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Anisotropy and Relaxation in Ferrites

Anisotropy of Ferrous Ions in Spinels

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The magneto-crystalline anisotropy of single crystals of Ti substituted manganese ferrites $MnTi_xFe_{2-x}O_4$ for $x=0$, 0.15, 0.30 and 0.45 has been measured by the torque method between 4°K and 225°K. It appears that for increasing Ti content, which should produce an equal content of ferrous ions, K_1 becomes strongly positive and K_2 large and negative. At 4°K we find per ferrous ion $\Delta K_1 \cong 9\times10^6$ erg/c.c. and $\Delta K_2 \cong -14\times10^6$ erg/c.c.. This behaviour is similar to that of Co^{II} ions, from which it appears that the ground state of the ferrous ions in substituted $MnFe_2O_4$ also has orbital degeneracy. This is made plausible by considering the factors determining the crystalline field.

Experimental Results

With the exception of Co ferrite all cubic ferrites so far investigated have a negative value of the magnetocrystalline anisotropy constant K_1. The anomalous behaviour of the anisotropy in the $MnFe_2O_4-Fe_3O_4$ system[1] for small ferrous ion content suggests, however, that the contribution of the Fe^{II} ions to K_1 is positive. With increasing Fe^{II} content the anomaly tends to disappear. At the same time the structure changes gradually from normal to inverse. Since we thought that this change in structure is important for the anisotropy, we increased the number of ferrous ions at constant manganese content by substituting Ti for Fe, so obtaining spinels with approximate compositions $Mn^{II}Ti^{IV}{}_xFe^{II}{}_xFe^{III}_{2-2x}O_4$. Single crystals for the Ti contents =0, 0.15, 0.27 and 0.44 were made by C. Kooy by a zone melting method[2] and annealed afterwards. The Fe^{II} contents in the single crystal bars (diameter 5-6 mm) were found to increase towards the centre. The measuring samples taken from the cores of the crystals were too small for the determination of the Fe^{II} content. That of larger pieces agreed to within 10% with the Ti content. For comparison a single crystal of $MnTi_{0.15}Co_{0.15}Fe_{1.7}O_4$ containing Co^{II} instead of Fe^{II}, was made. The magnetocrystalline anisotropy of these crystals between 4.2° and 225°K was measured in the (110) plane in a field of 32KOe on an automatic torque balance, constructed by U. Enz, based on a principle

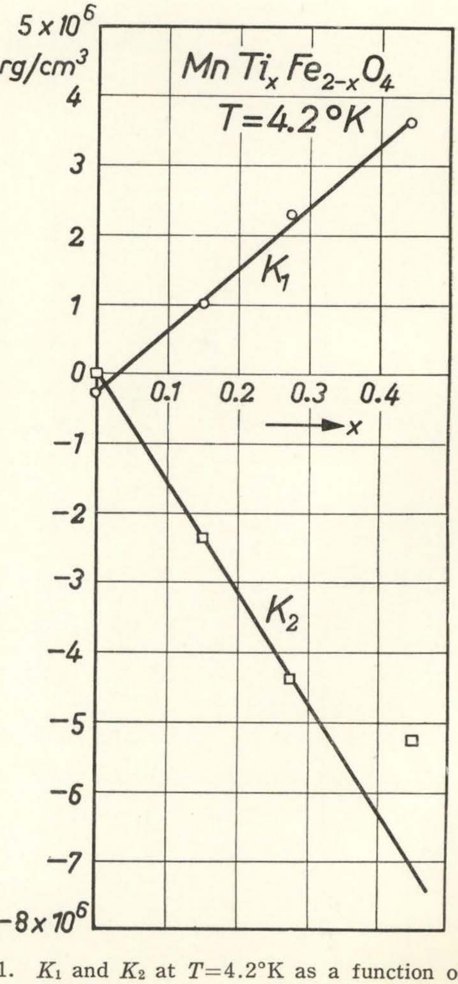

Fig. 1. K_1 and K_2 at $T=4.2$°K as a function of x for $MnTi_xFe_{2-x}O_4$.

