetic if R is a heavy rare earth. To investigate the strength of the R–T interaction by magnetization measurements, the latter type of compounds is very well suited, since the way in which the ferrimagnetic structure is affected by the applied field provides information about this coupling strength.

¹ Dedicated to Professor K.H.J. Buschow on his 60th birthday.

Usually, 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 [1,2]. In this installation, fields of 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.

Recently [3,4], an elegant method has been developed to derive quantitative information on the R–T interaction from the high-field magnetization of fine powder particles at low temperatures. The 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, so that they will be oriented by the applied field with their moments in the field direction.

Fig. 1. Schematic representation of M_R , M_T , M and B .

the Zeeman energy in an external field B . The angle between M_R and M_T is represented by

$$\cos \alpha = \sin \theta_R \sin \theta_T \cos(\varphi_T - \varphi_R) + \cos \theta_R \cos \theta_T, \quad (3)$$

The resultant magnetization is given by

$$M = \sqrt{M_R^2 + M_T^2 + 2 M_R M_T \cos \alpha}. \quad (4)$$

The equilibrium directions of M_R and M_T can be determined by minimizing the free energy in Eq. (1) with respect to the angles θ , φ and α , which has to be done numerically due to the complexity of the expressions for $E_R^{\text{an}}(\theta_R, \varphi_R)$ and $E_T^{\text{an}}(\theta_T, \varphi_T)$. In the case that the magnetization is considered of a single crystal which is free to rotate into its minimum-energy direction in the external field, the expression for the free energy sometimes becomes less complex and an analytical expression for the magnetization may be obtained. Below, the field dependence of the free-powder magnetization will be discussed for some particular cases of the R- and T-sublattice anisotropies.

3. Magnetization in the case of non-zero R-sublattice anisotropy and zero T-sublattice anisotropy

In general, at low temperatures, the R-sublattice anisotropy strongly dominates the T-sublattice ani-

2. Mean-field description of the magnetization

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

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

The first two terms represent the anisotropy energies of the R and T sublattices, respectively, and are given by

$$E_X^{\text{an}} = K_1^X \sin^2 \theta_X + K_2^X \sin^4 \theta_X + K_3^X \sin^6 \theta_X + K_4^X \sin^m \theta_X \cos m \varphi_X, \quad (2)$$

with $X = R$ or T and $m = 4$ for the tetragonal structure and $m = 6$ for the hexagonal structure. θ_R and θ_T are the polar angles and φ_R and φ_T the azimuthal angles of M_R and M_T (Fig. 1). The third term in Eq. (1) describes the 3d–4f exchange interaction and contains the inter-sublattice molecular-field coefficient n_{RT} . The last term in Eq. (2) represents

sotropy in R–T compounds. Therefore, usually the approximation is justified that the T-sublattice anisotropy can be neglected. Under these circumstances, in the magnetization process of a single crystal that can freely rotate in the applied field, the R-sublattice magnetization 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 magnetization process and Eq. (1) can be simplified to [3,4]

$$E = n_{RT} M_R M_T \cos \alpha - MB, \quad (5)$$

with M given by Eq. (4). The equilibrium directions of M_R and M_T can be determined by minimizing the free energy in Eq. (5) with respect to α . The corresponding magnetization is depicted in Fig. 2. At low fields, the configuration of the moments of the two sublattices is perfectly antiparallel and the magnetization $M = |M_T - M_R|$. Above a first critical field, $B_{cr,1} = n_{RT} |M_T - M_R|$, the moments start to bend towards each other. The magnetization is then represented by

$$B/M = n_{RT}, \quad (6)$$

which allows for a straightforward determination of the parameter n_{RT} . Beyond a second critical field, $B_{cr,2} = n_{RT}(M_T + M_R)$, the forced ferromagnetic alignment of the two sublattice moments, corresponding to a magnetization equal to $M = M_T + M_R$ is reached. It is worth noting that in the case that E_R^{an} and E_T^{an} are both equal to zero, the free energy is also presented in Eq. (5). The corresponding free-powder magnetization (and in this case, because of the absence of anisotropy, also the magnetization of a crystal oriented in any direction with respect to the external field) is also represented in Fig. 2.

