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Magnetic behaviour of heavy rare earth compounds of the type $RFe_{10}Cr_2$

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Abstract

Lattice constants, high field magnetic isotherms at 4.2 K, Curie temperatures and spin reorientation temperatures are reported for $RFe_{10}Cr_2$ compounds with $R \equiv Y$, Gd, Tb, Dy, Ho, Er, Tm, Lu. The value of the rare earth–transition metal (T) magnetic coupling constant J_{RT}/k derived by a mean field analysis of the Curie temperatures is about -15 K. This value is larger than the value of about -9 K obtained in a mean field analysis of the effect of the departure of the perfect collinear ferrimagnetic orientation of the sublattice magnetizations occurring in high magnetic fields. A tentative spin phase diagram for the $RFe_{10}Cr_2$ series is presented.

1. Introduction

Recently, many groups have investigated the iron-rich ternary compounds of the type $R(Fe,T)_{12}$ in which R is a rare earth element and T is a stabilizing element such as titanium, vanadium, chromium, silicon, etc. All these compounds crystallize in the $ThMn_{12}$ type of structure [1]. In particular, the compounds of the type $Sm(Fe,Ti)_{12}$ have relatively high values for the saturation magnetization, Curie temperature and magnetocrystalline anisotropy, which opens possibilities for application as permanent magnet materials.

The earliest studies of the structural and magnetic properties of $R(Fe,Ti)_{12}$ alloys have been carried out by Ohasi *et al.* [2], Buschow [3], Li Hong-shuo *et al.* [4], Moze *et al.* [5] and Hu *et al.* [6]. The properties of $RFe_{10}V_2$ alloys were studied by Buschow [3], de Boer *et al.* [7], Helmholdt *et al.* [8] and Gubbens *et al.* [9]. Stefanski *et al.* [10] and Buschow and de Mooij [11] studied the structural and magnetic properties of the $RFe_{10}Cr_2$ series.

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In this contribution we present additional information regarding the magnetic properties of $RFe_{10}Cr_2$ compounds in which R is a heavy rare earth, using high field magnetization measurements and a.c. susceptibility measurements.

2. Experimental details

Polycrystalline samples of nominal composition $RFe_{10}Cr_2$ where R is yttrium or one of the heavy rare earths (R≡Gd, Tb, Dy, Ho, Er, Tm, Lu) were prepared by arc melting of stoichiometric amounts of the constituent elements (99.9 wt.% purity or better) under an argon atmosphere. The ingots were melted several times to ensure homogeneity. After this the ingots were wrapped in tantalum foil, sealed in evacuated quartz tubes, annealed for several weeks between 900 and 950 °C and then rapidly cooled to room temperature.

Standard measurements of the initial susceptibility were performed between 4.2 and 350 K. Magnetization measurements were performed in the temperature range from 77 to 1100 K in a Faraday balance in fields up to 1 T and between 4.2 and 300 K in an extraction magnetometer in fields up to 7 T. In the High Field Installation at the University of Amsterdam [12] magnetization measurements were carried out at 4.2 K in fields up to 35 T. The high field measurements were made on powder samples of cylindrical shape prepared by aligning powder particles parallel and perpendicular to the cylinder axis in a magnetic field of 1 T at room temperature and by fixing their direction with epoxy resin. The magnetic isotherms were recorded with the external field applied either parallel or perpendicular to the alignment direction of the powder particles. In order to simulate the results of easy axis magnetization measurements on single crystals, measurements were also made on powder particles free to orient themselves in the applied field. The spin reorientation temperatures T_{sr} were derived from initial susceptibility measurements.

3. Experimental results and discussion

X-ray diffraction showed all compounds to crystallize in the $ThMn_{12}$ structure with α-Fe as a second phase. It turned out to be impossible to prepare samples that were completely single phase. The lattice constants, derived from the X-ray diffraction patterns by means of a least-squares fitting, are listed in Table 1. The ytterbium compound could not be prepared owing to the high vapour pressure of ytterbium metal.

