discussed above. They may, however, become appreciable at higher temperatures.

The foregoing analysis shows that the mechanism suggested here is of importance in the relaxation processes involving the ordered spin and lattice systems. Although the estimates have been made for iron, the process may have wider validity for other systems, such as the ferrites and the garnets. That such mixing of excited states with ground states owing to certain types of vibrations does occur is vindicated by the absorption spectra study of systems containing the transition metal ions.[19]

We briefly discuss the mechanism in this paper in relation to those suggested earlier.[3,7] The coupling terms arising out of the expansion of exchange interaction energy in powers of displacements[3] or strain tensors[7] do not provide an unambiguous atomistic picture of the physical process and the terms are difficult to evaluate from first principles. On the other hand, the interaction terms in the present paper stem from a change in electron-lattice potential energy due to crystal field oscillations which in turn leads to

$$^{\alpha}J(R_{lm}) = \langle \phi_{\alpha}\phi_m | g_{12} | \phi_m\phi_l \rangle \langle \phi_{\alpha} | V^h | \phi_l \rangle / (E_{\alpha} - E_l),$$

and thus determines the strength of the phonon-magnon interactions. Such factors occurring in (4.3) can be calculated explicitly in principle. Also, they furnish a clear physical picture of the microscopic processes involved.

Further, the one-phonon process in the phenomeno-logical theory is written as

$$\lambda_{iklmrs} \int \frac{\partial M_i}{\partial x_k} \frac{\partial M_l}{\partial x_m} u_{rs} dV,$$

where the M_i'S are the components of the vector density of the magnetic moment of the whole crystal, λ_{iklmrs} is a coupling constant, and $u_{rs} = \frac{1}{2}(\partial u_r/\partial x_s + \partial u_s/\partial x_r)$ is the strain tensor, u being the displacement vector. Since such interaction terms may be considered as the expansion of the exchange energy in power of strain tensors, the expression [e.g., Eq. (25) of reference 7] contains an additional wave-vector factor compared to our expression [cf. (3.11)]. Thus, at low temperatures the mechanism considered in the present work would seem to be more effective. A more explicit comparison between the two approaches is, however, not possible in that it does not seem appropriate to express the present mechanism in terms of the phenomenological concepts.

The motivation behind our study is more towards understanding the exchange of energy between the phonon and magnon systems in relation to certain physical properties such as thermal conductivity and absorption of sound rather than to the microwave absorption. The details of the calculations for such studies including the spin-orbit interaction, anharmonic coupling of lattice vibrations, etc., will be considered in another paper.

ACKNOWLEDGMENTS

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Curie Point and Origin of Weak Ferromagnetism in Hematite

A. Aharoni, E. H. Frei, and M. Schieber
Department of Electronics, The Weizmann Institute of Science, Rehovoth, Israel
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The Curie point of α-Fe$_2$O$_3$ is found by differential thermal analysis (DTA) to be at 725°C, rather than the value of 675°C known from magnetic measurements. Of the theories on the origin of the weak ferromagnetism in this material, only that of Dzialoshinskii can account for all the experimental data. The 675°C is argued to be a point at which the basal plane anisotropy (assumed nonsymmetric) changes sign.

HEMATITE, α-Fe$_2$O$_3$, is a rhombohedral natural crystal having the symmetry $R\bar{3}2/c$ with[1] $a = 5.4243$ Å and $\alpha = 55°17.5'$. It contains four iron ions per unit cell, which are located along the [111] direction. The material is, to a first approximation, antiferromagnetic. Below $\sim 250°$K, the magnetization of the sub-lattices is parallel to [111], while above 250°K it is in the (111) plane.[2]

It is known[3] that a weak ferromagnetism is superimposed on the antiferromagnetism of this material and this is most pronounced in the (111) plane, and in the

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temperature range 250 to 950°K. Many theories have been suggested to explain this weak ferromagnetism. They all assumed, however, that the point at which the weak ferromagnetism disappears, namely 675°C, is the antiferromagnetic Curie point, although magnetic scattering of neutrons[2] does not vanish at this temperature, and still persists at 710°C.

