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Abstract. Microwave resonance measurements are reported of the contribution to the magnetocrystalline anisotropy fields arising from substitution of gadolinium by holmium in the ferromagnetic phase of GdAl$_2$. The whole temperature range of interest, down to 2 K, is covered. The single-crystal specimen employed has 0.2% holmium replacing gadolinium. The results are compared with calculations based upon a single-ion molecular-field theory. Calculations correctly predict that $\langle 100 \rangle$ and $\langle 111 \rangle$ crystallographic directions are both hard directions of magnetisation and $\langle 110 \rangle$ are easy at low temperatures. Agreement between the measured and calculated magnitudes and temperature dependences of the anisotropy fields is not close if, in the calculations, crystal-field and exchange-field parameters based upon published values for HoAl$_2$ and GdAl$_2$ are employed. When values for these parameters are derived by fitting the theory to our measurements they differ substantially from the published values. However, they are in good agreement with the parameters derived from measurements of NMR of holmium substituted for 1% of gadolinium in GdAl$_2$. This shows that the interaction of a holmium ion with its neighbour differs in dilute substitution from that in HoAl$_2$.

1. Introduction

In this paper we report an extension of our study of the change in the magnetocrystalline anisotropy that is caused by the substitution of a small fraction of gadolinium by holmium in the ferromagnetic intermetallic compound GdAl$_2$. For several reasons this is a favourable host into which to place the anisotropic rare-earth ions such as holmium for study of their anisotropy. The crystallographic site occupied by the anisotropic ion is cubic and this means that, in the theory, crystal-field effects can be expressed in terms of only two parameters. Furthermore, the cubic symmetry of the crystal structure is helpful, as indicated below, in simplifying the analysis of experimental data in terms of contributions to the magnetocrystalline anisotropy fields from the substituted ion. Also, the gadolinium provides a fairly strong exchange field (the Curie temperature is 170 K) whilst contributing very little anisotropy. Hence the effect of a very small substitution of the anisotropic ion is readily measured whilst using crystals for which the magnetocrystalline anisotropy remains small enough throughout the temperature range for convenient measurement by microwave resonance methods. A further advantage of specimens with a low anisotropic ion substitution is that the ferromagnetic resonance absorption line

remains relatively narrow and is not distorted down to the lowest temperatures of interest. This contrasts with our experience with specimens with higher levels of substitution.

Our earlier work on this topic was reported by Pelegrini *et al* (1984). They found that a single-ion molecular-field theory of the anisotropy gave a fairly good account of the measured anisotropy fields at 5 K, for terbium- and erbium-substituted samples of GdAl$_2$, but for holmium and dysprosium the fit between theory and experiment was poor. However, the comparison was unsatisfactory for holmium because the theoretical calculations were for 0 K whereas the measurements were conducted at 20 K for the crystallographic [111] direction and 10 K for the [001].

These were the lowest temperatures at which we were able to make measurements on the available sample, which had 2% of the gadolinium replaced by holmium. At lower temperatures the ferromagnetic resonance line became weak and distorted and the magnetocrystalline anisotropy rose to inconveniently large values. It was clear, as seen in figure 1 of the paper referred to, that the measured anisotropy due to holmium increases very rapidly as the temperature is lowered through the temperatures quoted above. Hence, measurements at lower temperatures were required for comparison with theory for 0 K, which is a useful beginning. In the present investigations we employed a sample with 0.2% holmium substitution. This was the holmium content of the starting material, from which a single crystal was grown by the Czochralski method. No independent analysis of the crystal is available, but earlier experience with more heavily doped crystals suggests that the crystal composition corresponds closely to that of the starting mixture. Measurements are reported throughout the temperature range in which the holmium has a significant effect upon the anisotropy. The theory has been extended to finite temperatures, thus allowing explanation of the very rapid temperature variation of the anisotropy fields, a fuller test of the theory and much better opportunity for the determination of values for theoretical parameters by fitting theory to experiment.

2. Experimental procedure and results

Ferromagnetic resonance measurements were made at about 8.42 Ghz in a conventional transmission cavity microwave spectrometer. The specimens were circular discs of diameter 3 mm and thickness about 150 μm. The disc plane was parallel to a (110) crystallographic plane and the ferromagnetic resonance line was observed with the steady magnetic field oriented along various crystallographic directions within the disc plane. The resonance lines were satisfactory throughout the temperature range. The fields for resonance are given in figure 1. In this figure the large decrease in field for resonance, which occurs as the temperature is reduced below the Curie temperature, 170 K, arises from the microwave-frequency demagnetising field, $4\pi M_S$ in equation (1) below. The rapid change in anisotropy as the temperature is reduced below 40 K is due to the holmium ion, whereas the relatively small anisotropy at higher temperatures arises from the gadolinium. The demagnetising field in the plane of the disc was measured to be 375 Oe at low temperatures.

