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ELSEVIER

Invited paper

4f–3d interaction and magnetic anisotropy in ThMn_{12} -type rare-earth transition-metal compounds

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Abstract

Rare-earth (R) transition-metal (T) compounds of the R(T,M)_{12} -type with $\text{R} = \text{Y}$ or one of the heavy-rare-earth elements, $\text{T} = \text{Fe}$ or Co and $\text{M} = \text{Ti}$, V , Mo or Si , have been studied at 4.2 K in the Amsterdam High-Field Installation in magnetic fields up to 38 T and at temperatures between 4.2 and 1000 K in other magnetometers. The 4f–3d interaction is derived from magnetization measurements on single-crystalline particles that are free to rotate in the applied fields. The stabilizing element M is shown to have a pronounced influence on the 4f–3d interaction strength in these compounds. The large variation in Curie temperatures of the Y compounds and the different types of magnetic anisotropy found in the Y compounds demonstrate that the element M plays an important role in establishing these properties as well.

Keywords: R(T, M)_{12} -type compounds; Free-powder magnetization; 4f–3d interaction; 3d anisotropy

1. Introduction

The exchange interaction between the rare-earth (R) and transition-metal (T) moments in R–T compounds, the 4f–3d interaction, is of particular importance for the magnetic properties of these compounds. This interaction is of relatively small importance for the Curie temperature which is primarily determined by the 3d–3d interaction, but finds its interest in the fact that it couples the strongly anisotropic magnetization of the R sublattice to the much less anisotropic magnetization of the T sublattice.

Quantitative information about the strength of this interaction can be obtained by various experimental techniques, e.g. magnetic measurements, neutron scattering, Mössbauer experiments. In recent years, a method has been developed [1] to derive the 4f–3d interaction from magnetic isotherms measured in very high magnetic fields on fine single-crystalline powder particles that are free to rotate in the applied magnetic field. By means of this so-called free-powder technique (Section 2), the 4f–3d interaction has recently been investigated in the Amsterdam High-Field Installation at the University of Amsterdam [2] for a large variety of different R–T systems. A detailed review of the results and systematic trends of the 4f–3d interaction within and amongst the series of R–T intermetallic compounds investigated, are presented in Ref. [3]. In the present paper, we will present results on the

4f–3d interaction strength in compounds of the R(T,M)_{12} -type in which R represents a heavy rare-earth, T is Fe or Co, and M (= Ti, V, Mo, Si) is a third element necessary to stabilize the ThMn_{12} structure in which the compounds crystallize. In particular, we will focus on the dependence of the 4f–3d interaction strength on the element M. Furthermore, we have determined the Curie temperatures and the types of magnetic anisotropy of the Y compounds in the above R(T,M)_{12} systems. It is found that the nature of the element M plays an important role in establishing all these quantities.

2. Determination of the 4f–3d interaction by the free-powder technique

We consider the magnetization process of a single crystal that can freely rotate in the applied external field. In R–T intermetallics, the T-sublattice anisotropy is usually negligible with respect to the R-sublattice anisotropy, so that the R-sublattice moment will remain in its easy direction during the entire magnetization process. For this case, a simple molecular-field description shows that three stages can be distinguished in the magnetization process [1]: (a) at low fields, the moments of the two sublattices are perfectly antiparallel and the magnetisation is $M = |M_{\text{T}} - M_{\text{R}}|$; (b) above a first critical field, $B_{\text{cr},1} = n_{\text{RT}}|M_{\text{T}} - M_{\text{R}}|$, where n_{RT} is the molecular-field coefficient, the sublattice moments start to bend towards each other and the magnetization is given by $B/M = n_{\text{RT}}$; (c) above a second critical field, $B_{\text{cr},2} = n_{\text{RT}}(M_{\text{T}} + M_{\text{R}})$, forced paral-

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lel alignment of the two sublattice moments and a magnetisation $M = M_T + M_R$ are reached.

The exchange-coupling constant J_{RT} , appearing in the interaction Hamiltonian $H_{\text{exch}} = -\sum 2J_{RT}S_R \cdot S_T$, is related to n_{RT} by

$$J_{RT} = -\frac{g_R}{g_R - 1} \frac{N_T \mu_B^2}{Z_{RT}} n_{RT},$$

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.