The Curie temperatures of the compounds were obtained from $M(T)$ measurements by means of M^2 *vs.* T plots. The T_C values derived are also listed in Table 1. The presence of α-Fe in the samples is clearly manifested by high temperature tails in the $M(T)$ curves which disappear around 1040

TABLE 1

Lattice constants a and c, ratios a/c, cell volumes V, Curie temperatures T_C and spin reorientation temperatures T_{sr} of $RFe_{10}Cr_2$ compounds

R	a (Å)	c (Å)	a/c	V (Å^3)	T_C (K)	T_{sr} (K)
Y	8.415	4.733	1.778	335.2	525	
Gd	8.503	4.757	1.787	343.9	580	
Tb	8.502	4.769	1.783	344.7	525	255, 290
Dy	8.497	4.769	1.782	344.3	495	75, 175
Ho	8.448	4.747	1.780	338.8	485	80
Er	8.426	4.742	1.777	336.7	475	55
Tm	8.416	4.732	1.778	335.2	465	
Lu	8.412	4.736	1.788	335.1	450	

K, the Curie temperature of iron. From the $M(T)$ curves the contribution of iron to the low temperature magnetization could be estimated. It was deduced that the presence of α-Fe in some of the samples amounts to about 10 wt.%, as already indicated by the X-ray diffraction results.

In order to derive information regarding the magnetic coupling constants J_{TT} and J_{RT} between the rare earth (R) and 3d (T) moments in the $RFe_{10}Cr_2$ series, we have performed a standard mean field analysis of the observed Curie temperatures. Values for J_{TT} can be deduced from the T_C values for the compounds $YFe_{10}Cr_2$ and $LuFe_{10}Cr_2$ which do not contain a magnetic rare earth ion by means of the expression

$$J_{TT}=\frac{3T_C}{2Z_{TT}S_T(S_T+1)} \tag{1}$$

where Z_{TT} represents the number of nearest-neighbour T atoms of a T atom and S_T is the quasi-spin of the T ions, defined by $\mu_T=2S_T$. For the crystal structure of the $RFe_{10}Cr_2$ compounds $Z_{TT}=10$. Owing to the large amount of iron present as impurity phase in the samples, it is not possible to extract very accurate values for μ_T from the magnetization measurements. As will be discussed later in this paper, 1.4 μ_B represents a plausible value for the average magnetic moment of the transition metal atoms in the $RFe_{10}Cr_2$ compounds. Hence $S_T=0.7$. Using the T_C values for $YFe_{10}Cr_2$ and $LuFe_{10}Cr_2$ presented in Table 1, we find by means of eqn. (1) values for J_{TT}/k in these two compounds equal to 66 and 57 K respectively.

Values for J_{RT} can be obtained by comparing the Curie temperatures of the compounds containing a magnetic rare earth element with those of $YFe_{10}Cr_2$ or $LuFe_{10}Cr_2$. If we consider the T_C values listed in Table 1, it is clear that the high value observed for $YFe_{10}Cr_2$ is not a value to be expected for an $RFe_{10}Cr_2$ compound in which R is a non-magnetic heavy rare earth, whereas the value for $LuFe_{10}Cr_2$ fits nicely into the sequence of observed T_C values. Therefore, in evaluating J_{RT} values, we will use the T_C value of $LuFe_{10}Cr_2$. The expression for J_{RT} reads [13]

$$\left(\frac{J_{\mathrm{RT}}}{k}\right)^2 = \frac{9T_{\mathrm{C}}^{\mathrm{R}}(T_{\mathrm{C}}^{\mathrm{R}} - T_{\mathrm{C}}^{\mathrm{Lu}})}{4Z_{\mathrm{RT}}Z_{\mathrm{TR}}S_{\mathrm{T}}(S_{\mathrm{T}}+1)G} \tag{2}$$