In figure 2 the marked points, with uncertainties, show the contributions to the anisotropy fields, H_K, which are due to the holmium. These were obtained by simply subtracting the fields for resonance measured on a pure GdAl$_2$ sample from those measured on the holmium substituted sample after allowing for the small difference between the demagnetising fields, H_D, of the samples. The resonance relation when the
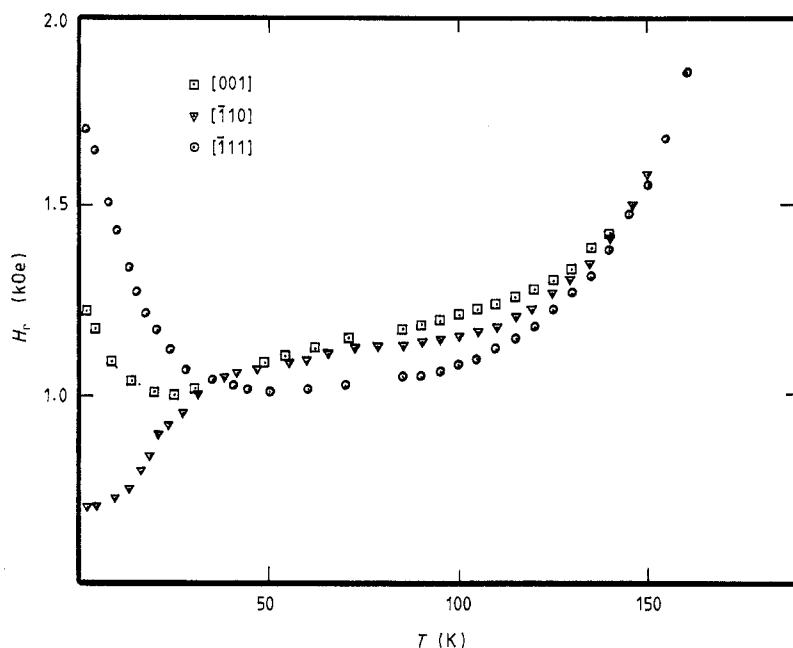
Figure 1. Fields for resonance, H_r, versus temperature for a sample of $Ho_{0.002}Gd_{0.998}Al_2$. Measurement frequency: 8.42 GHz.

applied field and magnetisation are aligned along the $[\bar{1}11]$ and $[001]$ directions, which lie in the disc plane, takes the form

$$(\omega/\gamma)^2 = (H_r + H_D + 4\pi M_S + H_K)(H_r + H_D + H_K) \tag{1}$$

where ω is the measurement frequency, H_r is the field for resonance, M_S the saturation magnetisation and H_D the demagnetising field in the disc plane. Hence the subtraction outlined above gives the change in H_K due to the holmium substitution provided the gyromagnetic ratio, γ, has the same value for the pure and doped samples. The 0.2% holmium substitution would not be expected to change γ significantly in the present context. When the applied field is oriented along crystallographic directions which are axes of symmetry lower than threefold, H_K assumes different values in the two brackets on the right-hand side of equation (1). It is then necessary to know each of the quantities in the equation before comparison between theory and experiment can be achieved. This applies to the $[110]$ direction. Similar complication arises for crystals of lower symmetry than cubic.

3. Discussion

A comparison of the anisotropy fields in figure 2 with those for holmium in figure 1 of the paper by Pelegrini *et al* (1984) shows that they are similar in their temperature variation (the unusual behaviour in the $[001]$ direction is seen for both samples) and the ratio of the anisotropy fields of the two samples at low temperatures is in fairly close agreement with the 1:10 ratio of the nominal holmium contents of the samples. The
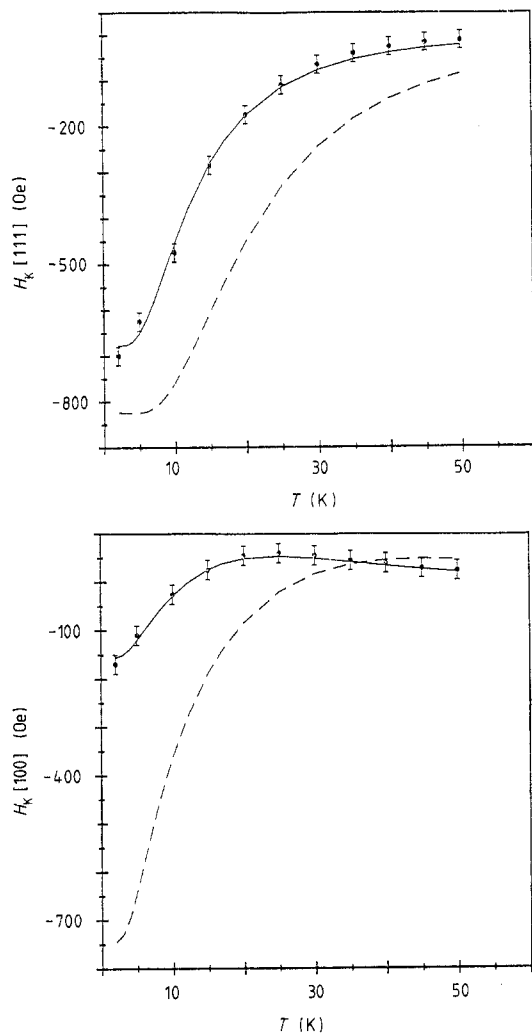
Figure 2. The change in the anisotropy fields due to substitution of 0.2% of the gadolinium by holmium in $GdAl_2$, as a function of temperature. The points are from experiment. The broken and full curves are computed from theory, the broken curves using the parameters in row 2 of table 1, and the full curves using those from row 1.