We have studied Fisher commercial powder of α-Fe$_2$O$_3$ by the DTA technique, using an apparatus described elsewhere,[4] to which was later added an arrangement similar to that described by Reisman,[5] for starting below room temperature (at about 90°K). Three transition points were observed for this material, at -30, at 675, and at 725°C. We did not observe the transitions at 320 and 500°C reported by Chevalier,[6] which were not observed by other workers either.

The first transition, at -30°C, is easily identified as the Morin transition[7,8] at which the sublattice magnetization rotates[2] by 90° and the weak ferromagnetism increases abruptly.[3] It is somewhat shifted with respect to magnetic data, but this is evidently caused[9] by the absence of magnetic field in this type of measurement. If the second transition at 675°C were the Curie point, as is generally accepted, one could hardly account for the other transition. We, therefore, assume that the true antiferromagnetic Curie point is 725°C, which is also supported by the neutron diffraction data,[2] and by Mössbauer effect measurements.[10] The problem now remains what is the transition at 675°C, at which the weak ferromagnetism vanishes (or at least is too small to be detected) leaving the material purely antiferromagnetic between this temperature and the Curie point. An answer to this question must be contained in the theory that explains the origin of the weak ferromagnetism and this should eliminate some of the theories that cannot account for such an extra transition.

Li[11] considered the possibility that the ferromagnetism originates from magnetic boundaries of antiferromagnetic domains, stabilized by inhomogeneities and imperfections. Some aspects of this assumption were studied by Jacobs and Bean.[12] Now that the second transition is found, this theory is definitely out of question, since one cannot imagine domains to nucleate and disappear always at a certain critical temperature.

Néel[3] assumed the composition was Fe$_{2-x}$O$_3$ with x small, either over all the material, or as local fluctuations in the composition averaging to Fe$_2$O$_3$. In both cases one could get very small particles, essentially magnetite, which are responsible for the weak ferromagnetism. The Curie point of these particles should be higher than that of magnetite (575°C) because of the exchange interaction with the anitferromagnetic regions, yet it need not coincide with that of the antiferromagnetic α-Fe$_2$O$_3$. A detailed study of oxidation and reduction[13] suggests the possibility of some ferromagnetism of this sort, which disappears by heat treatment, but also shows that the usually observed ferromagnetism is of a different nature. Also, the DTA is not very sensitive to small amounts, at least in a mixture. Normally we could observe the magnetite Curie point when mixed with other materials, only when it was at least about 10% of the mixture, so that it is very doubtful whether the necessary small amount of magnetite would yield the 675°C transition even in the kind of solid solution assumed. Besides, such a theory can hardly be expected to account for the weak ferromagnetism in other antiferromagnets having the same crystallographic structure as α-Fe$_2$O$_3$ which is easily understood by the Dzialoshinskii theory,[14,15] to be discussed in the following.

The last two arguments against Néel's hypothesis apply also to the hyptohesis[12,16] of special ferrimagnetic forms of Fe$_2$O$_3$, the so called β-Fe$_2$O$_3$, although there is some evidence[16] suggesting the formation of this phase in $\alpha \rightarrow \gamma$ transition.

One is left now with the theory of Dzialoshinskii,[14] who essentially postulated (from symmetry consideration) the existence of an interaction term of the form

$$\mathbf{D} \cdot [\mathbf{S}_i \times \mathbf{S}_j],$$

which tends to make the spins $\mathbf{S}_i$ and $\mathbf{S}_j$ at right angle to each other, and at right angles to a vector $\mathbf{D}$, which is related to the crystallographic directions. This assumption has been criticized[1] on the basis that dipole interaction is much too small to yield the magnitude of D necessary for the magnetization of α-Fe$_2$O$_3$. However, dipole interactions are anyway known not to suffice for the observed anisotropy in ferromagnets,[17] which originates mainly from spin-orbit interaction, and actually Moriya[15] has shown that spin-orbit interaction does yield the above mentioned $\mathbf{D}$, with the right magnitude to account for the weak ferromagnetism in α-Fe$_2$O$_3$, MnCO$_3$, CrF$_3$, and possibly FeF$_3$ and CoCO$_3$. The direction of $\mathbf{D}$ in α-Fe$_2$O$_3$ is[15] along [111]. Dzialoshinskii's argument is then essentially as follows.

