Interpretation of Magnetic Properties of Dysprosium*

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Dysprosium is ferromagnetic below 85°K, antiferromagnetic between 85 and 179°K, and paramagnetic above 179°K. The spontaneous magnetic moment lies always in the basal plane, and there is anisotropy in this plane below 110°K. In the present paper it is shown that the magnetic properties can be interpreted in terms of a two-sublattice model and a phenomenological theory similar to a theory proposed by Néel. Detailed agreement for the magnetization curves in the ferromagnetic and antiferromagnetic regions is obtained.

I. INTRODUCTION

THE magnetic properties of polycrystalline dysprosium were measured by Trombe,[1–3] and by Elliott, Legvold, and Spedding[4]; they found it to be ferromagnetic below 85°K, antiferromagnetic between 85°K and 179°K, and paramagnetic above 179°K. Recently Behrendt, Legvold, and Spedding[5] succeeded in growing a single crystal and measuring the magnetic properties as a function of direction in the crystal in all three regions. They found the material to be highly anisotropic, such that the spontaneous moments lie always in the basal plane. Above 110°K the dysprosium is isotropic in the basal plane but below that temperature it has a sixfold anisotropy with the $\langle 11\bar{2}0\rangle$ direction[6] easy. In their paper they gave the experimental results for the magnetization as a function of temperature, applied field, and direction in the basal plane for both the ferromagnetic and antiferromagnetic regions.

Néel[7] proposed a very interesting, partly phenomenological, theory to explain the properties in the ferromagnetic and antiferromagnetic regions. In his theory one considers the material to consist of two sublattices with strong ferromagnetic exchange forces within each sublattice and with weak interactions between them. The interactions between the sublattices determine which type of ordering, parallel or antiparallel, minimizes the free energy. When a field is applied, one writes the total energy as a sum of the interaction with the applied field, an exchange energy between the sublattices, and a magnetocrystalline energy. The last item is the energy associated with the axis of magnetization. The equilibrium configuration, and thus the magnetization curve, is found by minimizing the total energy with respect to the orientations of the magnetic moments of the sublattices. To explain the ferro-antiferromagnetic transition Néel assumed the magnetocrystalline energy to be of the form

$$E_M=-\tfrac{1}{2}K_0(\cos^2\theta_A+\cos^2\theta_B)-K_1\cos\theta_A\cos\theta_B,$$

where θ_A, θ_B are the orientations of the sublattice magnetic moments with respect to the axis of magnetization. The saturation moment of a sublattice, the magnetocrystalline energy constants, and the exchange energy parameter are chosen to give agreement with the experimental data at each temperature.

It is clear that Néel's original calculations do not apply for dysprosium because the single crystals showed properties inconsistent with his initial assumptions. In fact, between 110°K and 179°K a unique axis of magnetization does not exist because all directions in the basal plane are equivalent magnetically.

Above 110°K the isotropy in the basal plane suggests that the interaction between the sublattices depends only on the angle between their magnetic moment vectors. Thus instead of Néel's magnetocrystalline energy terms, one may assume a two term Fourier expansion for the interaction energy,

$$E_I=a\cos(\phi_A-\phi_B)+b\cos2(\phi_A-\phi_B).$$

The second term is necessary to explain the antiferro-ferromagnetic transition. This assignment, though not unique, does give a consistent fit with the experimental magnetization curves at all temperatures and orientations.

II. BASIC EQUATIONS AND EVALUATION OF PARAMETERS

The following expression is postulated for the angular dependence of the magnetic interaction energy per unit volume of the material:

$$E=-\tfrac{1}{2}MH\cos\phi_A-\tfrac{1}{2}MH\cos\phi_B+a\cos(\phi_A-\phi_B)+b\cos(2\phi_A-2\phi_B)\pm\tfrac{1}{2}k\cos6\phi_A\pm\tfrac{1}{2}k\cos6\phi_B. \quad (1)$$

Here the subscripts A, B refer to the two sublattices; $\frac{1}{2}M$ is the magnetic moment per unit volume of each sublattice; H is the internal magnetic field in either the $\langle 10\bar{1}0\rangle$ or $\langle 11\bar{2}0\rangle$ direction; ϕ_A and ϕ_B are the angles

