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Temperature Dependence of the Magnetization of Dysprosium Metal*

KAZUO NIIRA†

Institute for Atomic Research and Department of Physics, Iowa State University of Science and Technology, Ames, Iowa

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In this paper the experimental fact that the temperature dependence of the saturation magnetic moment of dysprosium metal shows a marked departure from the Bloch $T^{\frac{3}{2}}$ law at low temperatures is interpreted as due to magnetic anisotropy. The calculation is in the spin-wave approximation and gives a result which agrees well with the observed temperature dependence of the magnetization if the magnitude of the magnetic anisotropy is suitably chosen. A discussion on the atomic origin of the magnetic anisotropy is given.

I. INTRODUCTION

THERE are several interesting features in the magnetic properties of dysprosium metal.[1] The material has a hexagonal close-packed crystal structure. It is ferromagnetic below 85°K, and is antiferromagnetic from 85°K up to 178.5°K. Its spontaneous magnetization always lies in the basal plane of the hexagonal crystal, and the magnetic moment of the metal is a linear function of an external magnetic field applied parallel to the direction of the *c* axis of the crystal over the entire range of the temperature and of the applied magnetic field ($\sim 10^4$ gauss), i.e., the crystal is very hard magnetically in the direction of the *c* axis. At low temperature the direction of easy magnetization is in the $[11\bar{2}0]$ directions (the directions along the line joining nearest neighbors in the basal plane of the hexagonal lattice), but above 110°K the magnetization is isotropic in the basal plane.

The temperature dependence of the decrease of the saturation magnetic moment of dysprosium appears to be proportional to T^2 instead of $T^{\frac{3}{2}}$ (the Bloch law) at low temperature. Such anomalous behavior of the magnetization, which is also observed in erbium and holmium metals[2] can be interpreted by the spin-wave theory, taking account of the magnetic anisotropy. The result is the $T^{\frac{3}{2}}$ law modified by a factor with exponential dependence on the inverse temperature. This factor comes from the fact that, if there is a preferred direction of magnetization in the crystal due to magnetic anisotropy, it requires a finite amount of energy to excite even a long-wavelength spin wave.

II. EFFECT OF ANISOTROPY ON THE TEMPERATURE DEPENDENCE OF THE MAGNETIZATION

It is commonly believed that in the rare-earth metals the magnetic moments of the tripositive ions are due to the *f* electrons in the ions, since the other electrons still form closed shells.

As the spin-orbit couplings between the *f* electrons in the rare-earth ions are stronger ($1000 \sim 2000$ cm^{-1})[3] than perturbations due to the crystalline field, it is plausible to assume that the magnitude of the total angular momentum $\mathbf{J}$ of the *f* electrons in the ion is quantized even in the metal and to take into account only the lowest level of the ground term of the ion, the state in which $\mathbf{J}$ is constant and the magnitude of $\mathbf{J}$ corresponds to the maximum possible value for rare earths with more than seven *f* electrons. Inside $\mathbf{J} =$ constant the operator equivalence holds between $\mathbf{J}$ and the total spin $\mathbf{S}$ of the *f* electrons:

$$\mathbf{S} = (g-1)\mathbf{J}, \tag{1}$$

where g is the Landé g factor. Equation (1) gives an interesting correlation between the paramagnetic Curie temperatures (or the Néel temperatures) of various rare-earth metals and their spins.[4]

To discuss the magnetic properties of dysprosium, it is useful to consider the whole crystal of the hexagonal close-packed structure as consisting of two interpenetrating hexagonal sublattices (the primed and unprimed in the following equation) and to assume that the exchange coupling between magnetic ions is

$$H_{\text{ex}} = -J_1 \sum_{j>k} (\mathbf{J}_j \cdot \mathbf{J}_k) - J_1 \sum_{j'>k'} (\mathbf{J}_{j'} \cdot \mathbf{J}_{k'}) - J_2 \sum_{j,j'} (\mathbf{J}_j \cdot \mathbf{J}_{j'}), \tag{2}$$

where the first two terms represent the exchange couplings between the nearest neighbors in the same sublattice and the last gives the couplings between the two sublattices. The last summation over j' is to be taken over nearest neighbors of ions j on the other sublattice. In Eq. (2) different values (J_1 and J_2) of the exchange couplings for the two kinds of pairs with nearly equal distances[5] are assumed, as would result from the indirect exchange couplings of the spins of the ions via conduction electrons[6] [see Sec. III (i)]. This assumption is not essential for the discussion in this section, but is important for the interpretation of

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† On leave from Tokyo Institute of Technology, Tokyo, Japan.