described in ref.[3] The constants K_1 and K_2 were derived from the relations

$$K_1=4(E_{110}-E_{100})\quad K_2=9(3E_{111}-4E_{110}+E_{100})\,,$$

where the energies are obtained by integration of the torque curves. With these two constants the curves could be described to within a few percents. The values of K_1 and K_2 at $T=4.2$°K as a function of x are plotted in Fig. 1. The anisotropy constants are approximately linear in x. The decrease of the positive contribution to K_1 with increasing x, found in $\mathrm{Mn}_{1-x}\mathrm{Fe}_{2+x}\mathrm{O}_4$[1], is not observed, suggesting the importance of the normal structure for positive anisotropy. The anisotropies per ferrous ion and cobalt ion, given in Fig. 2 as a function of temperature, are deduced from the values in $\mathrm{MnTi}_{0.3}\mathrm{Fe}_{1.7}\mathrm{O}_4$ and $\mathrm{MnTi}_{0.15}\mathrm{Co}_{0.15}\mathrm{Fe}_{1.7}\mathrm{O}_4$ respectively, corrected for the anisotropy of the ferric ions using the values of $\mathrm{MnFe_2O_4}$. The energy difference $E_{111}-E_{100}$ per $\mathrm{Fe^{II}}$ ion at $T=4.2$°K is $0.9\,\mathrm{cm}^{-1}$ and per $\mathrm{Co^{II}}$ ion $2.5\,\mathrm{cm}^{-1}$. A very characteristic feature is that in both cases K_2 is large and negative.

Discussion

The large values of K_1 and K_2 of $\mathrm{Co^{II}}$ substituted in $\mathrm{Fe_3O_4}$ have been explained by Slonczewski,[4] assuming an orbital doublet as ground state. The theory predicts a positive value of K_1 and an even larger but negative value of K_2 so that $E_{111}-E_{100}\cong 15\,\mathrm{cm}^{-1}$ at

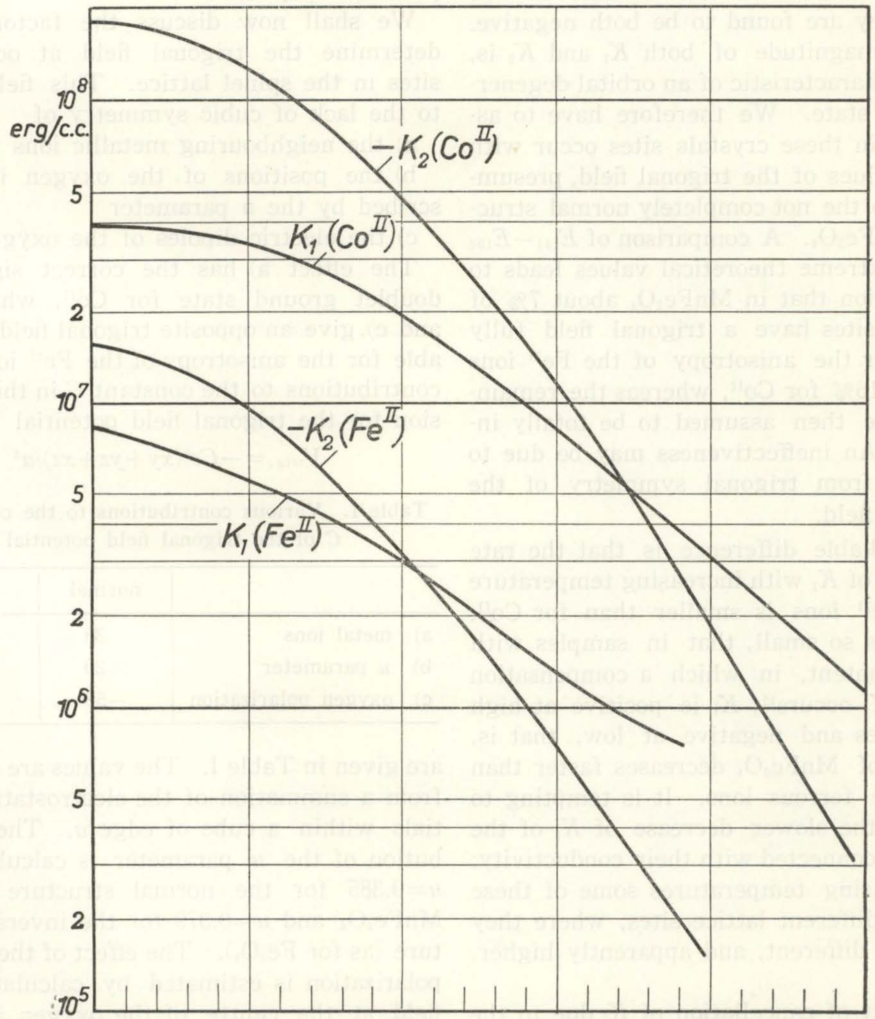

Fig. 2. K_1 and K_2 per $\mathrm{Fe^{II}}$ and $\mathrm{Co^{II}}$ ion as a function of temperature.

$T=0°K$. This doublet ground state is a consequence of the splitting, by a trigonal field, of a triplet, existing in a cubic field, into a doublet and a singlet. The sign of this trigonal field determines which of the latter two has the lowest energy. If the singlet is lowest, for a not too large energy splitting K_1 is still appreciable and positive, but K_2 is then positive[5], so that the observed sign of K_2 indicates the sequence of the levels.