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[1] F. Trombe, Compt. rend. **221**, 19 (1945).
[2] F. Trombe, J. phys. radium **12**, 22 (1951).
[3] F. Trombe, Compt. rend. **236**, 591 (1953).
[4] Elliott, Legvold, and Spedding, Phys. Rev. **94**, 1143 (1954).
[5] Behrendt, Legvold, and Spedding, Phys. Rev. **109**, 1544 (1958).
[6] The same notation for directions in the hexagonal lattice is used as in reference 5.
[7] L. Néel, Compt. rend. **242**, 1549, 1824 (1956).

between the sublattice magnetizations and the magnetic field; a, b are the interlattice interaction constants; k is the anisotropy constant; and the plus sign applies when H is in the $\langle 10\bar{1}0\rangle$ direction and the minus when H is in the $\langle 11\bar{2}0\rangle$ direction.

For most purposes the dependence of M on H may be ignored. An estimate of this dependence can be made from the Weiss formula

$$M=M_sL[(\mu/kT)(H+\lambda M)], \tag{2}$$

where M_s is the saturation magnetization, L is the Langevin function, μ is the magnetic moment per ion, and λ is the molecular field constant. From the paramagnetic susceptibility data,[5] one estimates μ to be 10.6 Bohr magnetons and λ to be 470. The dependence of M on H is found to be negligible except at temperatures higher than 130°K. The Weiss formula is used

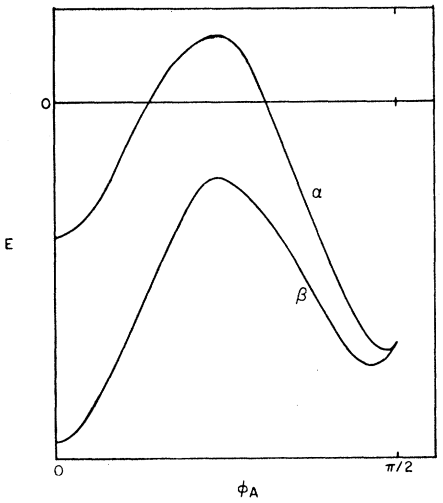

FIG. 1. Typical dependences of E on ϕ_A, as given by Eq. (5). For weak fields H, case α applies and the least value of E is near $\phi_A=\frac{1}{2}\pi$. For strong fields case β applies and the least value is at $\phi_A=0$.

below to give $M(H)$ at these higher temperatures when the magnetization is parallel to the field and otherwise the dependence of M on H is ignored.

The parameters M, a, b, k (and M_s at temperatures above 130°K) are to be chosen to give agreement with the experimental data at each temperature.

First the temperature range 110°K to 179°K will be considered. The material is isotropic in the basal plane so one can put k equal to zero. Equation (1) can be written as

$$E=-MH\cos\tfrac{1}{2}(\phi_A+\phi_B)\cos\tfrac{1}{2}(\phi_A-\phi_B)+a\cos(\phi_A-\phi_B)+b\cos 2(\phi_A-\phi_B), \tag{3}$$

and then the minimization is easily carried out by regarding $\phi_A+\phi_B$ and $\phi_A-\phi_B$ as the independent variables. Physically it is clear that only $0\leq\phi_A\leq\frac{1}{2}\pi$ and $-\frac{1}{2}\pi\leq\phi_B\leq 0$ need be considered. From the dependence on $\phi_A+\phi_B$ one sees that, at the minimum,

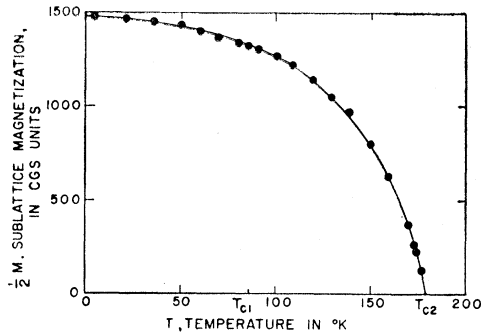

FIG. 2. Empirical values of sublattice magnetization at zero external magnetic field. T_{c1} is the ferromagnetic to antiferromagnetic transition temperature and T_{c2} is the antiferromagnetic to paramagnetic transition temperature. The points are values obtained by fitting the experimental magnetization curves with the formulas given in Sec. II and a smooth line is drawn through them.