[1] Behrendt, Legvold, and Spedding, Phys. Rev. **109**, 1544 (1958).

[2] S. Legvold (private communication).

[3] B. R. Judd, Proc. Phys. Soc. (London) **A69**, 157 (1956).

[4] P. G. de Gennes, Compt. rend. **247**, 1836 (1958).

[5] The distance between ions j and j' is slightly shorter than that between j and k in the rare-earth metals of hexagonal close-packed structure (3.50 A and 3.59 A in Dy, respectively).

[6] T. Kasuya, Progr. Theoret. Phys. (Kyoto) **16**, 45 (1956); K. Yosida, Phys. Rev. **106**, 893 (1957).

magnetic properties in the antiferromagnetic temperature range.[7]

There may be several kinds of anisotropy energy with different atomic origins in the dysprosium. One of the most important terms is the one due to the crystalline field acting on each magnetic ion, which can be assumed within the manifold $\mathbf{J}=$constant to be

$$H_{\text{crys}}=\sum_j\{B\mathbf{J}_{zj}^2+D\mathbf{J}_{zj}^4+F\mathbf{J}_{zj}^6 \\ +\tfrac{1}{2}G[(\mathbf{J}_{xj}+i\mathbf{J}_{yj})^6+(\mathbf{J}_{xj}-i\mathbf{J}_{yj})^6]\}, \qquad (3)$$

where the summation extends over all the ions in the crystal, the z axis is chosen along the c axis of the hcp lattice and the x axis along the direction of easy magnetization (the direction joining nearest neighbors in the same sublattice in our case). Only the last term in Eq. (3) is responsible for anisotropy in the basal plane (we assume $G<0$). Other kinds of interactions, such as the electric quadrupole-quadrupole ones between ions, will contribute appreciably to the anisotropy energy of the dysprosium, but as even when they are included the qualitative features of the following discussion remain unchanged [see Sec. III, (ii)], they are for simplicity neglected here.

Next, the exchange couplings between the ions are assumed to be ferromagnetic ($J_1,J_2>0$), and the eigenvalues of the Hamiltonian

$$H=H_{\text{ex}}+H_{\text{crys}} \qquad (4)$$

are calculated by the spin-wave approximation. The easy axis of the magnetization is the x axis, so one defines

$$\begin{aligned} &\mathbf{J}_{xj}=J-a_j^*a_j, \quad \mathbf{J}_{xj'}=J-b_{j'}^*b_{j'}, \\ &\mathbf{J}_{+j}=(2J)^{\frac{1}{2}}a_j, \quad \mathbf{J}_{+j'}=(2J)^{\frac{1}{2}}b_{j'}, \\ &\mathbf{J}_{-j}=(2J)^{\frac{1}{2}}a_j^*, \quad \mathbf{J}_{-j'}=(2J)^{\frac{1}{2}}b_{j'}^*, \\ &\qquad(\mathbf{J}_\pm=\mathbf{J}_y\pm i\mathbf{J}_z) \end{aligned} \qquad (5)$$

where a_j^* and $b_{j'}^*$ are creation operators, a_j and b_j, are destruction operators of spin deviation, and J is the inner quantum number of the ions ($J=15/2$ for Dy). As in the usual treatment in the spin-wave approximation, the terms of third order or higher in the spin deviation operators a_j, etc. will be neglected. In this procedure, when there is ambiguity in the order of operators, products of noncommuting operators like a_j^* and a_j in the D and F terms of H_{crys} will be rearranged in such an order (the normal order) that the creation operators are always written to the left of the destruction ones. As this ambiguity only concerns an estimation of the numerical value of the parameter D' defined by Eq. (7) (and further, the magnitudes of the quantities D and F are expected to be smaller than that of B; see Sec. III) this assumption is not important for the following discussion. Introduce the Fourier transforms of a_j, a_j^* and $b_{j'}$,$b_{j'}^*$,