3. The influence of the element M on the 4f–3d interaction

As explained in Section 2, the bending of the R- and T-sublattice moments in R–T intermetallics starts at a critical field given by $B_{\text{cr},1} = n_{RT}|M_T - M_R|$. In the $R(\text{Fe}, \text{M})_{12}$ compounds, the moment of the T (= Fe, M)-sublattice is usually much larger than the R-sublattice moment. This implies that, for these compounds, the values of $B_{\text{cr},1}$ exceed in most cases our experimentally available field of 40 T. The system $R\text{Fe}_{10}\text{Mo}_2$ forms an exception. In these compounds, the introduction of Mo reduces the T (= Fe, Mo)-sublattice moment so strongly that it approaches the R-sublattice moment, making the bending process observable in fields below 40 T (see Fig. 1) [4]. For some of the compounds, deviations are found from the linear behaviour predicted in Section 2. Presumably, this should be attributed to a non-zero anisotropy of the T-sublattice in these compounds. The values for J_{RT}/k derived from the magnetic isotherms are presented in Table 1. Since we do

Fig. 1. Free-powder magnetization at 4.2 K of $R\text{Co}_{10}\text{Mo}_2$ compounds with $R = \text{Dy}, \text{Ho}, \text{Er}$ and Tm .

Table 1

Values for $-J_{RT}/k$ (in K) in $R(\text{T}, \text{M})_{12}$ compounds

	Tb	Dy	Ho	Er	Tm	Ref.
$R\text{Fe}_{10}\text{Mo}_2$	—	9.3	6.9	5.4	5.7	[4]
$R\text{Co}_{11}\text{Ti}$	—	9.8	9.1	8.1	—	[5,6]
$R\text{Co}_{10}\text{Ti}_2$	11.5	9.4	9.9	8.5	—	[7]
$R\text{Co}_{10}\text{V}_2$	10.0	8.8	7.9	8.0	—	[8]
$R\text{Co}_{10}\text{Mo}_2$	8.7	7.7	7.5	6.7	—	[9,10]
$R\text{Co}_{10}\text{Si}_2$	—	6.8	6.5	6.1	5.1	[11,12]

not have available magnetization data from which J_{RT}/k values can be deduced for other $R\text{Fe}_{10}\text{M}_2$ compounds with M elements different from Mo, nothing can be said about the M dependence of J_{RT}/k in the Fe-based compounds.

In the case of $R(\text{Co}, \text{M})_{12}$ compounds, the situation is quite different. Here, the moment of the T (= Co, M)-sublattice has usually about the same size as the R-sublattice moment, allowing to observe the bending process. This process has been studied in detail for compounds in the systems $R\text{Co}_{11}\text{Ti}$ [5,6], $R\text{Co}_{10}\text{Ti}_2$ [7], $R\text{Co}_{10}\text{V}_2$ [8], $R\text{Co}_{10}\text{Mo}_2$ [9,10] and $R\text{Co}_{10}\text{Si}_2$ [11,12]. In Fig. 2, as example, the results on Dy compounds are shown. In $\text{DyCo}_{10}\text{Ti}_2$ and $\text{DyCo}_{10}\text{Mo}_2$, the Dy-sublattice moment and the T-sublattice moment practically compensate and $B_{\text{cr},1}$ is close to zero, whereas in $\text{DyCo}_{10}\text{Si}_2$ and $\text{DyCo}_{10}\text{V}_2$ the two moments are slightly different and $B_{\text{cr},1}$ adopts substantial values. In the case of $\text{DyCo}_{11}\text{Ti}$, the T-sublattice moment exceeds the Dy-sublattice moment. In Table

Fig. 2. Free-powder magnetization at 4.2 K of $\text{DyCo}_{11}\text{Ti}$ and $\text{DyCo}_{10}\text{M}_2$ compounds with $M = \text{Ti}, \text{V}, \text{Mo}$ and Si . The symbols stand for results obtained with step-wise field versus time profiles and the dots represent results obtained in fields that decrease linearly with time.

Fig. 3. The magnetic-coupling strength J_{RT} in $RCo_{10}M_2$ compounds.

1, the values for J_{DyT} derived from the magnetization curves of the $DyCo_{10}M_2$ compounds investigated are presented together with the J_{RT} values found for the other $RCo_{10}M_2$ compounds. A clear dependence of J_{RT} on the stabilizing element M is seen: for $RCo_{10}M_2$ compounds with a fixed rare-earth element, $|J_{RT}|$ decreases with M changing in the sequence Ti, V, Mo, Si. This dependence is visualized in Fig. 3.