$$\phi_A=-\phi_B, \tag{4}$$

so the problem reduces to finding the minimum of

$$E=-MH\cos\phi_A+a\cos 2\phi_A+b\cos 4\phi_A. \tag{5}$$

Depending on the size of H, E as a function of ϕ_A may have either of the dependences shown in Fig. 1. For small field H, case α applies and ϕ_A at the minimum of E is near $\pi/2$; for large field, case β applies and ϕ_A at minimum energy is zero. There is a discontinuity in the equilibrium value of ϕ_A as a function of H at the point where the two minima are at equal values of E. As long as the minimum is so near $\phi_A=\pi/2$ that an expansion for small $\cos\phi_A$ applies, one finds that at weak fields the equilibrium value of ϕ_A is given by

$$\cos\phi_A=MH/(4a-16b), \tag{6}$$

and that the discontinuity takes place at the field value given by

$$M^2H^2-8(a-4b)MH+16a(a-4b)=0. \tag{7}$$

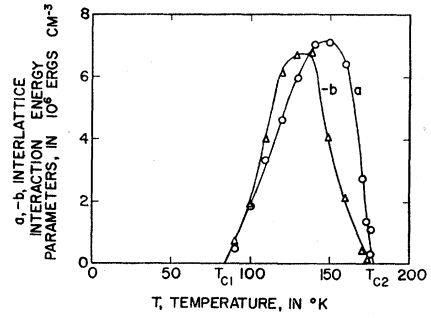

FIG. 3. Empirical values of interaction energy parameters a and b, as introduced in Eqs. (3) and (10). The points are values obtained by fitting the experimental magnetization curves with the formulas given in Sec. II and smooth lines are drawn through them.

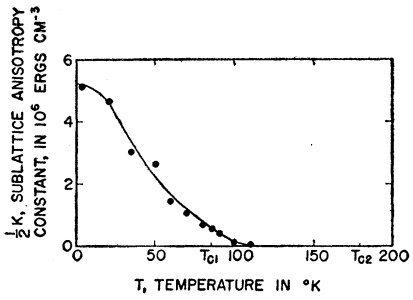

FIG. 4. Empirical values of the anisotropy constant for the sixfold anisotropy of a sublattice in the basal plane. The points are values obtained by fitting the experimental magnetization curves with the formulas given in Sec. II. The smooth line indicates a temperature dependence of $[M(T)]^{21}$, as predicted by Zener's theory.

The net magnetization of the material σ is given by

$$\sigma=\tfrac{1}{2}M\cos\phi_A+\tfrac{1}{2}M\cos\phi_B, \tag{8}$$

where ϕ_A, ϕ_B are the angles at which E is a minimum. Equations for the magnetization curves are then

$$\sigma=M^2H/(4a-16b) \tag{9}$$

for weak fields, Eq. (2) for strong fields, and with a discontinuous jump between at a field value given by Eq. (7). In Figs. 2 and 3 the values of M, a, and b which give the best agreement between theoretical and experimental magnetization curves are plotted and the actual agreement for three of the magnetization curves is shown in Fig. 5(A).

Next the temperature range 85°K to 110°K will be considered. The problem is now more complicated because of the anisotropy. When the magnetic field is in the $\langle 10\bar{1}0\rangle$ direction, Eq. (1) can be rewritten as

$$\begin{aligned}E=&-MH\cos\tfrac{1}{2}(\phi_A+\phi_B)\cos\tfrac{1}{2}(\phi_A-\phi_B)\\&+a\cos(\phi_A-\phi_B)+b\cos 2(\phi_A-\phi_B)\\&+k\cos 3(\phi_A+\phi_B)\cos 3(\phi_A-\phi_B).\end{aligned} \tag{10}$$