$$\begin{aligned} a_j&=(2/N)^{\frac{1}{2}}\textstyle\sum_\lambda a_\lambda\exp(-i\boldsymbol{\lambda}\cdot\mathbf{R}_j), \\ b_{j'}&=(2/N)^{\frac{1}{2}}\textstyle\sum_\lambda b_\lambda\exp(-i\boldsymbol{\lambda}\cdot\mathbf{R}_{j'}), \\ a_j^*&=(2/N)^{\frac{1}{2}}\textstyle\sum_\lambda a_\lambda^*\exp(i\boldsymbol{\lambda}\cdot\mathbf{R}_j), \\ b_{j'}^*&=(2/N)^{\frac{1}{2}}\textstyle\sum_\lambda b_\lambda^*\exp(i\boldsymbol{\lambda}\cdot\mathbf{R}_{j'}), \end{aligned}$$

where N is the total number of ions in the crystal and the wave vectors $\boldsymbol{\lambda}$ belong to the lattice reciprocal to each crystal sublattice. Then, one finds

$$\begin{aligned} H&=\tfrac{1}{2}N[JB+\tfrac{3}{2}J^2D+(15/4)J^3F+2J^6G-15J^5G] \\ &\qquad -\tfrac{1}{2}NJ^2(zJ_1+z'J_2)+\textstyle\sum_\lambda H_\lambda, \\ H_\lambda&=[JD'+(z-\gamma_\lambda)JJ_1+z'JJ_2](a_\lambda^*a_\lambda+b_\lambda^*b_\lambda) \\ &\quad -\tfrac{1}{2}JD''(a_{-\lambda}a_\lambda+a_{-\lambda}^*a_\lambda^*+b_{-\lambda}b_\lambda+b_{-\lambda}^*b_\lambda^*) \\ &\qquad -JJ_2(\gamma_\lambda'a_\lambda b_\lambda^*+\gamma_\lambda'^*a_\lambda^*b_\lambda). \end{aligned} \qquad (6)$$

Here z and z' are the number of nearest neighbors of an ion on the same sublattice and on the other sublattice, respectively ($z=z'=6$ in our case), and

$$\begin{aligned} D'&=B+3JD+(45/4)J^2F-21J^4G, \\ D''&=D'+36J^4G. \end{aligned} \qquad (7)$$

The quantities γ_λ and γ_λ' are defined by

$$\begin{aligned} \gamma_\lambda&=\textstyle\sum_k\exp[i\boldsymbol{\lambda}\cdot(\mathbf{R}_j-\mathbf{R}_k)], \\ \gamma_\lambda'&=\textstyle\sum_{j'}\exp[i\boldsymbol{\lambda}\cdot(\mathbf{R}_j-\mathbf{R}_{j'})], \end{aligned} \qquad (8)$$

where the summation is taken over the nearest neighbors as in Eq. (2). Although γ_λ is real, γ_λ' is complex, as the hexagonal close-packed structure is not a Bravais lattice. By a series of successive canonical transformations[8] the Hamiltonian (6) is brought into the form

$$\begin{aligned} H&=N-[(3/4)J^2D+(15/4)J^3F+(J^6+3J^5)G] \\ &\qquad -\tfrac{1}{2}NzJ(J+1)J_1-\tfrac{1}{2}Nz'J(J+1)J_2+\textstyle\sum_\lambda H_\lambda, \\ H_\lambda&=\tfrac{1}{2}J\sum_{i=1,2}\{(D'-D''+f_{i\lambda})Q_{i\lambda}^2 \\ &\qquad\qquad +(D'+D''+f_{i\lambda})P_{i\lambda}^2\}, \\ &\qquad [Q_{i\lambda},P_{k\lambda'}]=i\delta_{ik}\delta_{\lambda\lambda'}, \end{aligned} \qquad (9)$$

where

$$\begin{aligned} f_{1\lambda}&=(z-\gamma_\lambda)J_1+(z'-|\gamma_\lambda'|)J_2, \\ f_{2\lambda}&=(z-\gamma_\lambda)J_1+(z'+|\gamma_\lambda'|)J_2. \end{aligned} \qquad (10)$$

From (9) the frequencies $\omega_{i\lambda}$ of the spin waves are found to be

$$\hbar\omega_{i\lambda}=J[(D'-D''+f_{i\lambda})(D'+D''+f_{i\lambda})]^{\frac{1}{2}}, \quad (i=1,2) \qquad (11)$$

and the eigenvalues of the Hamiltonian (9) are

$$E=\sum_{i=1,2}\hbar\omega_{i\lambda}(N_{i\lambda}+\tfrac{1}{2}), \quad N_{i\lambda}=0,1,2,\cdots. \qquad (12)$$

In consequence of the two-sublattice model, the frequencies of the spin waves fall into two branches.

