FIG. 3. Deviation of critical field curves of several superconductors from parabolicity. For clarity the curves for individual samples of tin and indium are not shown (since the differences in D amount to 0.0014 or less).

found in $-dH_c/dT^2$ as temperature is lowered. Whether this behavior will extend into the range below 1°K remains to be seen.[12]

[12] It should be pointed out that the work of E. A. Lynton, B. Serin, and M. Zucker on tin indicates that a value of γ in better agreement with calorimetric data results if critical field data are extrapolated to 0°K by means of an expression which takes explicit account of the exponential temperature dependence of the superconducting electronic specific heat.

The deviation, $D(t)$, of the critical field curve from parabolicity is defined as the difference between the true critical field curve and a parabola drawn through the experimental values of H_0 and T_c:

$$D(t) = \frac{H_c(t)}{H_0} - (1-t^2),$$

Such curves are shown in Fig. 3 for the materials discussed here as well as for lead and mercury. It is clear that the differences among tin, indium, and tantalum are small. The amplitudes of these curves are sensitive to the choice of H_0 and thus are affected by the uncertainty in the extrapolation to 0°K. Measurements below 1°K will be required before the differences in amplitude of $D(t)$ for these elements can be considered to be clearly established. Further measurements, if extended to sufficiently low temperatures to yield reliable γ values, will also permit the deduction of the temperature dependence of C_{es} (the superconducting electronic specific heat) from the shape of $D(t)$.

IV. ACKNOWLEDGMENTS

Anisotropic Superexchange Interaction and Weak Ferromagnetism

TÔRU MORIYA*
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received May 25, 1960)

A theory of anisotropic superexchange interaction is developed by extending the Anderson theory of superexchange to include spin-orbit coupling. The antisymmetric spin coupling suggested by Dzialoshinski from purely symmetry grounds and the symmetric pseudodipolar interaction are derived. Their orders of magnitudes are estimated to be $(\Delta g/g)$ and $(\Delta g/g)^2$ times the isotropic superexchange energy, respectively. Higher order spin couplings are also discussed. As an example of antisymmetric spin coupling the case of $CuCl_2 \cdot 2H_2O$ is illustrated. In $CuCl_2 \cdot 2H_2O$, a spin arrangement which is different from one accepted so far is proposed. This antisymmetric interaction is shown to be responsible for weak ferromagnetism in α-Fe_2O_3, $MnCO_3$, and CrF_3. The paramagnetic susceptibility perpendicular to the trigonal axis is expected to increase very sharply near the Néel temperature as the temperature is lowered, as was actually observed in CrF_3.

INTRODUCTION

WEAK ferromagnetism of mainly antiferromagnetic crystals, represented by α-Fe_2O_3 and the carbonates of Mn and Co, has been a controversial problem for a decade. Néel[1] proposed an explanation of this phenomena based on an impurity effect, possibly magnetite. Many years later, Li[2] proposed a different explanation based on antiferromagnetic domains with magnetized walls. As he pointed out, however, the formation of antiferromagnetic domains is not energeti-

---

* On leave of absence from Tokyo Metropolitan University, Tokyo, Japan.

[1] L. Néel, Ann. phys. 4, 249 (1949).
[2] Y. Y. Li, Phys. Rev. 101, 1450 (1956).

cally advantageous and may be possible only when some imperfections of structural or chemical nature stabilize the domains. From these impurity mechanisms, we expect the magnetic properties to change from sample to sample depending on their purity.

However, it seems to be natural to raise the following question: Is weak ferromagnetism an intrinsic property of α-Fe$_2$O$_3$ or not? An affirmative answer was first given by Dzialoshinski.[3] His argument is phenomenological and is as follows: He first showed that when the spins are perpendicular to the trigonal axis, an α-Fe$_2$O$_3$ crystal with the antiferromagnetic spin arrangement has the same symmetry as that with a canted spin arrangement which has a net magnetic moment perpendicular to the trigonal axis. The next step was to write down the free energy of the system in terms of spin variables, the magnetic moments of the four sublattices. Among the terms of the form allowed under this crystal symmetry there was a term which favors the canted spin arrangement rather than the antiferromagnetic one and therefore is essential to the weak ferromagnetism. This term is expressed by

$$\mathbf{D}\cdot[\mathbf{S}_1\times\mathbf{S}_2],\qquad(1.1)$$

where $\mathbf{D}$ is a constant vector. In α-Fe$_2$O$_3$, $\mathbf{D}$ is parallel to the trigonal axis. This theory, however, is a phenomenological one and does not clarify how this interaction arises and how $\mathbf{D}$ can be calculated.