At low temperature [111] is an easy axis, as is clear from the neutron diffraction data.[2] An arrangement in which the sublattice magnetizations are antiparallel and along the [111] axis, is, therefore, clearly an energy

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minimum for both magnetocrystalline anisotropy and exchange energies. The term with **D** tends to get the magnetization out of this direction, but since it has to work against the anisotropy, the change it can produce is negligibly small, and the equilibrium position is still very close to [111] and antiparallel orientation (Dzialoshinskii gets [111] as the equilibrium, but this is only because he uses power series in $\cos\vartheta$, which is not allowed when $\cos\vartheta = 1$). At the Morin transition, neutron diffraction shows[2] that the spins rotate into the (111) plane, evidently because the anisotropy passes through zero and changes sign, so that [111] becomes a hard direction. At temperatures above the Morin transition, the energy minimum for anisotropy and exchange energies is therefore an antiparallel arrangement in the (111) plane. [Again, Dzialoshinskii[14] gets actually a small inclination to the (111) plane, but this originates from an extra term which is not important to the present discussion. It essentially determines, however, the width of the Morin transition.] Now the **D** term need not work against the magnetocrystalline anisotropy, which tends to put the sublattice magnetizations in a direction perpendicular to **D**, but only against the exchange. It can, therefore, produce a measurable weak ferromagnetism, of the order of D/J, which would then decrease with temperature as the magnetization of the sublattice does.

If we now add to this picture some anisotropy in the (111) plane, which is known to exist in some hexagonal ferrites,[18] the sublattice magnetization would be rather close to one of the easy directions (there should be 6 of them, because [111] is a three fold axis). If this anisotropy is assumed to change sign at 675°C, a rearrangement of the magnetization should take place at this temperature, rotating the sublattice magnetization by about 30°, and this should be seen by DTA, in the same way as the Morin transition does. [It should also be noted that the change in the quadropole moment, as seen by Mössbauer effect, is very similar at this temperature[19] to that which is observed at the Morin transition.]

Dzialoshinskii[14] has also introduced anisotropy terms

in the (111) plane, but he took them to be sinusoidal. However, if the anisotropy energy in the (111) plane is not purely sinusoidal, and the 6 minima (below 675°C) are wider than the maxima, the magnetization above 675°C should be considerably smaller than below this point and the former could be smaller than the experimental error. This nonsymmetry need not be very large, since the transition takes place rather close to the Curie point, when the sublattice magnetization is already small, so that the weak ferromagnetism is rather small anyway. The transition at 675°C, accompanied by disappearance of the magnetic moment, is thus explained. It should also be noted that the anisotropy in the (111) plane is sufficient to explain the memory effects observed[20] in this material. Siratori et al.[21] have assumed a unidirectional anisotropy in the basal plane to account for this effect, but this cannot satisfy the crystal symmetry, and is therefore very unlikely, in particular in view of the independence of the memory effect on impurities,[22] which suggests it is an intrinsic property. However, it was argued above that the spins are not actually in the [111] direction at low temperatures. The small angle they make with this axis is modified by the six fold anisotropy in the (111) plane, and the spins can, therefore, "remember" the direction they came from.

It has recently been found[22] that the transition at 675°C can be shifted considerably by partially substituting Cr, Al, Ga, or Mn for the iron in $\alpha-Fe_2O_3$. According to the above-mentioned model this means that the temperature at which the basal plane anisotropy passes zero is shifted with the substitutions. This is a reasonable possibility for anisotropy in general, as can be concluded for example by comparing the 2 graphs on p. 207 of Smit and Wijn.[18]

The Dzialoshinskii theory thus accounts, qualitatively at least, for all the known facts about the weak ferromagnetism of α-Fe$_2$O$_3$. It also explains why weak ferromagnetism is observed in rhombohedral antiferromagnets whenever neutron diffraction shows that the sublattice magnetization is in the (111) plane, while no ferromagnetism is observed whenever the sublattice magnetization is along the [111] axis[14,15].

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