

Crystal Field Effects on the Magnetocrystalline Anisotropy in HoAl_2 *

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Recent work on the heat capacity of HoAl_2 revealed an anomaly at 20°K, the origin of which was not understood. It is now suggested that this anomaly originates from a change in the easy direction of magnetization brought about by a combined effect of crystalline electric field and exchange field. Calculations by the equivalent operator method have been performed employing reasonable combinations of crystal field parameters. The exchange field acting on Ho^{3+} is determined in a self-consistent manner. Results are presented to illustrate the expected occurrence of a change in the easy direction of magnetization for a range of crystal field parameters which are compatible with those found for other RAl_2 compounds. The magnetic moment on Ho^{3+} ion calculated on the basis of this model is in agreement with experiment.

Introduction

The RAl_2 (R = rare earth) intermetallic compounds crystallize in the cubic Laves phase (C15) structure (1). Most of these order ferromagnetically (2). The NMR studies in the ferromagnetic RAl_2 materials reported by Kaplan *et al.* (3) and the magnetization measurements on single crystals by Purwins *et al.* (4) suggested the occurrence of strong magnetocrystalline anisotropy in these compounds. Low-temperature heat capacities of several RAl_2 compounds have been reported by Deenadas *et al.* (5), Hill *et al.* (6), and Inoue *et al.* (7). The destruction of ferromagnetism gives rise, as expected, to an extra contribution to the heat capacity. The excess heat capacity consists of a single peak in all cases, with the single exception of HoAl_2 . The magnetic contribution to the heat capacity of HoAl_2 shows an unusual feature, exhibiting pronounced peaks at 20 and 28°K (Fig. 1). The peak at 28°K corresponds to the Curie temperature; however, the origin of the other

peak has not been clarified. It is now suggested that the low-temperature peak at 20°K may arise as a consequence of the change in the easy direction of magnetization due to a combined effect of crystalline electric field and exchange field. This is demonstrated by calculating the free energy of the system as a function of temperature and showing that for a certain range of crystal field parameters the easy direction of magnetization changes near 20°K. This change in the easy direction gives rise to an anomaly in the magnetic heat capacity. The crystal field parameters required to produce a change in easy direction in HoAl_2 at the observed temperature are compatible with those found for other RAl_2 compounds. We report for the first time calculations which explain the anisotropy behavior in cubic compounds using self-consistent methods.

Theory and Calculations

The Hamiltonian for the rare-earth ion in the presence of a crystal field term \mathcal{H}_{CF} and an exchange field H_{ex} is given by

$$\mathcal{H} = \mathcal{H}_{\text{CF}} + 2(g_J - 1)\mu_B J_z H_{\text{ex}}, \quad (1)$$

where μ_B is the Bohr magneton, g_J is the Landé g factor, and J_z is the z component of the total

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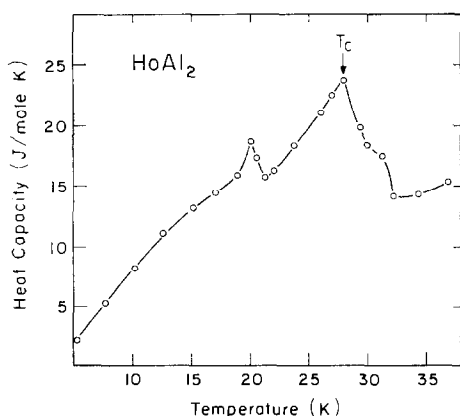


FIG. 1. Heat capacity vs temperature of HoAl_2 (from 6).

angular momentum of the rare-earth ion under consideration. The rare-earth ion in RAl_2 compounds occupies a site of local cubic symmetry. The crystal field term for the z -axis lying along the three cubic crystallographic directions may be expressed as follows (8, 9):

$$\mathcal{H}_{\text{CF}}^{(100)} = A_4 \langle r^4 \rangle \beta (\text{O}_4^0 + 5\text{O}_4^4) + A_6 \langle r^6 \rangle \gamma (\text{O}_6^0 - 21\text{O}_6^4) \quad (2)$$

$$\begin{aligned} \mathcal{H}_{\text{CF}}^{(110)} = & -A_4 \frac{\langle r^4 \rangle \beta}{4} (\text{O}_4^0 - 20\text{O}_4^2 - 15\text{O}_4^4) \\ & - \frac{1}{8} A_6 \langle r^6 \rangle \gamma \\ & \times (\text{O}_6^0 + \frac{10}{26} \text{O}_6^2 - \frac{10}{13} \text{O}_6^4 + \frac{2}{26} \text{O}_6^6) \end{aligned} \quad (3)$$

and

$$\begin{aligned} \mathcal{H}_{\text{CF}}^{(111)} = & -\frac{2}{3} A_4 \langle r^4 \rangle \beta (\text{O}_4^0 - 20\sqrt{2} \text{O}_4^3) \\ & + \frac{1}{9} A_6 \langle r^6 \rangle \gamma \\ & \times \left(\text{O}_6^0 + \frac{35\sqrt{2}}{4} \text{O}_6^3 + \frac{7}{8} \text{O}_6^6 \right). \end{aligned} \quad (4)$$