In order to compare the R–T coupling in different R–T systems it is worth transforming the n_{RT} values into the coupling constants J_{RT} appearing in the interaction Hamiltonian

$$H_{exch} = - \sum 2 J_{RT} S_R \cdot S_T,$$

which are independent of the number of T neighbours surrounding the R atoms and which are ex-

Fig. 2. Field dependence of the magnetization of a single crystal of a ferrimagnetic R–T compound free to rotate in the external field (from Ref. [5]). The magnetization 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. 3. Field dependence of the magnetization at 4.2 K of free powder particles of $\text{DyCo}_{12}\text{B}_6$ (from Ref. [6]).

pressed per (unit moment)² of a pair of R and T atoms. The relation between J_{RT} and n_{RT} reads

$$J_{\text{RT}} = -\frac{g_{\text{R}}}{g_{\text{R}} - 1} \frac{N_{\text{T}} \mu_{\text{B}}^2}{Z_{\text{RT}}} n_{\text{RT}}, \quad (7)$$

where g_{R} is 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 textbook example of a free-powder magnetization is $\text{DyCo}_{12}\text{B}_6$ [6] in which the complete bending process is observed below 40 T (Fig. 3). Such complete magnetization processes are not frequently observed, because the second critical field $B_{\text{cr},2}$ is usually much higher than the experimentally accessible fields. In practice, even the first critical field $B_{\text{cr},1}$ in most cases exceeds 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 win-

Fig. 4. Dependence of $-J_{\text{RT}}/k$ on the atomic number of the rare-earth element for a number of R-T series. In (a) and (b) open triangles represent Fe compounds, dashed triangles Co compounds and filled triangles Ni compounds.

Fig. 5. The coupling strength $-J_{\text{ErT}}/k$ in Er-T compounds as a function of the reciprocal volume per formula unit ErT_nM_m (from Ref. [7]).

dow 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 [7]. 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 (Fig. 4); this was first reported by Belorizky et al. [8] 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. Fig. 5 shows the coupling strength $-J_{\text{ErT}}/k$ in Er-T compounds plotted as a function of the reciprocal volume per formula unit normalized to one Er atom, i.e. ErT_nM_m . The correlation in Fig. 5 shows that $|J_{\text{ErT}}|$ increases with decreasing volume per unit ErT_nM_m , which may be understood since the 5d–3d hybridization increases in the same sense.

4. Influence of the T-sublattice anisotropy on the magnetization

In Section 3, an expression for the free-powder magnetization in the bending process was derived under the assumption that the anisotropy of the T

sublattice may be neglected. The influence of the T-sublattice anisotropy on the magnetization can be derived in analytical form [9] if only the first-order anisotropy terms are taken into account. In case the basal-plane anisotropy is neglected, M_R , M_T , M and B will be confined to one plane which contains the c -axis and φ_R will be equal to φ_T (see Fig. 1) and the free energy can be represented by

$$E = K_I^R \sin^2 \theta_R + K_I^T \sin^2 \theta_T + n_{RT} M_R M_T \cos \alpha - MB, \quad (8)$$

where M is the resultant magnetization as given by Eq. (4), and θ_R and θ_T are the angles between M_R and M_T and the c -axis, respectively (see Fig. 1). The angle α between M_R and M_T is then equal to $\alpha = \theta_T - \theta_R$, and Eq. (8) can be rewritten as

$$E = K_I^R \sin^2 \theta + K_I^T \sin^2 (\theta + \alpha) + n_{RT} M_R M_T \cos \alpha - MB \quad (9)$$

The equilibrium directions of M_R and M_T can be determined by minimizing the free energy with respect to θ and α . If at least one of the sublattices has easy-axis anisotropy, the following field dependence of the magnetization in the bending process is found [9]:

$$\frac{B}{M} = n_{RT} - \frac{2 K_I^R K_I^T \cos \alpha}{M_R M_T |K|}, \quad (10)$$

with

$$K = \sqrt{(K_I^R)^2 + (K_I^T)^2 + 2 K_I^R K_I^T \cos 2\alpha}.$$

From Eq. (10) it can be seen that the simple linear behaviour in the bending process as given in Eq. (6) is regained if K_I^R or K_I^T is zero. The correction term in Eq. (10) vanishes for $\alpha = \pi/2$. For this value of α , the magnetization curve crosses the straight line $B/M = n_{RT}$.