where Z_{TR} denotes the number of R neighbours to the T atom, Z_{RT} is the number of T neighbours to the R atom and G represents the de Gennes factor $(g_{\mathrm{R}}-1)^2J(J+1)$. For the $\mathrm{RFe_{10}Cr_2}$ compounds we have used $Z_{\mathrm{TR}}=2$ and $Z_{\mathrm{RT}}=20$. Inserting the above values in eqn. (2) and using the T_{C} values for $\mathrm{GdFe_{10}Cr_2}$ and $\mathrm{LuFe_{10}Cr_2}$, we find a value J_{GdT}/k equal to -15.0 K.

Figure 1 shows the temperature dependence of the initial susceptibility for the $\mathrm{RFe_{10}Cr_2}$ compounds with R ≡ Tb, Dy, Ho Er, Tm, Lu. For all compounds investigated we observed a small discontinuity in the $\chi(T)$ curve slightly below 300 K. This discontinuity is due either to the cryostat or to small amounts of an impurity phase common to all samples and therefore will be left out of consideration. Indications for a single spin reorientation were found in $\mathrm{RFe_{10}Cr_2}$ with R ≡ Ho, Er. There are two transition temperatures in the $\chi(T)$ curves of $\mathrm{TbFe_{10}Cr_2}$ and $\mathrm{DyFe_{10}Cr_2}$. The spin reorientation temperatures listed in Table 1 correspond to the arrows marking the phase

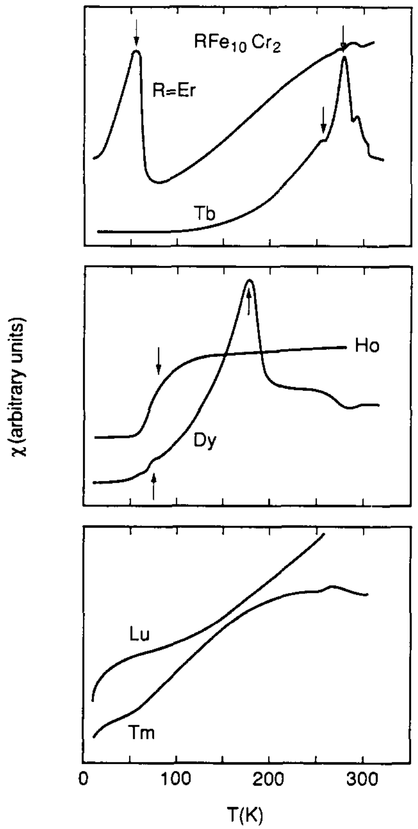
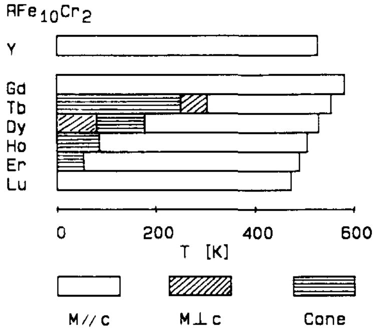


Fig. 1. Initial susceptibility in arbitrary units *vs.* temperature for the $\mathrm{RFe_{10}Cr_2}$ compounds with R ≡ Tb, Dy, Ho, Er, Tm, Lu.

transitions in Fig. 1. Having no information on the types of magnetic structures that are stabilized at the various spin reorientation temperatures, we assume that analogy exists with the behaviour of the isostructural $R(Fe,Ti)_{12}$ compounds [14]. In that case, with decreasing temperature, a transition in easy magnetization direction from the axial to complex structure occurs in the $RFe_{10}Cr_2$ compounds with R ≡ Ho, Er. $TbFe_{10}Cr_2$ and $DyFe_{10}Cr_2$ exhibit more complex behaviour. If the analogy mentioned is valid, the easy magnetization direction in $TbFe_{10}Cr_2$ changes with decreasing temperature, first from axial to planar at 290 K, then from planar to complex at 255 K. In $DyFe_{10}Cr_2$, the easy magnetization direction changes from axial to complex at 175 K and from complex to planar at 75 K. A tentative spin phase diagram of the $RFe_{10}Cr_2$ series is presented in Fig. 2.