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[7] L. Néel, Compt. rend. **242**, 1549, 1824 (1956); Suppl. Nuovo cimento **4**, 942 (1957); Liu, Behrendt, Legvold, and Good, Phys. Rev. **116**, 1464 (1959).

[8] T. Oguchi, Phys. Rev. **111**, 1063 (1958).

The higher one ($i=2$) corresponds to optical mode of coupling between two sublattices, and will be neglected in the following.

As the magnetization M of the whole crystal is given by

$$M/g\mu_B=\sum_j \mathbf{J}_{xj}+\sum_{j'} \mathbf{J}_{xj'}=NJ-\sum_j a_j{}^*a_j-\sum_{j'} b_{j'}{}^*b_{j'},$$

where μ_B is the Bohr magneton, its decrease due to the excitation of the spin waves is found to be expressed as

$$\Delta M/g\mu_B=\sum a_j{}^*a_j+\sum b_{j'}{}^*b_{j'}$$

$$=\tfrac{1}{2}\sum_{\lambda}\sum_{i=1,2}(Q_{i\lambda}{}^2+P_{i\lambda}{}^2)-\tfrac{1}{2}N$$

$$\simeq\sum_{\lambda}\sum_{i=1,2}\frac{J(D'+f_{i\lambda})}{\hbar\omega_{i\lambda}}N_{i\lambda},$$

where nondiagonal parts in the $N_{i\lambda}$ representation are omitted in the last equality. When the contribution from the higher frequency part ($\omega_{2\lambda}$) is neglected, the temperature dependence of the magnetization is given by

$$\frac{\langle\Delta M\rangle}{g\mu_B}=J\sum_{\lambda}\frac{D'+f_{1\lambda}}{\hbar\omega_{1\lambda}}\frac{1}{\exp(\hbar\omega_{1\lambda}/kT)-1}. \qquad (13)$$

At low temperature where only spin waves of small wave number are excited, $f_{1\lambda}$ can be approximated by

$$f_{1\lambda}\simeq\tfrac{1}{2}(3J_1+J_2)[(\lambda_1+\lambda_2)^2+\tfrac{1}{3}(\lambda_1-\lambda_2)^2]+\tfrac{3}{4}J_2\lambda_3{}^2,$$

where λ_1, λ_2, and λ_3 are components of $\boldsymbol{\lambda}$ along the basis vectors in the reciprocal lattice.

Since $f_{1\lambda}$ is proportional to the square of the wave number, for sufficiently small wave number it is smaller than Δ^2/D', where

$$\Delta=(D'^2-D''^2)^{\frac{1}{2}}, \qquad (14)$$

and Eq. (11) is written as

$$\hbar\omega_{1\lambda}\simeq J\Delta[1+(D'/\Delta^2)f_{1\lambda}].$$

Then Eq. (13) is reduced to

$$\frac{\langle\Delta M\rangle}{Ng\mu_B}=\frac{1}{2(2\pi)^3}\frac{D'}{\Delta}\int\frac{d\boldsymbol{\lambda}}{\exp\{J[\Delta+(D'/\Delta)f_{1\lambda}]/kT\}-1}$$

$$=\frac{1}{2\pi^2}\left(\frac{\Delta}{JD'}\right)^{\frac{3}{2}}\frac{1}{(3J_1+J_2)J_2{}^{\frac{1}{2}}}$$