We first note that the expression (1.1) is the antisymmetric part of the most general expression for bilinear spin-spin interaction. Only the symmetric interactions have been familiar to us so far. In insulators the known spin-spin interactions are isotropic superexchange interaction, magnetic dipole-dipole interaction and anisotropic superexchange interaction of pseudodipolar type. Among them the magnetic dipole-dipole interaction can make a contribution to the antisymmetric coupling in certain special cases because of the orbital moments. Its magnitude, however, is generally very small and it vanishes in the above mentioned trigonal crystals. The anisotropic superexchange interaction studied so far[4] is the so-called pseudodipolar interaction and is symmetric. However, the previous theories do not seem to be general.

We have developed a general theory of anisotropic superexchange interaction with the use of the new formalism recently developed by Anderson.[5] We take account of the spin-orbit coupling in the mechanisms of superexchange while the previous theories do not explicitly consider the mechanism of superexchange. We could show that when the crystal symmetry is sufficiently low, the largest term of the anisotropic

superexchange which is linear in the spin-orbit coupling has an antisymmetric form as was briefly reported.[6]

In this paper we discuss the anisotropic superexchange interaction to a fuller extent and the weak ferromagnetism of α-Fe$_2$O$_3$, the carbonates of Mn and Co and CrF$_3$.

ANISOTROPIC SUPEREXCHANGE INTERACTION

The anisotropic superexchange interaction is derived by extending the theory of superexchange interaction to include the effect of spin-orbit coupling. We use Anderson's new formalism[5] of superexchange interaction. The basic one electron wave functions are those localized at the positions of magnetic ions and are orthogonal to each other. The one electron part of the Hamiltonian is diagonalized within an ion, in this representation. These basic wave functions are denoted by

$$\psi_{n\uparrow}(r-R),\quad\psi_{n\downarrow}(r-R),$$

where $\uparrow$ and $\downarrow$ mean the spin almost up and almost down, respectively. As we take account of the spin-orbit coupling, these functions are not eigenfunctions of the spin component S_z but mixtures of $+$ and $-$ spin states. The one electron Hamiltonian is written in terms of annihilation and creation operators as follows:

$$E=\sum_R\sum_n\epsilon_n(R)[\alpha_{n\uparrow}{}^*(R)\alpha_{n\uparrow}(R)+\alpha_{n\downarrow}{}^*(R)\alpha_{n\downarrow}(R)]$$
$$+\sum_{R\neq R'}\sum_{n,n'}\{b_{n'n}(R'-R)[\alpha_{n'\uparrow}{}^*(R')\alpha_{n\uparrow}(R)$$
$$+\alpha_{n'\downarrow}{}^*(R')\alpha_{n\downarrow}(R)]+C_{n'n}{}^z(R'-R)[\alpha_{n'\uparrow}{}^*(R')\alpha_{n\uparrow}(R)$$
$$-\alpha_{n'\downarrow}{}^*(R')\alpha_{n\downarrow}(R)]+C_{n'n}{}^-(R'-R)\alpha_{n'\uparrow}{}^*(R')\alpha_{n\downarrow}(R)$$
$$+C_{n'n}{}^+(R'-R)\alpha_{n'\downarrow}{}^*(R')\alpha_{n\uparrow}(R)\},\quad(2.1)$$

where

$$b_{n'n}(R'-R)+C_{n'n}{}^z(R'-R)$$
$$=\int\psi_{n'\uparrow}{}^*(r-R')H_1\psi_{n\uparrow}(r-R)d\tau,$$
$$b_{n'n}(R'-R)-C_{n'n}{}^z(R'-R)$$
$$=\int\psi_{n'\downarrow}{}^*(r-R')H_1\psi_{n\downarrow}(r-R)d\tau,\quad(2.2)$$
$$C_{n'n}{}^-(R'-R)=\int\psi_{n'\uparrow}{}^*(r-R')H_1\psi_{n\downarrow}(r-R)d\tau,$$
$$C_{n'n}{}^+(R'-R)=\int\psi_{n'\downarrow}{}^*(r-R')H_1\psi_{n\uparrow}(r-R)d\tau,$$