The free-powder magnetization of $\text{ErCo}_{10}\text{Mo}_2$ at 4.2 K presents an example of a magnetization process that can be described by Eq. (10) [10]. In this compound, the Er sublattice has easy-plane anisotropy, whereas the Co-sublattice anisotropy is of easy-axis type. The Er and Co sublattices have approximately equal moments so that the bending process, which eventually leads to ferromagnetic alignment, starts already in low fields. The result of the fitting

Fig. 6. (a) Calculated free-powder magnetization (solid line) and experimental free-powder magnetization 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. [10]).

procedure is shown in Fig. 6(a), and the calculated field dependences of the moment orientations of the Er and Co sublattices are shown in Fig. 6(b). 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. Influence of the anisotropy within the basal plane on the magnetization

In the case that the R and T sublattices both possess easy-plane anisotropy, both magnetization vectors will remain in the basal plane during the entire magnetization process. In the absence of magnetic anisotropy within the basal plane, one will observe the simple magnetization shown in Fig. 2. In a number of compounds in which the R and the T sublattice both have easy-plane anisotropy, the free-

Fig. 7. Free-powder magnetization at 4.2 K of $\text{Er}_2\text{Fe}_{17}$ [11], $\text{ErFe}_7\text{Ni}_3\text{Si}_2$ [12] and $\text{ErCo}_{10}\text{Si}_2$ [13].

powder magnetization is observed to exhibit oscillatory behaviour in the field interval where the bending of the moments occurs. The oscillations are superposed on the linear magnetization. Examples of compounds exhibiting such oscillatory behavior of the magnetization are $\text{Er}_2\text{Fe}_{17}$ [11], $\text{ErFe}_7\text{Ni}_3\text{Si}_2$ [12] and $\text{ErCo}_{10}\text{Si}_2$ [13] (Fig. 7).

To understand this anomalous behaviour, the magnetic anisotropy within the basal plane has to be taken into account [14]. For a single crystal with a tetragonal crystal structure, in which both sublattice-magnetization vectors are confined to the basal plane, the free-energy expression reads [14]:

$$E = K_4^R \cos 4\varphi + K_4^T \cos 4(\varphi + \alpha) + n_{\text{RT}} \mathbf{M}_R \mathbf{M}_T \cos \alpha - BM. \quad (11)$$

Here, φ is the angle between $\mathbf{M}_R$ and the symmetry axis of the crystal and α is the angle between $\mathbf{M}_R$ and $\mathbf{M}_T$. For $\theta = \pi/2$, the θ -dependent terms in E_R^{an} and E_T^{an} in Eq. (11) are equal to the anisotropy constants K_i^R and K_i^T with $i = 1-3$. They have been omitted from Eq. (11) because they contribute an orientation-independent energy.

The equilibrium directions of $\mathbf{M}_R$ and $\mathbf{M}_T$ can be determined by minimizing the free energy in Eq. (11) with respect to φ and α . In doing this [14], the

following expression for the field dependence of the magnetization in the bending process is found:

$$\frac{B}{M} = n_{\text{RT}} - \frac{16 K_4^R K_4^T \cos \alpha \cos 2\alpha}{M_R M_T |K|}, \quad (12)$$

where

$$K = \sqrt{(K_4^R)^2 + (K_4^T)^2 + 2 K_4^R K_4^T \cos 4\alpha}.$$

The result in Eq. (12) differs from the result in Eq. (6) by the presence of a correction term which vanishes for $\alpha_1 = 3\pi/4$, $\alpha_2 = \pi/2$ and $\alpha_3 = \pi/4$. For these α values, the magnetization curve will cross the straight line $B/M = n_{\text{RT}}$ which is obtained in the absence of anisotropy within the basal plane. Between the crossing points, the magnetization will oscillate.

For compounds with the hexagonal structure the same procedure gives [14]

$$\frac{B}{M} = n_{\text{RT}} - \frac{12 K_4^R K_4^T \cos \alpha (4 \cos^2 \alpha - 3) (4 \cos^2 \alpha - 1)}{M_R M_T |K|}, \quad (13)$$

where

$$K = \left[(K_4^R)^2 + (K_4^T)^2 + 2 K_4^R K_4^T \cos 6\alpha \right]^{1/2}.$$

In this case, the correction term vanishes for five values of α .

Although the occurrence of the oscillations of the magnetization curves shown in Fig. 7 can safely be attributed to the presence of anisotropy within the basal plane, the observed behaviour cannot be described with the formalism presented above only. Closer inspection of the experimental magnetization curves tells us that the experimentally observed number of oscillations exceeds the number predicted by expressions (12) and (13) for tetragonal and hexagonal compounds, respectively.

6. Conclusions

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

simple way be determined from the free-powder magnetization 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 magnetization can properly be analyzed, providing information regarding the magnetic-coupling strength as well as the anisotropy constants.

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