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Effect of Crystalline Electric Fields on Ferromagnetic Anisotropy*

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The effect of the electrostatic crystalline field has been considered for a magnetic crystal in which the ions are strongly coupled by ferromagnetic exchange. On the basis of the one-ion approximation that the exchange can be represented by a Weiss molecular field, it is possible to derive expressions for the anisotropy constants, $K_i(T)$, in terms of the parameters occurring in the spin Hamiltonian of the isolated ions, and the magnetization of the lattice at the temperature, T. The treatment assumes that the magnetic electrons can be considered as localized on the individual ions, and thus applies primarily to nonmetallic substances such as ferrites. The presence of more than one aligned sublattice is easily taken into account if the magnetization of each sublattice can be calculated from the Néel equations.

INTRODUCTION

ALTHOUGH the importance of crystalline electric fields has long been recognized in connection with the anisotropy of antiferromagnetic crystals,[1] only very recently[2,3] has this mechanism been invoked to explain the observed anisotropy energies of nonmetallic ferro- (or ferri-) magnetic materials such as ferrites. The reason for this lies partly in the fact that up to a few years ago theories of ferromagnetism were concerned mainly with metals, for which the concept of localized magnetic electrons subjected to an electrostatic field from the surrounding lattice is of dubious validity. However, for ferrites and similar crystals this type of model seems to be much more justified, since, even if the binding with the neighbors is not entirely ionic but to some extent covalent, it is still meaningful to talk of the properties of isolated magnetic ions located in a crystal lattice.

The purpose of this note is to show in a very simple way how the anisotropy energy of such a system may be determined in terms of the parameters which represent the effect of the crystalline electric field in the spin Hamiltonian of the individual paramagnetic ions. The expressions also involve the strength of the exchange interaction with neighboring magnetic ions and we shall assume that this can be represented by a Weiss molecular field. This effective molecular field is closely related to the spontaneous magnetization of the sublattice to which a particular ion belongs, and if this can be deduced from magnetic moment and susceptibility measurements, by using Néel's treatment, the temperature variation of the ferromagnetic anisotropy can be found. The present discussion is restricted to the consideration of the contributions to the anisotropy from ions whose orbital angular momentum is zero or quenched. These, however, include Fe^{3+}, Mn^{2+}, Gd^{3+} (as well as Ni^{2+} and Cr^{3+} in certain compounds) so that the result is of fairly wide applicability.

The mechanism considered here, which is the same in some respects as one of those considered recently by Yosida and Tachiki,[2] is fundamentally different from those previously invoked for ferromagnetic metals,[4] in that it assumes that the anisotropy is a "one-ion" property, whereas it had previously been assumed that the anisotropy resulted from an anisotropic coupling between the magnetic ions. Such anisotropic coupling no doubt also takes place, but for many ferrites it will be very small since it is roughly proportional[5] to $(g-2)^4$ and g is often extremely close to 2.

THE ONE ION SPIN HAMILTONIAN

The form of the spin Hamiltonian of an ion depends on the symmetry of its surroundings as well as on the magnitude of its spin. For many compounds the environment of the ions is primarily cubic, consisting of either 4 or 6 almost equidistant anions, but there are nearly always some departures from this symmetry. To a first approximation, the departure from cubic symmetry is usually axial in nature, although there are often also small terms of lower symmetry. These nonaxial terms we shall neglect here, although with a little more algebra they could readily be carried through. With this approximation and dropping constant terms, the most general spin Hamiltonian for a spin $S\leq\frac{5}{2}$ is[6]

$$\mathcal{H}=\beta\mathbf{H}\cdot g\cdot\mathbf{S}+\tfrac{1}{6}a(S_x^4+S_y^4+S_z^4)+DS_\alpha^2+fS_\alpha^4,\quad(1)$$

where α denotes the direction of the axial distortion. For paramagnetic salts D is often considerably larger than a, while f is negligibly small. We shall therefore neglect this term also in the present calculation, although it must be borne in mind that f might sometimes be large if the departure from cubic symmetry is very large. Again the inclusion of this term affects the amount of algebra, but not the general form of the final

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[1] See, e.g., Nagamiya, Yosida, and Kubo, in *Advances in Physics* (Francis and Taylor, Ltd., London, 1955), Vol. 4, p. 1.