In the above expressions A_n are the n th-order crystal field parameters, $\langle r^n \rangle$ is the expectation value of the n th power of the $4f$ -electron radius, and β and γ are the Stevens operator equivalent factors for fourth- and sixth-order terms, respectively, in the Hamiltonian (9).

In the molecular field approximation, the exchange field which the rare-earth ions exert on one another can be written as

$$2\mu_B H_{\text{ex}} = -\mathcal{J}_{ff}(g_J - 1) \langle J_z \rangle_{\text{av}}, \quad (5)$$

where $\langle J_z \rangle_{\text{av}}$ denotes the Boltzmann average of the expectation value of the operator over all the levels. The exchange constant \mathcal{J}_{ff} is related to the paramagnetic Curie temperature θ_P by

$$3k_B \theta_P = \mathcal{J}_{ff}(g_J - 1)^2 J(J + 1). \quad (6)$$

From Eq. (5) we note that H_{ex} is proportional to $\langle J_z \rangle_{\text{av}}$, which in turn depends implicitly on H_{ex} through the eigenfunctions and the energy eigenvalues obtained after diagonalizing the Hamiltonian given by Eq. (1). Thus, the exchange field has to be determined self-consistently for a given value of \mathcal{J}_{ff} , for each set of crystal field parameters $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$, and for each temperature. In an actual calculation, the Hamiltonian of Eq. (1) is diagonalized for a set of parameters for an approximate value of H_{ex} . The resultant eigenvalues and eigenfunctions are utilized to evaluate $\langle J_z \rangle_{\text{av}}$. This value is used to calculate H_{ex} employing Eq. (5), and this iterative process is repeated until self-consistency is achieved. These eigenvalues are used to calculate the Helmholtz free energy of the system using the expression

$$F = -k_B T \ln Z,$$

where

$$Z = \sum_i e^{-E_i/k_B T}.$$

The easy direction of magnetization at any given temperature corresponds to the one possessing the lowest free energy. The above procedure was used to calculate the temperature dependence of the free energy for Ho^{3+} ion for H_{ex} directed along the three major symmetry directions in a cube. Various combinations of $A_4 \langle r^4 \rangle$, $A_6 \langle r^6 \rangle$, and \mathcal{J}_{ff} were used.

Results and Discussion

The variation of free energy with temperature for a typical set of crystal field parameters

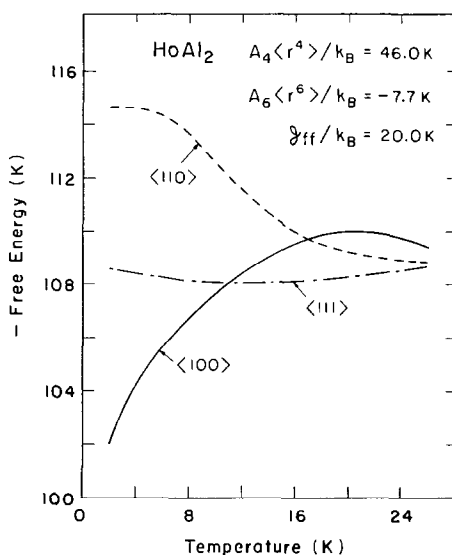


FIG. 2. Calculated free energy vs temperature for Ho^{3+} ion. The parameters used in the calculation are shown in figure.

and exchange constant is plotted in Fig. 2. The exchange constant is calculated using Eq. (6) and the experimental value of θ_p reported by Wallace (2). The crystal field parameters are chosen on the basis of the work of Inoue *et al.* (7). We note from Fig. 2 that the free energy along the $\langle 110 \rangle$ direction is the lowest at low temperatures. This implies that the twofold axis is the easy direction of magnetization at these temperatures. However, at about 20°K , the free energy along $\langle 100 \rangle$ becomes lowest. This results in a spontaneous change in the easy direction of magnetization. The magneto-crystalline anisotropy is expected to decrease with increasing temperature. This is evident from the trends of the three curves in Fig. 2.