crossing of the curves for the [111] and [001] directions in the earlier publication arises because the relatively small anisotropy fields of pure $GdAl_2$ were not subtracted from the measured anisotropy fields of the substituted sample and above 70 K the anisotropy is dominated by the host crystal.

The widely used single-ion molecular-field theory of the magnetic anisotropy (see, for example, Waind *et al* 1983) may be summarised as follows. The energy levels of the anisotropic rare-earth ion are calculated from the interaction of the total angular momentum $\hbar J$ of the ion with its surroundings, given by the sum of exchange and crystal-field contributions to the Hamiltonian:

$$\mathcal{H} = \mathcal{H}_{ex} + \mathcal{H}_{CF}$$

where

$$\mathcal{H}_{ex} = -\alpha J \qquad \alpha = -(g-1)\mathcal{J}_{eff}\boldsymbol{\sigma}\cdot\boldsymbol{J}$$

where $g = \frac{5}{4}$ is the Landé g-factor of Ho^{3+}, $\boldsymbol{\sigma}$ is the thermally averaged spin of the host Gd^{3+} ion and $\mathcal{J}_{eff}$ is an effective exchange constant for Ho^{3+} in GdAl$_2$. It is implicit in this model that the exchange is isotropic and the exchange field is parallel to the magnetisation of the gadolinium, which is essentially equal to the saturation magnetisation of the sample.

$$\mathcal{H}_{CF} = B_4^0(O_4^0 + 5O_4^4) + B_6^0(O_6^0 - 21O_6^4)$$

where B_4^0 and B_6^0 are crystal-field parameters and the brackets contain crystal-field operators. The magnetic anisotropy field, due to the R ion, (holmium in our study) is calculated as

$$H_K = (N/M_S)\partial^2 F/\partial\Theta^2.$$

N is the number of R ions per unit volume and M_S is the saturation magnetisation, which was taken from measurements by Lee and Montenegro (1981). $F = kT\ln Z$ is the free energy of the R ion. Z, the partition function, is calculated from the energy levels of the R ion. Θ is a small angular rotation of the direction of the effective exchange field, from the crystallographic direction, [001] or [$\bar{1}$11], for which H_K is calculated.

The broken curves in figure 2 give the anisotropy fields computed using the values of crystal-field parameters B_4^0 and B_6^0, described as the weighted mean in table 2 of the paper by Prakash *et al* (1984). These values were derived from a number of publications which describe a variety of experiments with their interpretation. In this calculation, following the suggestion of Waind *et al* (1983) $\mathcal{J}_{eff}$ was taken to be equal to $\sqrt{\mathcal{J}_0(Gd)\mathcal{J}_0(Ho)}$ where $\mathcal{J}_0(Gd)$ is the value for the exchange parameter derived from measurements on pure GdAl$_2$ and $\mathcal{J}_0(Ho)$ is that derived from HoAl$_2$. Values for $\mathcal{J}_0(Gd)$ and $\mathcal{J}_0(Ho)$ were taken from the paper by these authors. Clearly the fit between the broken curves and the measured values of H_K is not very close, although the calculation does predict that both the $\langle 100\rangle$ and $\langle 111\rangle$ directions are hard directions of magnetisation at low temperatures in agreement with the negative sign of H_K for both of these orientations of the magnetisation. $\langle 110\rangle$ directions, not illustrated in the figure, are correctly predicted to be easy directions. The ratio between the measured holmium contributions to the [001] and [$\bar{1}$11] anisotropy fields at the lowest temperatures is 0.24 whereas the theory gives 0.86. This forms a test of the theory that is independent of the concentration of holmium in the crystal, of which we have no independent measurement.