[2] K. Yosida and M. Tachiki, Progr. Theoret. Phys. Japan **17**, 331 (1957).

[3] W. P. Wolf, Bull. Am. Phys. Soc. Ser. II, **2**, 117 (1957).

[4] J. H. Van Vleck, Phys. Rev. **52**, 1178 (1937).

[5] J. H. Van Vleck, Boston Magnetism Conference 6, 1956 (unpublished).

[6] See, e.g., B. Bleaney and K. W. H. Stevens, in *Reports on Progress in Physics* (The Physical Society, London, 1953), Vol. 16, p. 108.

answer. It should be noted that, within the various approximations mentioned above, (1) is the most general form for $\mathcal{H}$ and that terms in S_x^6, etc., and higher order reduce identically to terms of lower order if $S\leq\frac{5}{2}$. (For the case of Gd^{3+}, $S=\frac{7}{2}$ and a somewhat more complicated form must be used for $\mathcal{H}$.[6] The resulting contribution to the anisotropy energy will, however, be very similar to that for $S=\frac{5}{2}$.) If $S<2$, the term in a also vanishes identically and we are left with only the axial term, but as will be shown below, this must not be taken to imply that the crystal as a whole cannot have any cubic anisotropy, although the anisotropy will then usually be small.

The first term in $\mathcal{H}$, which in the paramagnetic case represents the effect of an applied magnetic field, in our case represents the effect of the exchange interaction of the ion with its magnetic neighbors. The magnitude of the effective molecular field acting on an ion of the ith sublattice can be treated as an experimentally measurable parameter since

$$M_i/M_{i0}=B_s(g\beta H_{\mathrm{eff}}/kT), \tag{2}$$

where M_i is the spontaneous magnetization at the given temperature, M_{i0} its value at $T=0$, and B_s is the Brillouin function. The direction which H_{eff} makes with the cubic axes will be denoted by (l,m,n) and its angle with the distortion direction α by θ. It is assumed here that the magnitude of H_{eff} does not depend on its direction relative to the crystal, as is implicit in the assumption that we have only isotropic exchange interaction of the form $\sum J\mathbf{S}_i\cdot\mathbf{S}_j$, acting on spins with quenched orbits.

CALCULATION OF THE FREE ENERGY

We now proceed to calculate the free energy of the ith sublattice, F_i, as a function of lmn and θ. The anisotropy energy of the whole crystal is then found by summing F_i over all the sublattices. To illustrate the method, let us specifically calculate the contribution from a simple sublattice of Fe^{3+} ions which have $S=\frac{5}{2}$. For one such ion, the energy levels are given by (1)[7,8] as

$$W_{\pm\frac{5}{2}}=\pm\tfrac{5}{2}g\beta H_{\mathrm{eff}}+\tfrac{1}{2}a(1-5\phi)+(5/3)D(3\cos^2\theta-1)$$
$$\pm\frac{D^2}{4g\beta H_{\mathrm{eff}}}[5+70\cos^2\theta-75\cos^4\theta],$$

$$W_{\pm\frac{5}{2}}=\pm\tfrac{3}{2}g\beta H_{\mathrm{eff}}-\tfrac{3}{2}a(1-5\phi)-\tfrac{1}{3}D(3\cos^2\theta-1)$$
$$\pm\frac{D^2}{4g\beta H_{\mathrm{eff}}}[9-66\cos^2\theta+57\cos^4\theta],$$

$$W_{\pm\frac{1}{2}}=\pm\tfrac{1}{2}g\beta H_{\mathrm{eff}}+a(1-5\phi)-\tfrac{4}{3}D(3\cos^2\theta-1)$$
$$\pm\frac{D^2}{4g\beta H_{\mathrm{eff}}}[4-40\cos^2\theta+36\cos^4\theta],$$

where $\phi=l^2m^2+m^2n^2+n^2l^2$, provided $a<D\ll g\beta H_{\mathrm{eff}}$ as they are in our case. Constant terms which are common to all six levels and therefore do not affect the anisotropy have been omitted.