There are several qualitatively different types of minimum energy configurations possible, depending on the relative sizes of the parameters. The one that leads to agreement with the experimental data has the sublattices oriented antiparallel before the transition and parallel after. An analysis similar to that of the previous paragraph gives the following equations for the net magnetization:

$$\sigma=M^2H/(4a-16b+36k), \tag{11a}$$

$$MH=36k[(\sigma/M)-(16/3)(\sigma/M)^3+(16/3)(\sigma/M)^5], \tag{11b}$$

$$\sigma=M, \tag{11c}$$

where the first equation applies for weak fields, the second for intermediate fields, and the third for strong fields. An analytical formula for the field at the transition from Eq. (11a) to Eq. (11b) would be complicated; the actual values were found numerically in each case. The transition from Eq. (11b) to Eq. (11c) takes place at $MH=36k$. Figures 2, 3, and 4 exhibit the values of the parameters chosen and Fig. 5(B) shows the agreement with the experimental data at 100°K.

The next consideration is the temperature range 85°K to 110°K with the field in the $\langle 11\bar{2}0\rangle$ direction. Equation (1) applies with the minus signs. One can see that the simple relationship

$$\phi_A=-\phi_B$$

does not hold because it would imply that at small field the magnetic moments are perpendicular to the field in the hard direction of magnetization $\langle 10\bar{1}0\rangle$. In the absence of an external field, the spontaneous moments lie in $\langle 11\bar{2}0\rangle$ directions so that the equilibrium conditions are

$$\phi_A-\phi_B=\pi,\quad \phi_A=0,\ \pm\tfrac{1}{3}\pi,\ \pm\tfrac{2}{3}\pi,\ \pi.$$

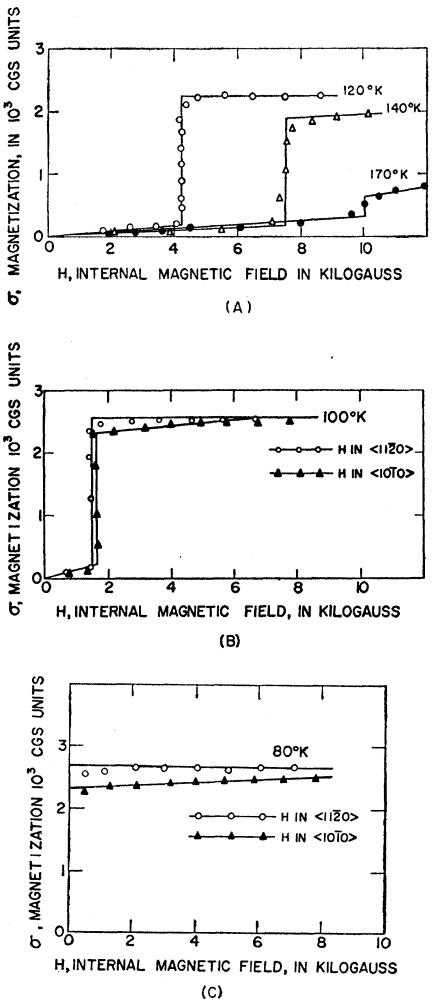

FIG. 5. Comparison of typical theoretical and experimental magnetization curves: A and B in the antiferromagnetic region, and C in the ferromagnetic region. The solid lines are the theoretical curves and the marked points show the experimental results from reference 5.

The first condition gives the minimum exchange energy and the second the minimum of anisotropy energy. When k is large enough the system is at $\phi_A \approx \frac{1}{3}\pi$, $\phi_B \approx -\frac{2}{3}\pi$ (or a physically equivalent orientation) for small H, and then there is a discontinuous jump to $\phi_A=0$, $\phi_B=0$ when H exceeds a certain value. One can discuss the magnetization curves by making expansions about these configurations. In terms of the angles δ and ϵ, defined by

$$\phi_A+\phi_B=-\tfrac{1}{3}\pi+\delta, \quad \phi_A-\phi_B=\pi+\epsilon,$$

the energy before the jump is

$$E=-a+b-k+\tfrac{1}{4}\sqrt{3}MH\epsilon+\tfrac{1}{2}(a-4b+9k)\epsilon^2 +\tfrac{1}{8}MH\delta\epsilon+(9/2)k\delta^2, \quad (12)$$