In view of the imperfect fit seen above, calculations were made using a computer program to determine the values of parameters B_4^0, B_6^0 and α that gave the best fit between theory and experiment. The values so obtained, with their uncertainties which were calculated from the uncertainties in the experimental quantities, are displayed in row one of table 1. Table 2 gives the correlation matrix. The full curves in figure 2, which fit the measured values given by the points very well, are calculated using these parameters. Row two of the table gives the values for these parameters used for the calculation of the broken curves, as explained above. Clearly the two sets of values are markedly different. However, we derive confidence in this surprising outcome of our calculations because the values for these three parameters derived by McMorrow (1987), and quoted in the third row of table 1, are in quite close agreement with those derived from our best-fit calculations. McMorrow derived these values from the interpretation of NMR of holmium in 1% solution in GdAl$_2$. Measurements made with the applied field

Table 1. Value of α, $10^4 B_4^0$ and $10^6 B_6^0$ (in K). The figures in brackets are the uncertainties calculated from the experimental uncertainties. The values in row 1 are derived from ferromagnetic resonance, while those in row 3 are derived from nuclear magnetic resonance. Those in row 2 are the *a priori* expectations, deduced from published work on $GdAl_2$ and $HoAl_2$.

Alloy	α	$10^4 B_4^0$	$10^6 B_6^0$
$Ho_{0.002}Gd_{0.998}Al_2$	16.1(0.9)	−6.3(0.4)	4.4(0.3)
	23.9	−8.7	7.7
$Ho_{0.01}Gd_{0.99}Al_2$	18.2(0.9)	−6.3(0.4)	4.9(0.4)

Table 2. The correlation matrix of FMR parameters. The reduced $\chi^2 = 0.4$.

	α	B_4^0	B_6^0
α	1.0		
B_4	−0.666	1.0	
B_6	0.784	−0.911	1.0

in [001] and [011] directions were analysed. It seems that there is evidence from two quite different experiments that $\mathscr{J}_{eff}$ for holmium when dilutely substituted into $GdAl_2$ is not given by $\sqrt{\mathscr{J}_0(Ho)\mathscr{J}_0(Gd)}$ and that the crystal-field parameters for holmium in dilute substitution differ from those in $HoAl_2$. The geometric-mean expression for the effective exchange constant has also been questioned by Ross *et al* (1983). A critical discussion will be given by McMorrow and McCausland (1989).

The values of the parameters and their uncertainties quoted in row one of table one were calculated assuming that precisely 0.2% of gadolinium had been substituted by holmium in our sample. Because this was the concentration in the starting mixture and we were unable to check the sample by chemical analysis, calculations were performed to investigate the effects of departure from this figure. When a figure of 0.18% was assumed calculation gave the best fit to experiment with $\alpha = 17.2$, $10^4 B_4^0 = -6.1$ and $10^6 B_6^0 = 4.5$. The departure from 0.2% is unlikely to exceed this. The ratio of the measured $H_K[111]$ to $H_K[001]$, which is independent of holmium concentration, is very well explained if the parameters in row one of table one are adopted. This is apparent from the fit in figure 2.

4. Conclusion

Measurements of the magnetocrystalline anisotropy field due to holmium doping in $GdAl_2$ have been extended down to 2 K. This was achieved by employing a specimen with 0.2% of the gadolinium replaced by holmium. In contrast to the case for more heavily doped samples, the ferromagnetic resonance absorption line was narrow and undistorted down to the lowest temperatures and the anisotropy fields were of a magnitude convenient for measurement by the resonance technique. Measurements at 2 and 4 K make it clear that no further significant increase in the anisotropy fields is to be anticipated at lower temperatures.

The single-ion molecular-field theory correctly predicts that $\langle 110 \rangle$ directions are easy directions of magnetisation at low temperatures as can be seen from the behaviour illustrated in figure 1 where the [110] direction has the lowest field for resonance at low temperatures. However, the anisotropy fields in the hard directions, $\langle 100 \rangle$ and $\langle 111 \rangle$, and their temperature dependence are explained only qualitatively if the crystal-field parameters in the theory are taken as the weighted mean of published values for $HoAl_2$ and $\mathcal{J}_{\text{eff}}$ is taken as the geometric mean of the exchange parameters in $GdAl_2$ and $HoAl_2$.

When values for crystal-field and exchange parameters are computed by fitting theory to the experiment it is found that an excellent fit can be obtained throughout the temperature range of interest using values that differ markedly from those mentioned above. These values do however agree quite closely with those obtained from interpretation of NMR of holmium substituted dilutely into $GdAl_2$. This suggests that the interaction of a holmium ion with its neighbours differs when in dilute solution from the one that obtains in the pure $HoAl_2$ compound.

Acknowledgments

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