$$\times\int_0^\infty\frac{\lambda^2d\lambda}{\exp[(J\Delta+\lambda^2)/kT]-1}$$

$$=\frac{1}{4\pi^2}\left(\frac{\Delta}{JD'}\right)^{\frac{3}{2}}\frac{(kT)^{\frac{3}{2}}}{(3J_1+J_2)J_2{}^{\frac{1}{2}}}\int_0^\infty\frac{\xi^{\frac{1}{2}}d\xi}{e^{x+\xi}-1}, \qquad (15)$$

where

$$x=J\Delta/kT.$$

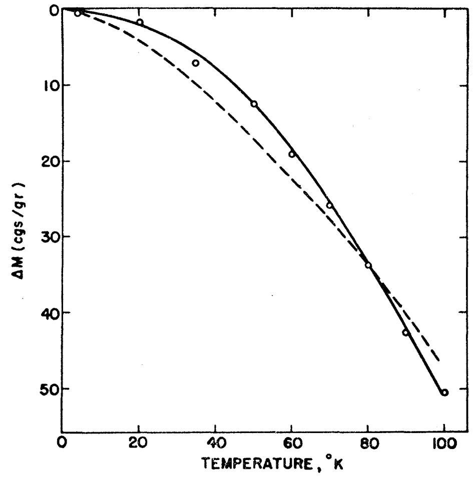

FIG. 1. Temperature dependence of saturation magnetic moments. Circles show the experiment[1] and the solid curve is the plot of Eq. (15) with $J\Delta=20$°K chosen to fit the experiment at 80°K. The dashed curve shows the $T^{\frac{3}{2}}$ law chosen to fit the experimental data at 80°K.

Since

$$\int_0^\infty\frac{\xi^{\frac{1}{2}}d\xi}{e^{x+\xi}-1}=\sum_{n=1}^{\infty}e^{-nx}\int_0^\infty\xi^{\frac{1}{2}}e^{-n\xi}d\xi$$

$$=\frac{\pi^{\frac{1}{2}}}{2}\sum_{n=1}^{\infty}\frac{e^{-nx}}{n^{\frac{3}{2}}}$$

has roughly exponential dependence on the inverse temperature, the predicted temperature dependence of the magnetization deviates from the Bloch $T^{\frac{3}{2}}$ law even at low temperature, and when the value of $J\Delta$ is chosen as 20–40°K Eq. (15) agrees well with the experiment for dysprosium (Fig. 1). Since $J\Delta$ as given by Eq. (14) is roughly a geometrical mean of the magnetic anisotropy energy for the c direction ($K_2\simeq J^2B$) and the one for the $[11\bar{2}0]$ (or x) direction ($K_6\simeq J^6|G|$), a qualitative formula

$$\Delta M\simeq\text{const}T^{\frac{3}{2}}\exp[-(K_2K_6)^{\frac{1}{2}}/kT] \qquad (16)$$

might be useful to estimate the temperature dependence of the magnetization in hexagonal close-packed crystal at low temperature. As for the dysprosium K_2 and K_6 are of the order of magnitude of 10^8 erg/cm^3 (100°K per ion) and 10^6 erg/cm^3 (1°K per ion), respectively,[7] the above estimated value (20–40°K) of $J\Delta$ seems to be reasonable. The observed T^2 law in erbium and holmium metals[2] may perhaps be interpreted in the same way. As ions in gadolinium metal are in s states so that the magnetic anistropy is very small, the magnetization is expected to obey the $T^{\frac{3}{2}}$ law as observed. Incidentally, it is interesting to note that in the case of vanishing anisotropy in the basal plane ($G=0$) $\hbar\omega_{1\lambda}$ is proportional to λ and the T^2 law holds for the magnetization.[9]

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[9] This remark is due to Mr. S. Liu.

III. DISCUSSION

(i) The exchange interaction $H_{\text{ex}}(i,j)$ between rare-earth ions i and j represents the indirect exchange coupling via conduction electrons. If the conduction electrons are assumed to be plane waves, $H_{\text{ex}}(i,j)$ is expressed by an oscillating function of $k_f R_{ij}$ (so that it can be either ferromagnetic or antiferromagnetic), where R_{ij} is the distance between i and j and k_f is the wave number corresponding to the Fermi energy E_f[10]:

$$E_f = (\hbar^2/2m)k_f^2. \tag{17}$$

If one chooses the magnitude of the exchange integral between conduction electrons and f electrons to be 0.1 ev, $H_{\text{ex}}(i,j)$ is found to be, for the nearest neighbor pair, $-7.5(\mathbf{S}_i\cdot\mathbf{S}_j)$ in °K (ferromagnetic), where $\mathbf{S}_i$ and $\mathbf{S}_j$ are the spins of the ions i and j.[4] This choice gives the correct order of magnitude of the Curie (and the Néel) temperature of the dysprosium.