Using these expressions, we can write down explicitly the partition function of a sublattice of N such ions as

$$Z=\left[\sum_{m=-\frac{5}{2}}^{m=\frac{5}{2}}\exp(-W_m/kT)\right]^N, \tag{3}$$

and from this we can calculate the free energy $F_i=-kT\ln Z$. If we expand those terms in $\exp(-W_m/kT)$ which contain the crystal field parameters (whose magnitudes are small compared to kT at all but the very lowest temperatures), and retain only leading terms, we get

$$F_i=N\left\{F_0(y)+D\cos^2\theta p(y)+\frac{D^2}{g\beta H_{\mathrm{eff}}}\cos^4\theta q(y)\right.$$
$$+a(l^2m^2+m^2n^2+n^2l^2)r(y)-\frac{1}{2}\frac{D^2}{kT}\cos^4\theta s(y)$$
$$\left.+\frac{1}{2}\frac{D^2}{kT}\cos^4\theta[p(y)]^2\right\}, \tag{4}$$

where

$$p(y)=(1/Z_0)(5-y-4y^2-4y^3-y^4+5y^5),$$
$$q(y)=(1/4Z_0)(75-57y-36y^2+36y^3+57y^4-75y^5),$$
$$r(y)=(5/2Z_0)(-1+3y-2y^2-2y^3+3y^4-y^5),$$
$$s(y)=(1/Z_0)(25+y+16y^2+16y^3+y^4+25y^5),$$
$$Z_0=1+y+y^2+y^3+y^4+y^5,$$
$$y=\exp(-g\beta H_{\mathrm{eff}}/kT).$$

This can be condensed to

$$F_i=N\{F_0(y)+D\cos^2\theta p(y)+a(l^2m^2+m^2n^2+n^2l^2)r(y)$$
$$+(D^2/kT)\cos^4\theta t(y)\}, \tag{5}$$

where

$$t(y)=-q(y)/\ln y-\tfrac{1}{2}s(y)+\tfrac{1}{2}[p(y)]^2. \tag{6}$$

F_0 denotes the large part of the free energy which is independent of the direction of the exchange field and therefore of no interest in connection with anisotropy. The value of y at any particular temperature is most simply obtained from M_i by writing the Brillouin function in Eq. (2) in the form

$$\frac{M_i}{M_{i0}}=\sum_s^{-s}my^{-m}\bigg/\left(S\sum_s^{-s}y^{-m}\right), \tag{2a}$$

and solving graphically. The functions $p(y)$, $r(y)$ and $t(y)$ plotted against M_i/M_{i0} are shown in Fig. 1. Analogous functions for the cases of $S=1$, $S=\frac{3}{2}$, and $S=\frac{7}{2}$ are shown in Figs. 2, 3, and 4.[9] As T tends to zero

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[7] R. de L. Kronig and C. J. Bouwkamp, Physica **6**, 290 (1939).

[8] B. Bleaney and D. J. E. Ingram, Proc. Roy. Soc. (London) **A205**, 336 (1951).

[9] The full expressions for these functions, together with tabulated values, are given in an Air Force Cambridge Research Center Scientific Report, AFCRC-TN-57-594 (unpublished).

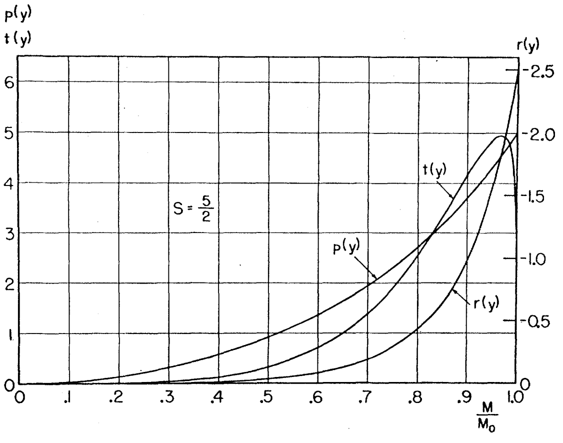

FIG. 1. Variation of $p(y)$, $r(y)$, and $t(y)$ as a function of relative sublattice magnetization for a spin $S=\frac{5}{2}$.

the last term in Eq. (5) tends to 0/0; the correct limit for this term is found in the usual way to be $75D^2 \cos^4\theta / 4g\beta H_{\text{eff}}$, as is obvious also by inspection of the energy levels in Eq. (3).