Also the Fe^{II} ion in an octahedral cubic field has a lower lying orbital triplet which is split by a trigonal field; but in this case for the same trigonal field the sequence of the doublet and singlet is reversed. The sign of K_2 of Co^{II} and Fe^{II} should thus be opposite. We have seen that in fact in our crystals they are found to be both negative. The large magnitude of both K_1 and K_2 is, however, characteristic of an orbital degenerate ground state. We therefore have to assume that in these crystals sites occur with opposite values of the trigonal field, presumably due to the not completely normal structure of $MnFe_2O_4$. A comparison of $E_{111}-E_{100}$ with the extreme theoretical values leads to the conclusion that in $MnFe_2O_4$ about 7% of the lattice sites have a trigonal field fully effective for the anisotropy of the Fe^{II} ions and about 16% for Co^{II}, whereas the remaining 77% are then assumed to be totally ineffective. An ineffectiveness may be due to deviations from trigonal symmetry of the crystalline field.

A remarkable difference is that the rate of decrease of K_1 with increasing temperature for the Fe^{II} ions is smaller than for Co^{II}. In fact it is so small, that in samples with low Fe^{II} content, in which a compensation point for K_1 occurs[1], K_1 is positive at high temperatures and negative at low, that is, the $|K_1|$ of $MnFe_2O_4$ decreases faster than that of the ferrous ions. It is tempting to think that the slower decrease of K_1 of the Fe^{II} ions is connected with their conductivity: with increasing temperatures some of these will go to different lattice sites, where they can have a different, and apparently higher, anisotropy.

The effect of cancellation of K_1 due to the Fe^{II} ions is of great technical importance for the understanding of the high permeability peak (~5000) near room temperature of Mn-Zn ferrites containing about 0.05 Fe^{II} ions per formula unit. It was previously thought that the role of the ferrous ions was solely the reduction of the magnetostriction, but we are now led to the conclusion that they can also serve to make $K_1=0$ at a certain temperature. From magnetostriction measurements carried out by Enz[6] on this polycrystalline material it can be deduced that this is indeed the case. The sign of K_1 can be found because λ_{111} and λ_{100} have opposite sign, and the initial magnetostriction is determined by whichever of these applies to the easy direction. A similar cancellation of K_1 is found in Co substituted ferrites. In that case the Co anisotropy predominates at low temperatures ($K_1>0$).

We shall now discuss the factors which determine the trigonal field at octahedral sites in the spinel lattice. This field is due to the lack of cubic symmetry of

a) the neighbouring metallic ions
b) the positions of the oxygen ions, described by the u parameter
c) the electric dipoles of the oxygen ions.

The effect a) has the correct sign for a doublet ground state for Co^{II}, whereas b) and c) give an opposite trigonal field, favourable for the anisotropy of the Fe^{II} ions. The contributions to the constant C in the expression for the trigonal field potential

$$V_{\text{trig.}}=-Ce^2(xy+yz+xz)/a^3$$

Table I. Various contributions to the coefficient C of the trigonal field potential.

	normal	inverse
a) metal ions	38	28
b) u parameter	−20	− 8
c) oxygen polarization	−58	− 5

are given in Table I. The values are obtained from a summation of the electrostatic potentials within a cube of edge a. The contribution of the u parameter is calculated for $u=0.385$ for the normal structure (as for $MnFe_2O_4$) and $u=0.379$ for the inverse structure (as for Fe_3O_4). The effect of the oxygen polarization is estimated by calculating the field at the centre of the oxygen ion from the dependence of the Madelung energy on the u parameter[7]. This field appears to be quite strong for the normal structure and if we take for the oxygen polarizability 1.66 A^3 it should be even decisive for the sign of the trigonal field. Because of symmetry there is no net dipole-dipole interaction.

It may be remarked that the corresponding polarization energy of the oxygen ions amounts to $-8e^2/a$ per formula unit for the normal structure, and practically zero for the inverse one. Adding this to the Madelung energy[7] gives rise to the result that, from purely electrostatic considerations, the normal structure should always be the stable one.

In conclusion we can say that, although the calculations have little quantitative significance, they at least indicate that the trigonal field, favourable for a degenerate ground state of the Fe^{II} ion, is more likely to occur in the normal than the inverse structure.

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DISCUSSION

S. KRUPIČKA: What do you think about possible contribution of ordering in *A* positions to both trigonal field and magnetic anisotropy in MnFe ferrites?

J. SMIT: I do not think that the magnetic ordering contributes appreciably to the trigonal field on *B* sites, as is inferred from calculation of the Coulomb energy. Therefore any influence on the anisotropy of the *B* site ions is not clear.