and

$$H_1=p^2/2m+V(r)$$
$$+(\hbar/2m^2c^2)\mathbf{S}\cdot[\mathrm{grad}V(r)\times\mathbf{p}],$$
$$C_{n'n}{}^\pm(R'-R)=C_{n'n}{}^x(R'-R)\pm iC_{n'n}{}^y(R'-R),$$

[3] I. Dzialoshinski, J. Phys. Chem. Solids 4, 241 (1958).

[4] J. H. Van Vleck, J. phys. radium 12, 262 (1951); T. Moriya and K. Yosida, Progr. Theoret. Phys. (Kyoto) 9, 663 (1953); T. Nagamiya, K. Yosida, and R. Kubo, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1955), Vol. 4, p. 1.

[5] P. W. Anderson, Phys. Rev. 115, 2 (1959).

[6] T. Moriya, Phys. Rev. Letters 4, 228 (1960).

$\alpha_{n\uparrow}(R)$ and $\alpha_{n\uparrow}{}^*(R)$ are the annihilation and the creation operators of the electrons in the state $\psi_{n\uparrow}(r-R)$, etc. The most important contribution to the superexchange comes from the configuration mixing of the polar states due to the transfer terms of (2.1). By the second order perturbation calculation we get the usual isotropic superexchange from the b^2 terms, the interaction of the form (1.1) from the bC terms and pseudodipolar interaction from the C^2 terms. We have for the interaction between the spins at R and R'

$$E_{R,R'}{}^{(2)} = J_{R,R'}{}^{(2)}(\mathbf{S}(R)\cdot\mathbf{S}(R'))$$
$$+\mathbf{D}_{R,R'}{}^{(2)}\cdot[\mathbf{S}(R)\times\mathbf{S}(R')]$$
$$+\mathbf{S}(R)\cdot\Gamma_{R,R'}{}^{(2)}\cdot\mathbf{S}(R') \quad (2.3)$$

where the scalar, vector and tensor quantities: $J_{RR'}{}^{(2)}$, $\mathbf{D}_{R,R'}{}^{(2)}$, and $\Gamma_{RR'}{}^{(2)}$ are given in the case of one electron per ion as follows:

$$J_{R,R'}{}^{(2)} = 2|b_{nn'}(R-R')|^2/U, \quad (2.4a)$$

$$\mathbf{D}_{R,R'}{}^{(2)} = (4i/U)[b_{nn'}(R-R')\mathbf{C}_{n'n}(R'-R)$$
$$- \mathbf{C}_{nn'}(R-R')b_{n'n}(R'-R)], \quad (2.4b)$$

$$\Gamma_{RR'}{}^{(2)} = (4/U)[\mathbf{C}_{nn'}(R-R')\mathbf{C}_{n'n}(R'-R)$$
$$+\mathbf{C}_{n'n}(R'-R)\mathbf{C}_{nn'}(R-R')$$
$$-(\mathbf{C}_{nn'}(R-R')\cdot\mathbf{C}_{n'n}(R'-R))\mathbf{1}]. \quad (2.4c)$$

The expression for $J_{RR'}{}^{(2)}$ has been obtained by Anderson.[5] We assumed here that the ground state of an ion is nondegenerate except for being a Kramers' doublet. n and n' represent the ground states of the ions at R and R', respectively, and U is the energy required to transfer an electron from an ion to its nearest neighbor, thus making a polar state.