If the crystal as a whole has cubic symmetry it follows that there must be several ions in unit cell, all similar except for the direction of the axial distortion relative to the crystal axes, and we must therefore average the terms in $\cos\theta$ over this set of directions. The mean value of $\cos^2\theta$ for any set of distortion axes with cubic symmetry is $\frac{1}{3}$ so that the term linear in D does not contribute to the total measured anisotropy. The term in $\cos^4\theta$ averages to a constant plus $\gamma(l^2m^2+m^2n^2+n^2l^2)$, where $\gamma=4/9$ if the distortions lie along the four [111] directions, and $\gamma=-\frac{2}{3}$ if they lie along the three [100] directions. If there are more than four inequivalent ions in the unit cell, smaller values of γ result. We shall assume that the cubic axes of each ion coincide with those of the crystal as a whole, though this is by no means always true. If they did not, we would then have to average over the differently oriented sets of cubic axes and this would decrease the total anisotropy arising from the term in a.

From Eq. (5) it follows that K_1, the first order cubic anisotropy coefficient as usually defined, is given by

$$K_1 = ar(y) + \gamma(D^2/kT)t(y). \tag{7}$$

Similar expressions for the higher order anisotropy coefficients can be obtained from Eq. (4) by retaining further terms in the series expansion. However, an order of magnitude calculation shows that values of K_2, etc., obtained in this way will be considerably smaller than K_1, in disagreement with some of the reported experimental values. This difficulty has also been encountered previously by Van Vleck in his calculation of the anisotropy arising from pseudodipolar and quadrupolar interaction. It appears, therefore, that there is some other mechanism contributing at least to higher order anisotropy, arising, maybe, from disorder in the crystal. This supposition finds some support in the fact that yttrium iron garnet, a ferrimagnetic substance with well-defined and perfectly regular crystal structure,[10] is reported to have no detectable second order anisotropy between 20°K and 540°K, though the magnitude of its K_1 is quite normal.[11]

For ions which are in an S state, the magnitudes of the coefficients a and D cannot be estimated from theory since even the physical mechanism giving rise to the crystal-field splittings is at present in doubt.[12] However, since they are properties of the individual magnetic ions depending only on the crystal structure of the compound, they can in principle be determined experimentally if there exists a diamagnetic compound which has the same structure as the magnetic one, since one can then carry out the usual paramagnetic resonance experiments to fit $\mathcal{H}$ for each type of ion present. From such experiments one could determine a and D (and also f and lower symmetry terms) for the different lattice sites, as well as α, the principal distortion direction.

In the absence of such data we can guess at the constants, assuming them to be of the same order of magnitude as usually found in paramagnetic salts, say, $a \sim 0.02$ cm^{-1}, $D \sim 0.2$ cm^{-1}. It then turns out that the term in a gives a contribution to K_1 close to the experimental values found in ferrites ($K_1/M \sim 100$ oersteds), as previously noted by Yosida and Tachiki,[2] while the terms in D^2 are considerably smaller. However, it must be stressed that ferrites are far less regular compounds than most paramagnetic salts as regards the microscopic symmetry of the individual ion sites, so that we should expect relatively much bigger effects from distortions, with values of D maybe an order of magnitude larger. In crystals whose over-all symmetry is not cubic, the anisotropy from the term linear in $D\cos^2\theta$ does not average to zero and an axial anisotropy of order D/atom results. The fact that uniaxial crystals, even those containing only magnetic ions in S states, (e.g.,

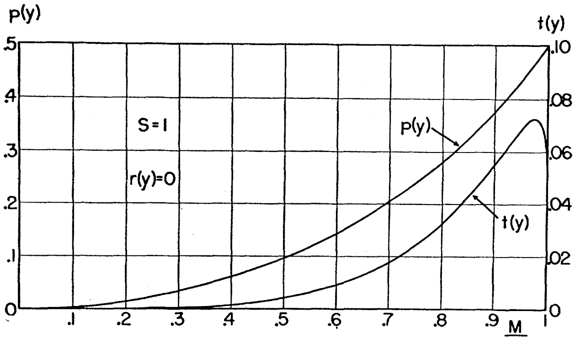

FIG. 2. Variation of $p(y)$ and $t(y)$ as a function of relative sublattice magnetization for a spin $S=1$.