where higher powers of δ and ϵ have been disregarded. Treating δ and ϵ as independent variables, one finds that at minimum energy

$$\epsilon=-\sqrt{3}MH/4(a-4b+9k),$$
$$\delta=+\sqrt{3}(MH)^2/288k(a-4b+9k).$$

The net magnetization is

$$\sigma=\tfrac{1}{2}M\cos\phi_A+\tfrac{1}{2}M\cos\phi_B$$
$$=-M(\sin\tfrac{1}{2}\epsilon)(\tfrac{1}{2}\sqrt{3}\cos\tfrac{1}{2}\delta+\tfrac{1}{2}\sin\tfrac{1}{2}\delta).$$

To the first order in H one finds

$$\sigma=3M^2H/16(a-4b+9k), \quad (13)$$

and this gives the initial slope of the magnetization curve. Similarly for high fields, one finds that the first order solutions for the equilibrium position are

$$\phi_A=\phi_B=0, \quad \sigma=M. \quad (14)$$

The transition takes place at the field

$$H=2a/M. \quad (15)$$

Figure 5(B) shows the comparison of the theory with the experimental data.

In the ferromagnetic temperature range, $T<85°$K, the constant a in the leading term of interlattice interaction energy is negative. The total energy is a minimum when

$$\phi_A=\phi_B,$$

and Eq. (1) becomes

$$E-MH\cos\phi_A+a+b\pm k\cos6\phi_A, \quad (16)$$

where the proper sign of the anisotropy energy should be chosen according to the direction of the magnetic field as explained under Eq. (1). Equation (8) becomes

$$\sigma=M\cos\phi_A.$$

If the field is applied in the easy direction, the material simply remains magnetized and $\sigma=M$. In fact, a finite field is required to magnetize the sample; this is probably an effect of domain structure. If the field is applied in the $\langle 10\bar{1}0\rangle$ direction, the plus sign in Eq. (16)

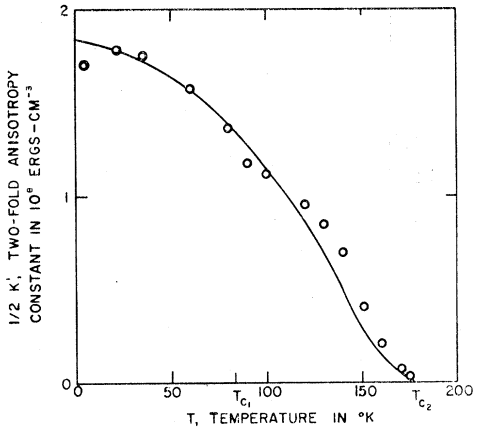

FIG. 6. Empirical values of the anisotropy constant for the twofold anisotropy of a sublattice relative to the c-axis. The points are values obtained by fitting the experimental susceptibility with Eq. (20). The smooth line indicates a temperature dependence of $[M(T)]^3$, as predicted by Zener's theory.

is to be used. The resulting magnetization curve is

$$MH=36k[(\sigma/M)-(16/3)(\sigma/M)^3 +(16/3)(\sigma/M)^5], \quad (17a)$$

$$\sigma=M, \quad (17b)$$

the saturation taking place at

$$MH=36k. \quad (18)$$

Figures 2 and 4 show the choice of M and k which gives best agreement with the data and a comparison of magnetization curves is given in Fig. 5(C).

In addition to the magnetization curves, this model can be used to discuss the large anisotropy relative to the c-axis. Assuming the field H is applied in the c-direction and considering the antiferromagnetic region, one may take the energy to be

$$E=-\tfrac{1}{2}MH\cos\theta_A-\tfrac{1}{2}MH\cos\theta_B+a\cos(\theta_A+\theta_B) +b\cos2(\theta_A+\theta_B)+\tfrac{1}{2}k'\cos2\theta_A+\tfrac{1}{2}k'\cos2\theta_B, \quad (19)$$

where θ_A, θ_B are the angles between the magnetization vectors of the sublattices and the c-axis, and k' is the anisotropy constant for this direction. Minimization of this energy for θ_A, θ_B near $\pi/2$ leads to the susceptibility

$$\chi=M^2/4(k'+a+4b). \quad (20)$$

The value of k' can be determined from the previously established values of M, a, b and the measured susceptibility.[5] The same formula with a, $b=0$ applies in the ferromagnetic region. The results are displayed in Fig. 6.