Under the above assumption of plane waves for the conduction electrons, $H_{\text{ex}}(i,j)$ is independent of the direction of the lattice vector $\mathbf{R}_{ij}$. However, if the detailed band structure were taken into account, $H_{\text{ex}}(i,j)$ would depend on the direction of $\mathbf{R}_{ij}$. For instance, suppose the energy of the conduction electron has the form

$$E = (\hbar^2/2m)(\alpha_\perp k_x^2 + \alpha_\perp k_y^2 + \alpha_{\parallel} k_z^2),$$

where the z axis is along the c axis of the hexagonal crystal and the α's are constants corresponding to the effective mass of the electron. Then $H_{\text{ex}}(i,j)$ is an oscillating function of $k_f\rho_{ij}$ (instead of $k_f R_{ij}$), where ρ_{ij} is defined by

$$\rho_{ij} = \left[\frac{R_{x,ij}^2 + R_{y,ij}^2}{\alpha_\perp} + \frac{R_{z,ij}^2}{\alpha_{\parallel}}\right]^{\frac{1}{2}}.$$

$H_{\text{ex}}(i,j)$ becomes dependent on the direction of $\mathbf{R}_{ij}$ and the oscillating feature of $H_{\text{ex}}(i,j)$ leads to different magnitudes of the exchange couplings for nearest neighbor pairs with different orientations in the crystal.

(ii) The magnetic dipolar interactions between the ions in dysprosium contribute to the anisotropy energy in the order of 10^6 erg/cm^3, but under the assumption of the molecular field approximation it is found that they are isotropic in the basal plane of the crystal and produce very small anisotropy energy in the c direction in the ferromagnetic state.

The electrostatic interactions between ions (together with strong spin-orbit coupling) will give an appreciable contribution to the magnetic anisotropy of dysprosium. Since the charge clouds of the ions are supposed not to overlap with each other, the electrostatic interactions between f electrons in an ion i and in an ion j can be expanded in terms of the spherical harmonics $Y_l^m(i)$ and $Y_l^m(j)$ around each nucleus[11] (the "two-center" expansion) and considered as consisting of multipole-multipole interactions. The $Y_0^0(i)$ term in the expansion (together with the contribution from the nucleus and closed shells) gives the "crystalline field" V_{crys} on the f electrons in the ion j when summed over $i(\neq j)$. For the hcp crystal V_{crys} can be expressed as

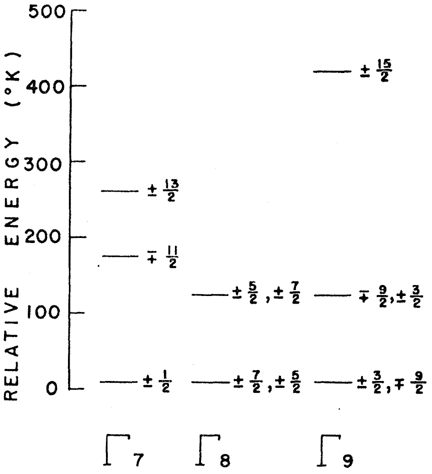

FIG. 2. Splitting of ground state of dysprosium ion ($J=15/2$) due to the crystalline field. The effective charge of ions is taken as 3. Each level is a mixture of states with J_z values (z parallel to the c axis) shown in the figure in decreasing order of their weights (states with negligible weights being omitted). Γ_i shows the irreducible representation of the hexagonal group [H. Bethe, Ann. Physik **3**, 133 (1929)] to which the level is specified.