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[10] F. Bertaut and F. Forrat, Compt. rend. **242**, 382 (1956).

[11] J. F. Dillon, Jr., Phys. Rev. **105**, 759 (1957).

[12] Hutchison, Judd, and Pope, Proc. Phys. Soc. (London) **B70**, 514 (1957).

$BaFe_{12}O_{19}$), have anisotropies one and often two orders of magnitude greater than cubic crystals supports the guess that in some ferrites D may be considerably larger than a, and larger than the D in hydrated paramagnetic salts.

IMPORTANCE OF NONCUBIC TERMS

In any case, the terms in D will be of prime importance for ions with $S<2$, since for these the cubic term in a in the spin Hamiltonian vanishes identically. It has always been assumed up to now[2–4] that crystalline field effects would not then contribute to the macroscopic anisotropy of a crystal with over-all cubic symmetry, but this we can see now is only true to first order. Since anisotropy only enters in these cases through terms in D^2/kT and $D^2/g\beta H_{\text{eff}}$, the contribution will usually be small, but in compounds with large local distortions from cubic symmetry their effect can become quite large.

The terms in D^2 will also be important at low temperatures in crystals in which H_{eff} is relatively weak, i.e., in crystals in which a particular sublattice begins to contribute to M only at low temperatures. This is because H_{eff} occurs in the denominator of the second order terms in the expressions for the energy levels, and also because the expansion of Z (and also F) converges more slowly at low temperatures for a given value of y. One substance in which this effect should be important is gadolinium iron garnet, for which it is known that the Gd^{3+} lattice is only weakly coupled to the strongly aligned Fe^{3+} lattices.[13] It might be pointed out that the converse of this effect is true quite generally, namely that a sublattice which is subjected to a weak exchange field will at moderately high temperatures contribute only very little to the anisotropy. This can readily be seen in Figs. 1, 2, 3, and 4 which show that the functions which multiply a and D^2/kT become very small for only moderately small values of M_i/M_{i0}. Unless a and D were exceptionally big, we would expect therefore that the Gd^{3+} ions in the compound cited above would contribute very little to the anisotropy at high temperatures and that K_1 should be very nearly the same as that of the analogous yttrium compound in which the anisotropy arises solely from the Fe^{3+} ions. Preliminary experiments have shown that this indeed seems to be the case.[14]

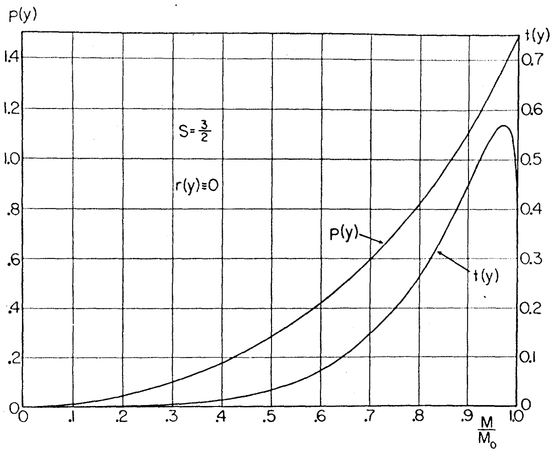

FIG. 3. Variation of $p(y)$ and $t(y)$ as a function of relative sublattice magnetization for a spin $S=\frac{3}{2}$.