In Fig. 3 the high field magnetization results at 4.2 K are shown for magnetically aligned samples of the $RFe_{10}Cr_2$ compounds with R ≡ Y, Gd, Lu with the field applied parallel or perpendicular to the alignment direction. Owing to the misalignment which is inevitably present, it is difficult to determine the anisotropy fields very accurately. For the yttrium and lutetium compounds the anisotropy fields are very similar, about 3 T; for the gadolinium compound it is around 5 T. The values of the saturation magnetization derived from the curves shown for $YFe_{10}Cr_2$ and $LuFe_{10}Cr_2$ are equal to 16.8 and 17.2 μ_B per formula unit respectively. From these values we derive an average value of the 3d moment in these compounds equal to 1.4 μ_B T per atom. The 4.2 K isotherms for the R ≡ Tb, Dy, Er, Tm compounds are shown in Fig. 4. In all these data there is little difference between the two alignment directions, which may be considered as confirmation of the occurrence of a complex structure at 4.2 K in most of these compounds. The high iron impurity level in the samples prevents us from establishing the intrinsic magnetization values of the various compounds accurately enough to apply the usual analysis in terms of antiferromagnetically coupled R and iron sublattice moments.



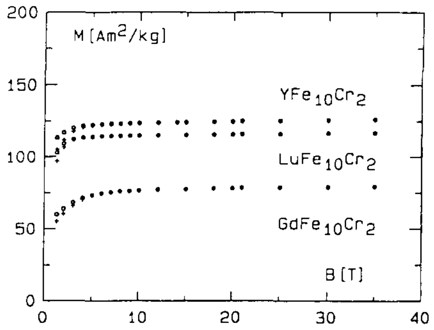


Fig. 2. Tentative phase diagram for the $RFe_{10}Cr_2$ series.

Fig. 3. High field magnetization curves at 4.2 K for magnetically aligned powder samples of $YFe_{10}Cr_2$, $GdFe_{10}Cr_2$ and $LuFe_{10}Cr_2$ with the external field parallel (O) and perpendicular (+) to the alignment direction.

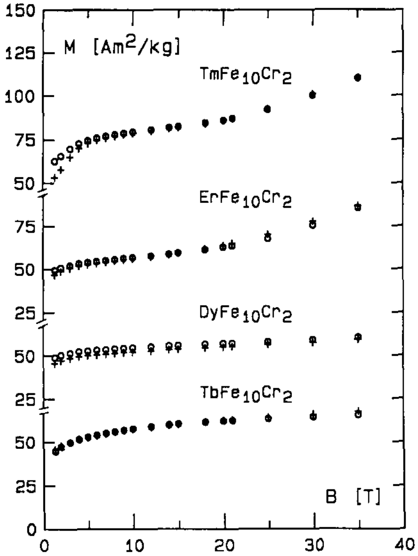
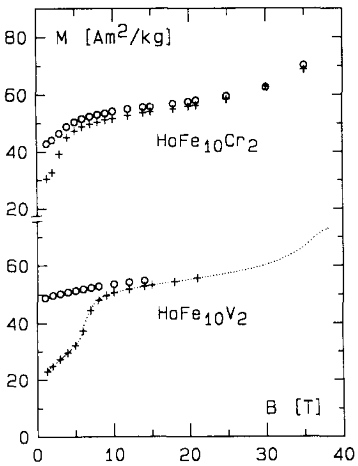


Fig. 4. High field magnetization curves at 4.2 K for magnetically aligned powder samples of $TbFe_{10}Cr_2$, $DyFe_{10}Cr_2$, $ErFe_{10}Cr_2$ and $TmFe_{10}Cr_2$ with the external field parallel (O) and perpendicular (+) to the alignment direction.