When the orbital level separation in an ion is larger than the spin-orbit coupling, we can calculate the transfer integrals b and C by a perturbation method. The b terms are the ordinary transfer integrals without spin-orbit coupling and the C terms are given up to the first order in the spin-orbit coupling as follows:

$$\mathbf{C}_{n'n}(R'-R) = -\frac{\lambda}{2}\left(\sum_{m'}\frac{\mathbf{l}_{m'n'}{}^*(R')}{\epsilon_{m'}(R')-\epsilon_{n'}(R')}b_{m'n}(R'-R)\right.$$

$$+\sum_m \frac{\mathbf{l}_{mn}(R)}{\epsilon_m(R)-\epsilon_n(R)}b_{n'm}(R'-R)\bigg)+\mathbf{c}(R'-R), \quad (2.5)$$

with

$$\mathbf{c}(R'-R) = \frac{\hbar}{4m^2c^2}\int\varphi_{n'}{}^*(r-R')$$
$$\times[\mathrm{grad}V(r)\times\mathbf{p}]\varphi_n(r-R)d\tau, \quad (2.6)$$

where n, n' represent the ground orbital states and m, m' the excited states, $\mathbf{l}_{mn}(R)$ the matrix element of the orbital angular momentum of the ion at R, λ the spin-orbit coupling constant, and $\varphi_n(r-R)$ the ground orbital wave function of the ion at R.

From (2.5) we see that the magnitude of the C terms is roughly $(\Delta g/g)$ times that of the b terms where

g is the gyromagnetic ratio and Δg is its deviation from the value for a free electron. Therefore the orders of magnitudes of $\mathbf{D}$ and Γ are estimated by

$$D\sim(\Delta g/g)J, \quad \Gamma\sim(\Delta g/g)^2 J. \quad (2.6)$$

The contribution of the next importance is the direct exchange interaction. This has the same form as (2.3) and the coefficients of the first two terms $J_{RR'}{}^{\mathrm{ex}}$ and $\Gamma_{RR'}{}^{\mathrm{ex}}$ are given as follows:

$$J_{RR'}{}^{\mathrm{ex}} = J_{RR'}(nn'nn'), \quad (2.7)$$

$$\mathbf{D}_{RR'}{}^{\mathrm{ex}} = 2i\lambda\left(\sum_m\frac{\mathbf{l}_{mn}(R)}{\epsilon_m(R)-\epsilon_n(R)}J_{RR'}(nn'mn')\right.$$

$$-\sum_{m'}\frac{\mathbf{l}_{m'n'}(R')}{\epsilon_{m'}(R')-\epsilon_{n'}(R')}J_{RR'}(nn'nm')\bigg). \quad (2.8)$$

The tensor coefficient $\Gamma_{RR'}{}^{\mathrm{ex}}$ of the last term has just the same form as that which has been discussed by the previous authors[4] though they regarded J to include superexchange implicitly. The exchange integral is given by

$$J_{RR'}(nn'mm') = \int\int\varphi_n{}^*(r_1-R)\varphi_{n'}{}^*(r_2-R')\frac{e^2}{r_{12}}$$

$$\times\varphi_m(r_2-R)\varphi_{m'}(r_1-R')dr_1dr_2, \quad (2.9)$$

where $\varphi_n(r-R)$, etc., are the orthogonal orbital wave functions obtained without the spin-orbit coupling. We see here again that the ratios of $D_{RR'}{}^{\mathrm{ex}}$ and $\Gamma_{RR'}{}^{\mathrm{ex}}$ to $J_{RR'}{}^{\mathrm{ex}}$ are approximately given by (2.6). Therefore, these terms are generally smaller than the corresponding second order superexchange terms as was shown by Anderson in the case of isotropic superexchange.

The third order perturbation which include transfer terms twice and the intra-atomic exchange interaction gives the same form of coupling as (2.3). The isotropic first term and the anisotropic second and third terms come from $b^2 J_0$, bCJ_0, and $C^2 J_0$ terms, respectively, J_0 being the intra-atomic exchange energy. All the three terms are generally J_0/U times smaller than the corresponding second order terms.