Previous studies of the factors that govern the preference in site occupation displayed by the different compounds of the $ThMn_{12}$ -type, have shown that the influence of the nearest-neighbour distance is comparatively unimportant but that the average distance between the atoms residing at the 8i, 8j and 8f sites may have some relevance [13]. Based on average distances the 8i site is preferred by M atoms with metallic radii larger than that of Co, while the 8j and 8f sites are preferred by M atoms of smaller size than the Co atoms. This can qualitatively explain the preference of Ti, V, and Mo for the 8i sites and the preference of Si for the 8f and the 8j sites. Alternatively, one may consider enthalpy effects as controlling factors for the site preference. The 8i sites in $RCo_{12-x}M_x$ have only one nearest-neighbour R atom whereas the 8f and 8j sites have two nearest-neighbour R atoms. Because the enthalpy of mixing of rare earth and M = Ti, V, and Mo is positive [14], these atoms prefer the sites with the lowest contact with the R atoms, which evidently are the 8i sites. By contrast, the mixing enthalpy between rare earth and Si is strongly negative, implying a reluctance of Si for the 8i sites. Our conclusion therefore is that, also when enthalpy effects play a dominant role in determining the site preference of the M atoms in the $RCo_{12-x}M_x$ compounds, one expects a different behaviour for Ti, V and Mo from that of Si.

The site preference discussed above may, at least partially, explain the behaviour of the intersublattice-coupling constant. As mentioned above, the 8f and 8j sites have two

R neighbours whereas the 8i sites have only one R neighbour. Therefore the number of R–Co contacts in the $RCo_{12-x}M_x$ compounds is most effectively reduced in the compounds with Si which substitutes on the 8f and 8j sites. Consequently, the 5d–3d hybridization, responsible for the intersublattice coupling, can be expected to be lower in the Si compounds than in the compounds with Ti, V and Mo. This may explain why the intersublattice-coupling constants reach the lowest values in the Si compounds.

It can also be seen in Fig. 3 that, in each $RCo_{10}M_2$ series, the magnetic-coupling strength $|J_{RT}/k|$ decreases with increasing atomic number Z of the R element involved. This decreasing behaviour has first been reported by Belorizky et al. [15] and explained in terms of an increasing 4f–5d distance and therefore decreasing 4f–5d interaction with increasing Z. This dependence of J_{RT} is commonly encountered in R–T compounds, because it outweighs the opposite effect in which J_{RT} increases with Z due to increasing 5d–3d hybridization [3].

4. The influence of the element M on the 3d anisotropy

The rare-earth-sublattice anisotropy in intermetallic compounds with $ThMn_{12}$ -type structure can be adequately described by means of crystal field theory [13]. By contrast, no such parametrised tool is available for describing the 3d-sublattice anisotropy in these materials. Similar difficulties in describing the 3d-sublattice anisotropy are found in almost all 3d intermetallics, whatever their crystal structure. An impression of these difficulties can be obtained from results of recent band-structure calculations made for the compound YCo_5 [16], showing that the correlation between the presence of anisotropy and the presence of an orbital moment on the 3d atoms is too simple a picture.

Fig. 4. Anisotropy diagram of $Y(Fe,M)_{12}$ and $Y(Co,M)_{12}$ compounds. References: $YFe_{11}Ti$ [13], $YFe_{10}V_2$ [18], $YFe_{10}Cr_2$ [19], $YFe_{10}Mo_2$ [19], $YFe_{10.8}W_{1.2}$ [19], $YFe_{10}Si_2$ [19], $YCo_{11}Ti$ [20], $YCo_{10}Ti_2$ [7], $YCo_{10}V_2$ [8], $YCo_{10}Mo_2$ [9,21], $YCo_{10}Si_2$ [12].

In several of the 3d-based intermetallics, the interesting observation was made that Co and Fe atoms give rise to anisotropies of opposite sign when occupying the same type of sites in a given crystal structure [17]. Well-known examples are $Y\text{T}_3$, $Y_2\text{T}_{17}\text{N}_3$ and $Y_2\text{T}_{14}\text{B}$. The latter compounds have easy-plane anisotropy for $\text{T} = \text{Co}$ and easy-axis anisotropy for $\text{T} = \text{Fe}$. The opposite behaviour is observed in the first two compounds. For the ThMn_{12} -type of compounds studied in the course of the present investigation, this controversial behaviour between Co and Fe compounds is seen in Fig. 4 to be only found in the compounds formed with Si and V.

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