Figure 3 shows the range of crystal field parameters for which our calculations predict a change in the easy direction of magnetization and the temperature at which this change will occur. The magnitudes of $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$ have been chosen to obtain an overall splitting of $100\text{--}200^\circ\text{K}$ in the ground J manifold of Ho^{3+} ion. Various experimental results on RAl_2 compounds have shown that the overall splittings in these compounds lie within this range (2, 4, 7). In general, it may be mentioned that a change in the easy

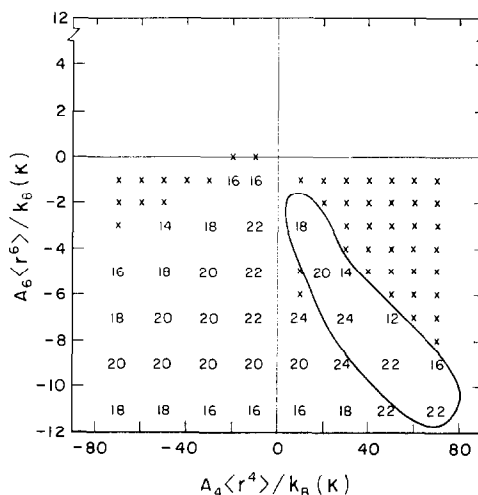


FIG. 3. The range of crystal field parameters $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$ for which the calculations predict a change in the easy direction. The portion enclosed in the contour indicates a change from the $\langle 110 \rangle$ to the $\langle 100 \rangle$ direction. The portion outside the contour indicates a change from the $\langle 110 \rangle$ to the $\langle 111 \rangle$. The temperature where the transition takes place is marked in the figure. x 's are indicated to define the limits.

direction is predicted for all values of $A_4 \langle r^4 \rangle$ and only negative values of $A_6 \langle r^6 \rangle$. We predict $\langle 110 \rangle$ as the easy direction at low temperatures for all the combinations examined. However, for the range of parameters enclosed

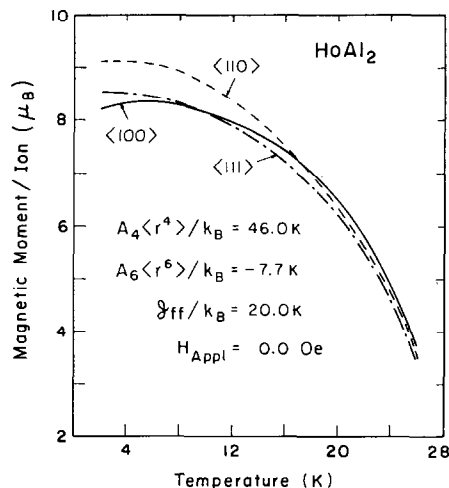


FIG. 4. Magnetic moment of the Ho^{3+} ion calculated as a function of temperature.

in the contoured region in Fig. 3 the easy direction changes to $\langle 100 \rangle$ while for the other combinations it changes to $\langle 111 \rangle$ direction. Calculations were performed varying \mathcal{J}_{ff} for a fixed combination of $A_4 \langle r^4 \rangle$ and $A_6 \langle r^6 \rangle$. These indicate that the transition temperature increased as a function of \mathcal{J}_{ff} .

Zero-field magnetization values of Ho^{3+} ion are plotted in Fig. 4 as a function of temperature along the three directions for a set of crystal field parameters. It may be noted that the conclusions drawn from Fig. 2 also apply in this instance. However, the differences in the magnetization along the three directions are rather small. We obtain a value of $9.2 \mu_B$ at 4.2°K along the $\langle 110 \rangle$ direction compared to the value of $8.2 \mu_B$ from neutron diffraction experiments on polycrystalline material (10). Measurements of magnetization on single crystals of HoAl_2 are highly desirable to confirm our results.

In conclusion, we feel that the best choice of crystal field parameters of $A_4 \langle r^4 \rangle = 46^\circ\text{K}$ and $A_6 \langle r^6 \rangle = -7.7^\circ\text{K}$ for HoAl_2 obtained in our calculations are compatible with other RAl_2 compounds. These parameters predict $\langle 110 \rangle$ as the easy direction below 20°K and $\langle 100 \rangle$ above this temperature. The origin of the peak at 20°K in the heat capacity curve reported by Hill *et al.* (6) in HoAl_2 may thus be related to this change in the easy direction. Similar anomalous behavior in the experimental heat capacity curves as a consequence of changes in anisotropy have been reported in RCO_5 (11), Dy_3Al_2 (12), and RCO_2 (13). Calculations have also been performed in RCO_2 compounds which are isostructural to

HoAl_2 and the results will be reported elsewhere.

Note added in proof. We wish to draw attention to a recent paper entitled "Magnetic behavior of HoAl_2 single crystal," by B. Barbara, M. F. Rossignol, and J. X. Boucherle published in *Physics Letters* **55A**, 321 (1975). Their experimental results support the conclusions drawn in our paper.

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