P. K. BALTZER: Recently we have made calculations of the contribution from the Co^{2+} ion in spinels. These calculations are similar to those of Slonczewski but differ mainly in that the spin-orbit coupling and crystalline electric fields are treated in a more rigorous way. We find that Co^{2+} has a positive K_1 and negative K_2 contribution even for a trigonal field that produces a singlet orbital ground state (see Baltzer, P. in these Proceedings).

J. SMIT: If this is true it would give a very simple explanation for the observed negative value of K_2 both for the Fe^{II} and the Co^{II} ions in $MnFe_2O_4$. The origin of the negative value of K_2 for a non-degenerate ground state is, however, not clear.

J. KANAMORI: The experiment on $Ni^{2+}_{1-x}Fe^{2+}_x Fe^{3+}_2O_4$ for small x by Miyata indicates that the anisotropy constant K_1 per Fe^{2+} at octahedral sites is positive. This seems to contradict with the negative sign of K_1 in magnetite. The single ion energy of fourth order of Fe^{2+} calculated by Yosida and Tachiki yields the negative sign, whereas the second order contribution of the single ion energy of second order pointed out by Wolf yields the positive sign. As a plausible origin of the apparent discrepancy mentioned above, I should like to point out that the electron transfer in magnetite will quench Wolf's mechanism to some extent. Supposing two ions whose single ion energies of second order have different principal axes, we can show that the electron transfer between the two ions tends to make the contribution of Wolf's mechanism smaller than that which would be expected in the absence of the electron transfer. (Similar comment was also made by M. Tachiki.)

J. SMIT: The positive anisotropy observed in Ni ferrites is about 10 times smaller and is caused by different terms in the perturbation calculus, which have not to be considered for the large effects for degenerate or nearly degenerate states.

G. T. RADO: I would like to comment on the remark in your preprint that the difference in line width between ordered and disordered lithium ferrite may be caused by ferrous ions. Recent experimental work by Schnitzler, Folen and Rado, to be reported at the Phoenix Magnetism Conference in November, 1961, shows that (except when the static field is near the [110] direction) this difference is independent of oxidation and hence does not arise from ferrous ions. We believe that, in our present samples, this difference is due to the different crystalline fields experienced by certain rapidly relaxing ions in ordered and disordered lithium ferrite.

In regard to your remark on the cause of the difference in anisotropy between ordered and disordered lithium ferrite, I should mention that Folen has concluded that this difference is caused not by ferrous ions but by the different crystalline fields existing in ordered and disordered lithium ferrite. This conclusion is based partly on the result of his recent paramagnetic resonance experiments on ferric ions introduced (in a low concentration) into both ordered and disordered lithium aluminate, a crystal which is isostructural with lithium ferrite. Folen's work will also be reported at the Phoenix Conference.

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Magnetocrystalline Anisotropy of W-Type Hexagonal Barium-Cobalt-Iron Oxides

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The magnetocrystalline anisotropy of cobalt-iron W-type hexagonal oxides ($BaCo_y Fe_{18-y}O_{27}$) is investigated over the temperature range from 77° to 500°K by the torque method. The materials with intermediate cobalt concentration ($0.4<y<1.0$) display cones of easy magnetization at some temperatures. The sample $y=0.9$ shows the unusual behavior of the preferred direction changing from axis to cone to plane to cone as temperature decreases. All torque curves are well fitted by an anisotropy expression which consists of three terms of a series expansion in spherical harmonics. Each of the coefficients in the expansion is found to be linear in y. The values of each of the coefficients are found to be consistent with Slonczewski's theory of cobalt ion anisotropy throughout the observed ranges of temperature and composition.

It is well known that cobalt has a large influence on the magneto-crystalline anisotropy of ferrimagnetic oxides. In the case of hexagonal oxides with structures similar to that of magnetoplumbite, cobalt adds a large negative contribution to the principal anisotropy constant. If cobalt is present in sufficient concentration, the easy directions of magnetization lie in the basal plane or in cones of revolution[1]. Rather unusual torque curves not reducible to a simple harmonic series are sometimes observed[2].

This paper reports an investigation of the intrinsic anisotropy of hexagonal oxides in the composition system $BaCo_yFe_{18-y}O_{27}$ (denoted by $Co_yFe_{2-y}W$). The W crystal structure, viewed along the *c*-axis, consists of layers with cubic spinel structure sandwiched between non-cubic, barium-containing layers. A previous publication[3] presents evidence that cobalt is located in the spinel portion of the lattice, where it responds to magnetic annealing in much the same way as it does in cobalt-substituted magnetite ($Co_xFe_{3-x}O_4$). The spinel layers of the W structure are twice as thick as those of the other related hexagonal oxides. Therefore the environment of cobalt ions in W should be most like their environment in spinels, and it should be possible to make a meaningful comparison with the anisotropy contributed by cobalt to spinels.