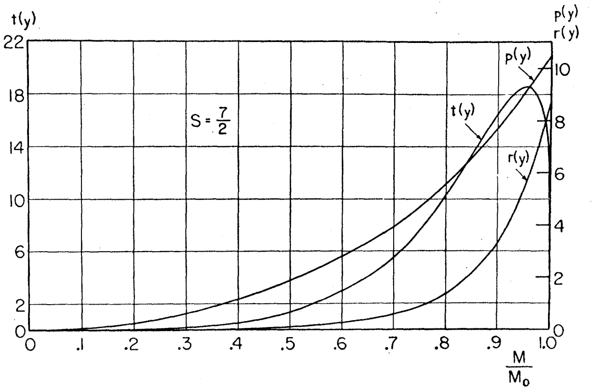

FIG. 4. Variation of $p(y)$, $r(y)$, and $t(y)$ as a function of relative sublattice magnetization for a spin $S=\frac{7}{2}$.

In addition to affecting the absolute magnitude of K_1, a term in D^2 can also radically affect its dependence on temperature, since the function by which it is multiplied, $t(y)$, varies very differently from $r(y)$, which multiplies a. (See Fig. 1.) This is a fact which must be borne in mind when considering the effect of internal strains on the anisotropy and in particular its temperature dependence. Since anisotropy measurements are invariably made under conditions of constant stress, rather than constant strain, this remark applies particularly to the contribution to the anisotropy arising from magnetostriction,[15] and results should therefore be corrected for this effect before any attempt is made to fit them to the above equations. In this respect Ni^{2+} might be expected to show the biggest effect, since D depends on the proximity of excited orbital states which will be much closer in Ni^{2+} than in, say, Mn^{2+} or Fe^{3+}.

In passing, it may be noted that there is yet another reason why nickel ferrites might show an anomalous anistropy. A Ni^{2+} ion in an octahedral surrounding has a ground state which is an orbital singlet and so behaves very much like a free spin. The crystalline field effects cited above are then the results of small perturbations. In a tetrahedral surrounding, however, (which still has cubic symmetry) the ground state would be an orbital triplet very similar to that of a Co^{2+} ion in an octahedral site.[16] This is known to give rise to extremely large anisotropy, of the order of 100 times that of an ion with a quenched ground state. It is

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[13] R. Pauthenet, Compt. rend. **242**, 1859 (1956).

[14] R. White (private communication) and B. A. Calhoun (private communication).

[15] C. Kittel, Revs. Modern Phys. **21**, 541 (1949).

[16] J. H. Van Vleck, Phys. Rev. **41**, 208 (1932).

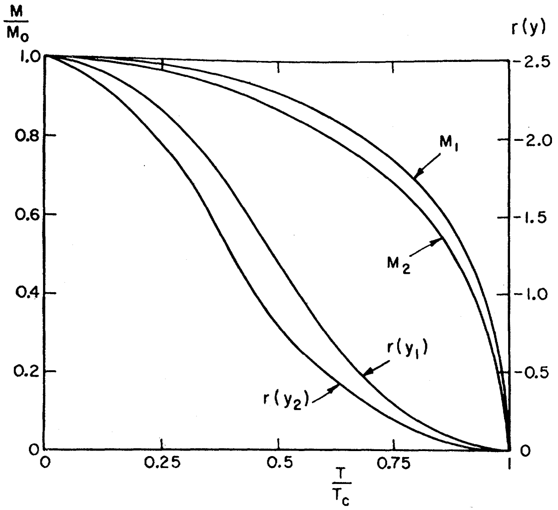

FIG. 5. Hypothetical two sublattice example, showing the difference between the two curves of $r(y)$ *versus* T/T_c corresponding to two assumed variations of M_i/M_{i0}. $M=\lambda M_1-\mu M_2$; $K=N[\lambda a_1 r(y_1)+\mu a_2 r(y_2)]=K_0[r(y_1)+\epsilon r(y_2)]$.

clear therefore that, if in the ferrite only a few Ni^{2+} ions occupy tetrahedral instead of their usual octahedral sites, an important contribution to the total anisotropy will result. It may be that this mechanism is responsible for the considerable differences between various nickel ferrite crystals which have been reported in the literature.[17]