III. DISCUSSION

The curve of the sublattice magnetization when plotted as a function of temperature (Fig. 2) resembles that obtained from the conventional molecular field theory. That the curve goes smoothly through the ferromagnetic to antiferromagnetic transition tempera-

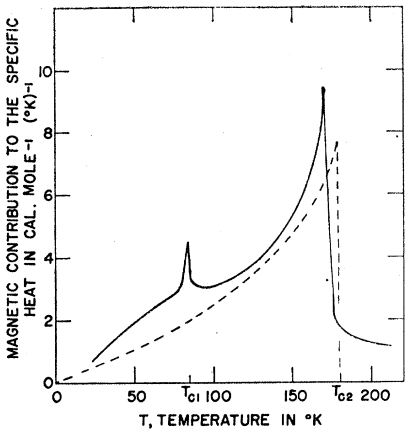

FIG. 7. Magnetic contribution to the specific heat. The solid line shows the experimental result and the dashed line the theoretical result, as given by Eq. (22).

ture gives support to the basic assumptions that the sublattices are ferromagnetic, but their interaction may create ferromagnetism or antiferromagnetism. The antiferromagnetic to paramagnetic transition temperature is the Curie temperature of a sublattice.

Figure 3 shows the temperature dependence of the interlattice interaction energy constants a and b. The strong temperature dependence of these parameters shows that the interaction is different in nature from the ordinarily assumed exchange energy,

$$\lambda'\mathbf{M}_A\cdot\mathbf{M}_B,$$

where λ' is almost temperature independent.

Figures 4 and 6 give the sublattice anisotropy constants as functions of temperature. The solid curves show the dependence predicted by Zener's theory[8] for a ferromagnetic lattice. In this theory the anisotropy constant depends on the temperature through the relationship

$$k(T)\propto[M(T)]^{\frac{1}{2}n(n+1)}, \tag{21}$$

where n is an integer. The agreement is good if $n=6$ for k and $n=2$ for k'. The M^{21} dependence of the sixfold anisotropy constant implies a spatial dependence of the anisotropy energy of the form $\frac{1}{2}k\cos^6\theta\sin6\phi$. This term does not appreciably affect the discussion of the magnetization curve when the external field is out of the basal plane because $k\ll k'$. The agreement of k' with M^3 shows that the assumed spatial dependence of this anisotropy energy is correct. However, one can not expect a very good agreement at low temperatures because k' is so strong that it can no longer be treated as a perturbation to the spin-wave system (see Pincus[8]). The application of a, b terms out of the basal plane also introduces some small corrections on k'. However the shape of the magnetization curves is too insensitive to the effect of the a, b terms to tell definitely whether the use of these terms out of the basal plane is sensible or not.

The specific heat of the dysprosium was measured by Griffel, Skochdopole, and Spedding.[9] The magnetic contribution to the specific heat can be found by subtracting the lattice and the electronic contributions from the experimental data as described in their paper. The resulting data are shown in Fig. 7, together with the curve

$$c_M=d(\tfrac{1}{4}\lambda M^2)/dT, \tag{22}$$

as suggested by the molecular field theory and using magnetization values from Fig. 2. As before, λ is taken to be 470. The effects of the interaction between sublattices, as estimated by the values of a and b, are negligible. The agreement is fair but this model gives no understanding of the anomaly at T_{c1}.

In conclusion, this model gives reasonably good agreement with almost all of the data. This agreement does not imply uniquely the types of anisotropy and interaction terms used above, but it does suggest the direction in which a more fundamental treatment of the problem should proceed.

[8] C. Zener, Phys. Rev. **96**, 1335 (1954). See also F. Keffer, Phys. Rev. **100**, 1692 (1955); and P. Pincus, Phys. Rev. **113**, 769 (1959).

[9] Griffel, Skochdopole, and Spedding, J. Chem. Phys. **25**, 75 (1956).