Interesting features are encountered in the high field curves of $HoFe_{10}Cr_2$ shown in Fig. 5. In both curves, in the curve with B perpendicular to the alignment direction in particular, one may recognize a jump-like increase in magnetization. This jump-like increase was also observed in $HoFe_{10}V_2$ and the corresponding magnetic isotherms have been included in Fig. 5. These jumps in the isotherms are interpreted as first order magnetization process (FOMP) transitions, giving evidence of field-induced transitions from one spin structure to another. In Fig. 6 the results are shown of high field magnetization measurements on fine powder particles of $HoFe_{10}Cr_2$, $ErFe_{10}Cr_2$ and $TmFe_{10}Cr_2$ free to be rotated into their minimum energy direction by the applied field. It has been shown [15] that the magnetization of small particles of R–T compounds with R a heavy rare earth element will increase linearly with the field in sufficiently high fields if the R anisotropy is infinitely large and the T anisotropy can be neglected. Under this condition the field dependence of the magnetization of a ferrimagnetic system can be described very simply. For relatively low fields the moment configuration is expected to be strictly antiparallel and the magnetization $M_S = |M_T - M_R|$. Beyond a critical field strength ($B_{crit} = |M_T - M_R| n_{RT}$) the exact antiparallel moments start to bend towards each other and the magnetic moment is described by $M = B/n_{RT}$. The quantity n_{RT} represents the intersublattice-coupling constant. It is seen in Fig. 6 that only for R≡Tm is there a tendency for the high field magnetization to depend linearly on the field, but that the extrapolations to zero field do by no means pass through the origin. This is very likely due to the large amount of iron impurity present in the samples. Using the



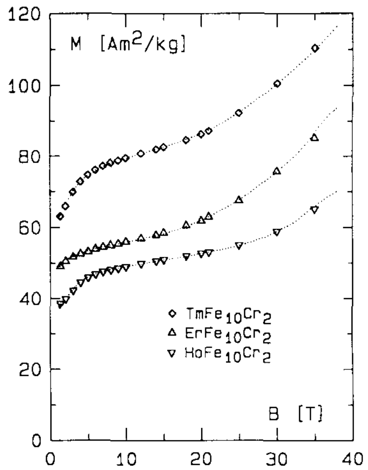


Fig. 5. High field magnetization curves at 4.2 K for magnetically aligned powder samples of $HoFe_{10}Cr_2$ and $HoFe_{10}V_2$ with the external field parallel (○) and perpendicular (+) to the alignment direction. The dotted curve corresponds to data taken during a controlled field pulse in which the field decreased linearly in time at about 55 T s^{-1}.

Fig. 6. High field magnetization curves at 4.2 K for powder particles of $HoFe_{10}Cr_2$, $ErFe_{10}Cr_2$ and $TmFe_{10}Cr_2$ free to orient themselves in the applied magnetic field. The dotted curves correspond to data taken during controlled field pulses in which the field decreased linearly in time at about 55 T s^{-1}.

expression

$$\frac{dM}{dB}=\frac{1}{n_{RT}} \tag{3}$$

and using for dM/dB the slope of the $M(B)$ curve observed for $TmFe_{10}Cr_2$ at the highest field applied, we obtain $n_{TmT}=3.33$ T formula units per μ_B. From the n_{RT} value the corresponding J_{RFe} value can be derived by means of the expression

$$J_{RT}=\frac{N_T{\mu_B}^2 g_R}{Z_{RT}(1-g_R)}\,n_{RT} \tag{4}$$

where N_T represents the number of T atoms per formula unit.

For $ErFe_{10}Cr_2$ the value for J_{ErT}/k is found to be equal to about −9 K. This value is appreciably lower than that obtained in the T_C analysis for $GdFe_{10}Cr_2$ but is close to the value derived from high field data on $R(Fe,V)_{12}$ compounds [16].

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