As well as affecting the anisotropy, noncubic terms with distortion directions which differ for various sets of ions throughout the crystal may also provide a mechanism for line width broadening. If it were not for the effect of exchange, ions at different lattice sites would resonate at frequencies varying over a range of order D cm^{-1}, the exact spread depending on the relative orientations of the applied field and the distortion axes. Under the influence of exchange, this spread is reduced by a factor of order $D/g\beta H_{\text{eff}}$,[18] but even so we might still expect a contribution to the line width of order $D^2/g\beta H_{\text{eff}}$. Even if one takes a conservative value for $D\sim 0.2$ cm^{-1} and $g\beta H_{\text{eff}}\sim 100$ cm^{-1}, this gives $\Delta H\sim 4$ oersteds which is not negligible when one is trying to explain the experimentally observed values in yttrium iron garnet which are of the order of 10 oersteds. Moreover, we have neglected numerical factors of the order of $2S$ which in an exact calculation would push up the value almost another order of magnitude. An interesting fact which should be noted regarding this mechanism is that the effect will be anisotropic, since it depends on the relative angles between H and the distortion axes. Along certain directions of high macroscopic symmetry, (e.g., the [100] axis in a cubic crystal), several sets of ions may become equivalent and this will lead to a decrease in line broadening. The effect will obviously be large in crystals in which the local distortions are large, but it will probably be even more important in crystals in which there are ions with only a partially quenched orbital angular momentum, for which the individual g values can be highly anisotropic. The rare earth iron garnets may well present a set of compounds for which this is the case, but at present too little is known about the behavior of the individual rare earth ions to make any definite predictions.

EFFECT OF MORE THAN ONE SUBLATTICE

In any particular crystal the combined effect of several sublattices can be calculated only if the respective parameters of the one-ion spin Hamiltonians are known, as well as the respective sublattice magnetizations. However, we can already get some idea of the great variety of K_1 *versus* T curves possible if we examine a simple fictitious example involving only two sublattices having cubic field parameters a_1 and a_2 and negligible D's. We shall assume that the sublattice magnetization curves are as shown in Fig. 5 and we shall examine the variation of the K_1 *vs* T curve as a function of the ratio $\epsilon=\mu a_2/\lambda a_1$, where λ and μ represent the fractions of the total number of magnetic ions, respectively on the 1 and 2 sublattices. We shall show that in certain cases, the total anisotropy can be extremely sensitive to the value of this ratio, emphasizing again the very likely possibility of considerable discrepancies between crystals having slightly different stoichiometries.

From Eqs. (4) and (7) the total first order cubic anisotropy for the two sublattice model is given by

$$K_1=N[\lambda a_1 r(y_1)+\mu a_2 r(y_2)]=N\lambda a_1[r(y_1)+\epsilon r(y_2)],$$

where the variations of $r(y_1)$ and $r(y_2)$ based on the assumed variation of M_1 and M_2 are shown in Fig. 5. The curves of K_1, expressed in units of $K_0=N\lambda a_1$, as a function of T for various values of ϵ is shown in Fig. 6. It will be seen that for a range of values of ϵ near -1 the shape of the curves is very sensitive to the actual value of ϵ, and that for some values the anisotropy even changes sign as a function of temperature.

Although we have attempted here to give only the crudest outline of what can happen, it might be pointed out that one would expect ϵ to have a negative value of the order of unity in many cases. This is because the main difference between the A and B sites in a ferrite lies in the fact that the A sites have 4 nearest O^{2-} neighbors while the B sites have 6, and from a simple point charge model it can be shown that the coefficients of the cubic electric potential produced by these two types of arrangements will be of the same order of magnitude with, however, opposite signs. This fact has been noted by Yosida and Tachiki, and it has also

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[17] D. W. Healy, Jr., Phys. Rev. **86**, 1009 (1952); Yager, Galt, and Merritt, Phys. Rev. **99**, 1203 (1955).

[18] See, e.g., P. W. Anderson and P. R. Weiss, Revs. Modern Phys. **25**, 269 (1953).

recently been observed experimentally by Folen and Rado[19] in their measurements on Mg ferrite.