$$V_{\text{crys}}(j) = e^2 Z \sum_\mu [v_2^0\langle r^2\rangle Y_2^0(\theta_\mu) + v_4^0\langle r^4\rangle Y_4^0(\theta_\mu) + v_6^0\langle r^6\rangle Y_6^0(\theta_\mu) + v_6^6\langle r^6\rangle Y_6^6(\theta_\mu,\varphi_\mu)], \tag{18}$$

where Z is an effective charge of the ions, the summation is taken over all the f electrons in the ion j, and $\langle r^n\rangle$ is the average value of r^n of the f electron. The same coordinate axes are taken in Eq. (18) as before. Within the manifold of $\mathbf{J}=$ constant $\sum_j V_{\text{crys}}(j)$ is equivalent to H_{crys} of Eq. (3) except for terms independent of the direction of $\mathbf{J}$.[12] From the computed values of the v's[13] in Eq. (18) one can evaluate the splitting of the energy level of the dysprosium ion ($J=15/2$) due to the crystalline field. The results are shown in Fig. 2.[14] It was assumed for the estimation of the values of $\langle r^n\rangle$ that the wave functions of f electrons are hydrogen-like with an effective nuclear charge suitably adjusted

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[10] References 4 and 6, and M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954).

[11] For the explicit form of the expansion, see Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (J. Wiley and Sons, New York, 1954), p. 843; B. C. Carlson and G. S. Rushbrooke, Proc. Cambridge Phil. Soc. **46**, 626 (1950).

[12] K. W. H. Stevens, Proc. Phys. Soc. (London) **A65**, 209 (1952).

[13] T. Murao, Progr. Theoret. Phys. (Kyoto) **20**, 277 (1958); T. Kasuya and A. Yanase, Progr. Theoret. Phys. (Kyoto) (to be published).

[14] With the computed values for v and $\langle r^n\rangle$ the values of B, D, F, and G in Eq. (3) are found to be $34.3Z$, $-0.17Z$, $0.19Z$, and $-21.1Z$ in °K, respectively.

to experiment[15]:

$$\langle r^2\rangle=0.508\ \text{A}^2,\quad \langle r^4\rangle=0.381\ \text{A}^4,\quad \langle r^6\rangle=0.392\ \text{A}^6.$$

From Fig. 2 it is seen that the larger the magnitude of J_z the higher the energy of the state, and this is consistent with the observed magnetic anisotropy in the direction of the c axis in dysprosium. As the Curie-Weiss law with the free ion value of the Curie constant holds for dysprosium above 200°K,[1] the over-all splitting of the level due to the crystalline field must be smaller than 200°K. This leads one to infer that the effective charge Z of the dysprosium ion in the metal should have a value less than 1.5 as the result of a shielding effect of the conduction electrons. Since the lower levels in Fig. 2 are spaced close to each other it is difficult to predict correctly the relative spacing of these levels. Furthermore as the quadrupole-quadrupole interactions (and the exchange couplings) between ions are probably not small (see below), it is unlikely that the "one ion model" is adequate.

The terms other than the crystalline field in the electrostatic interactions between ions are multipole-multipole interactions (up to the 2×6 pole interactions), in which the main term would be the quadrupole-quadrupole interaction H_{qq}. It is expressed within $\mathbf{J}=$ constant as

$$\begin{aligned}H_{qq}=\textstyle\sum_{i,j}(e^2/R_{ij}{}^5)\langle r^2\rangle^2\alpha^2[&(105/4)\mathbf{J}_{\zeta i}{}^2\mathbf{J}_{\zeta j}{}^2\\&-(15/4)\mathbf{J}_{\zeta i}\mathbf{J}_{\zeta j}(\mathbf{J}_i\cdot\mathbf{J}_j)-(15/4)(\mathbf{J}_i\cdot\mathbf{J}_j)\mathbf{J}_{\zeta i}\mathbf{J}_{\zeta j}\\&-(15/4)\mathbf{J}_{\zeta i}(\mathbf{J}_i\cdot\mathbf{J}_j)\mathbf{J}_{\zeta j}-(15/4)\mathbf{J}_{\zeta j}(\mathbf{J}_i\cdot\mathbf{J}_j)\mathbf{J}_{\zeta i}\\&-(15/4)\mathbf{J}_{\zeta i}{}^2\mathbf{J}_j{}^2-(15/4)\mathbf{J}_i{}^2\mathbf{J}_{\zeta j}{}^2+\tfrac{3}{2}(\mathbf{J}_i\cdot\mathbf{J}_j)^2\\&+\tfrac{3}{4}\mathbf{J}_i{}^2\mathbf{J}_j{}^2],\end{aligned}\tag{19}$$