CONCLUSION

We have shown how crystalline field effects of the kind known to act on the ions of paramagnetic salts can lead to a macroscopic anisotropy in ferro- (and ferri-), magnetic crystals in which the ions are coupled by isotropic exchange. We have neglected the possibility of anisotropic coupling on the grounds of a crude order of magnitude estimate, which indicates that it will be small if the orbital contribution to the magnetic moment (g value) is highly quenched by the crystalline field. This will certainly not be true for ions in which the main part of the crystal field does not remove all the orbital degeneracy, but for ions which are in S states, the approximation should be good. The importance of the *local* symmetry of the magnetic ion sites has been emphasized, since even in macroscopically cubic crystals relatively small, local distortions can affect the overall anisotropy appreciably in some cases. The physical reason for this lies in the fact that the leading term in the expansion of an axial crystalline potential is one of second order, which in the calculation of the crystalline field splitting is multiplied by $\langle r^2 \rangle$, the mean square orbit, while the lowest order cubic potential acts only through $\langle r^4 \rangle$. Thus in a crystal in which the ionic environment is mainly cubic and only slightly distorted, the effect of an axial term may nevertheless be quite large, and this may well be the case in ferrites. The experimental approach to the solution of this problem which suggests itself is the systematic investigation of paramagnetic resonance of magnetically isolated ions dispersed in diamagnetic crystals which are isomorphous with the ferrimagnetic ones. This could be done presumably quite easily, but it must be born in mind that the results might not be quite unambiguous, since it is known that in paramagnetic salts the crystalline field splittings sometimes depend quite strongly on the particular diamagnetic diluent used. Further, it would be impossible to simulate the effect of magnetostriction which occurs in the ferromagnetic state and which cerntainly affects the measured anisotropy[14] if experiments are carried out, as always, under conditions of constant stress. However, the paramagnetic experiments would be useful in indicating a trend in the relative importance of the cubic and axial effects, as well as giving an order of magnitude for the two.

In ferrimagnetic crystals the effects from the various sublattices are additive and it has been shown by means of a simple example that a very wide variety of anisotropy *versus* temperature curves can then be obtained. The form of the curves can in some cases depend quite critically on the relative number of ions on the different sites and this fact may in part explain the large differences which have been reported for crystals of nominally the same material but with slightly different stoichiometries. It is also shown that it is quite possible for the anisotropy to change sign at a temperature at which the contributions from the various sublattices just cancels. The reversal in the trend of the K_1 *versus* T curve[20] of Fe_3O_4 is probably due to this effect since it occurs well above the temperature at which the observed change of phase sets in. This type of behavior is exactly analogous to different M *versus* T curves predicted by Néel's original theory of ferrimagnetism.

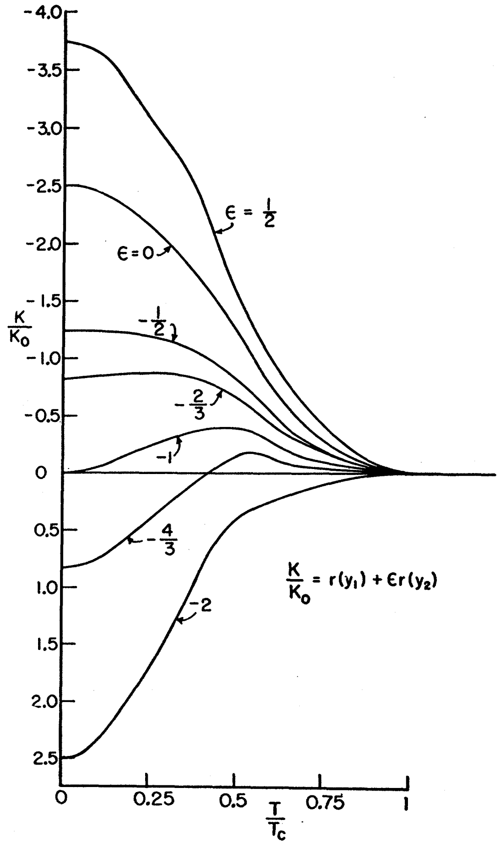

FIG. 6. Variation of first order anisotropy with temperature corresponding to different values of the parameter $\epsilon = \mu a_2/\lambda a_1$ and the two curves of $r(y)$ *versus* T/T_c shown in Fig. 5.

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