where the ζ axis is taken along $\mathbf{R}_{ij}$ and α is a numerical factor in the operator equivalence ($\alpha=-2/9\times45$ for Dy, $J=15/2$).[12] As H_{qq} is quadratic in $\mathbf{J}_i$, there is no difference in its magnitudes between ferromagnetic and antiferromagnetic orientations of the two sublattices. With the molecular field approximation the anisotropy energy (the difference of H_{qq} between the two states $\mathbf{J}_{xi}=\mathbf{J}_{xj}=J$ and $\mathbf{J}_{zi}=\mathbf{J}_{zj}=J$) due to H_{qq} is found to be

$$\Delta H_{qq}\approx-56\textstyle\sum_{ij}\alpha^2e^2\langle r^2\rangle^2J^4/R_{ij}{}^5,$$

where the ideal hcp crystal $[c/a=(8/3)^{\frac{1}{2}}]$ is assumed for the dysprosium. If one puts $\langle r^2\rangle$ at 0.5 A^2 (see above), then

$$\Delta H_{qq}\approx-1.05\times10^8\ \text{erg/cm}^3.$$

This corresponds to the correct order of magnitude of the anisotropy energy in the c direction, and is comparable to the splitting of the level of an ion due to the crystalline field ($\alpha^2e^2\langle r^2\rangle^2J^4/R^5=12.4$°K for a nearest neighbor pair). However, as in the case of the crystalline field, there would be a shielding effect due to a deformation of the charge cloud of conduction electrons from spherical symmetry around the ions. When the quadrupolar interactions between nearest neighbors are included in the Hamiltonian (4), the spin-wave treatment gives the Hamiltonian in the form of

$$\begin{aligned}&H=H_0+\textstyle\sum_\lambda H_\lambda,\\&H_\lambda=\Phi_{1\lambda}(a_\lambda{}^*a_\lambda+b_\lambda{}^*b_\lambda)+\Phi_{2\lambda}(a_{-\lambda}a_\lambda+b_{-\lambda}b_\lambda)+\text{H.c.}\\&\qquad+\Phi_{3\lambda}a_\lambda b_\lambda{}^*+\text{H.c.}+\Phi_{4\lambda}a_\lambda b_{-\lambda}+\text{H.c.},\end{aligned}\tag{20}$$

instead of Eq. (6), where each $\Phi_{i\lambda}$ contains a term coming from the quadrupolar interactions besides (6) and H.c. means the Hermitian conjugate terms. The eigenvalues of the spin waves are found to be

$$\begin{aligned}(\hbar\omega_\lambda)^2=&\Phi_{1\lambda}{}^2-\Phi_{2\lambda}{}^2+\Phi_{3\lambda}{}^2-\Phi_{4\lambda}{}^2\\&\pm2[|\Phi_{1\lambda}\Phi_{3\lambda}-\Phi_{2\lambda}\Phi_{4\lambda}|^2-(\text{Im}\Phi_{3\lambda}\Phi_{4\lambda}{}^*)^2]^{\frac{1}{2}},\end{aligned}$$

which gives the same result for the temperature dependence of the magnetization as Eq. (15):

$$\langle\Delta M\rangle\sim T^{\frac{3}{2}}\int_0^\infty\frac{\xi^{\frac{1}{2}}d\xi}{e^{x+\xi}-1},$$

where x is given by

$$x=J[(a+D')^2-(b+D'')^2]^{\frac{1}{2}}/kT\equiv\Delta'/kT.\tag{21}$$

In this expression, a and b stand for the contributions from the quadrupolar interaction. If the values of a and b are computed from Eq. (19) ($Ja=99.1$°K and $Jb=-57.2$°K) and the terms D' and D'' are omitted, the value of Δ' in Eq. (21) is found to be 80°K, which is much larger than the experimental value of 20–40°K. But again one might expect an appreciable amount of shielding by conduction electrons, perhaps enough to reduce the quadrupolar interactions by the required factor of $\frac{1}{2}$ or $\frac{1}{4}$.

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[15] T. Kasuya and A. Yanase, reference 13.