We shall here show only the coefficient of the second term. The first term is given in reference 5.

$$\mathbf{D}_{RR'}{}^{(3)} = -(i/U^2)\{\sum_{m'}J_{n'm'}(R')[b_{nm'}(R-R')$$
$$\times\mathbf{C}_{m'n}(R'-R)-\mathbf{C}_{nm'}(R-R')b_{m'n}(R'-R)]$$
$$+\sum_m J_{nm}(R)[b_{n'm}(R'-R)\mathbf{C}_{mn'}(R-R')$$
$$-\mathbf{C}_{n'm}(R'-R)b_{mn'}(R-R')]\}, \quad (2.10)$$

where $J_{nm}(R)$ represents an intra-atomic exchange integral in the ion at R, etc. We have considered above the most important three contributions to the superexchange interaction. As was seen, all the terms linear in the spin-orbit coupling have the form (1.1) which is antisymmetric for the interchange of two spins and the terms of second order in the spin-orbit coupling have the pseudodipolar form which is symmetric for the two
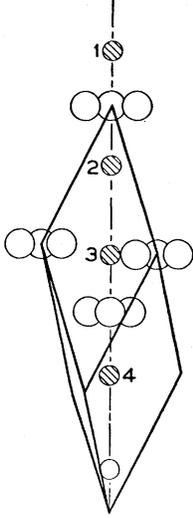
FIG. 1. Crystal structure of α-Fe$_2$O$_3$. The open circles represent O^{--} ions and the shadowed ones Fe^{3+} ions.

spins. The orders of magnitude of these anisotropic couplings are generally given in relation to the isotropic coupling by (2.6).

The crystal symmetry is of particular importance for the antisymmetric coupling (1.1). In crystals of high symmetry this coupling vanishes though it is important in crystals of low symmetry, particularly in relation to weak ferromagnetism. Discussion of the symmetry properties will be given in the following section.

Extension of the theory to the case of many-electron ions is straightforward only when the ground ionic state has a single configuration. In this case we need only to express the spin operators of the electrons by the equivalent operators of the ionic spins with some modifications in the coefficients. However, in the first transition group ions the term separation is much larger than the spin-orbit coupling and the ground states taking account of the spin-orbit coupling cannot generally be expressed by a single configuration. Moreover, in crystals of low symmetry in which the anti-symmetric coupling (1.1) is of particular importance, even the purely orbital states cannot generally be represented by a single configuration. The calculation, therefore, is very complicated even for the isotropic coupling and we would content ourselves with the expectation that also in this case the order estimation of (2.6) may be correct.

We shall now further discuss the contribution from the higher order perturbations qualitatively. For the one electron ions there are no other types of interaction between two ions than those given by (2.3). So the higher order perturbation calculation gives only minor corrections to the contributions treated above. On the other hand, for the ions with many electrons the couplings of more than fourth order in the spin variables come out from higher order perturbations. For example, from the fourth order perturbation we get

biquadratic forms of spin coupling (for $S \geq 1$) and couplings which are linear in one spin and of third order in the other (for $S \geq \frac{3}{2}$), in addition to the minor corrections to the bilinear terms. A representative term of the fourth order perturbation which contributes to the isotropic biquadratic coupling may be of the form:

$$\sum_{\substack{n,n' \\ m,m'}} U^{-3} \times b_{nn'}(R-R')b_{n'm}(R'-R)b_{mm'}(R-R')$$

$$\times b_{m'n}(R'-R) \sum_{\sigma,\sigma'} \sum_{\lambda,\lambda'} \alpha_{n\sigma}{}^*(R)\alpha_{n'\sigma}(R')\alpha_{n'\sigma'}{}^*(R')$$

$$\times \alpha_{m\sigma'}(R)\alpha_{m\lambda}{}^*(R)\alpha_{m'\lambda}(R')\alpha_{m'\lambda'}{}^*(R')\alpha_{n\lambda'}(R). \quad (2.11)$$

When the ground ionic state can be expressed by the numbers of electrons in the basic states, the first sum is over the singly occupied Kramers' doublets. In general, we should take the expectation value of (2.11) in the ground ionic state. The order of magnitude of the isotropic biquadratic coupling may be $(b/U)^2$ times the usual bilinear superexchange interaction.[7] Contributions to the anisotropic coupling can be obtained by replacing one, two or three b's in (2.11) by C's with the corresponding modifications of the spin suffixes of the annihilation and creation operators. From the order of magnitude relation: $C \sim (\Delta g/g) \cdot b$, we may estimate their magnitudes.

Though we will not discuss any further these higher order perturbations, we already see how to provide the mechanisms and to estimate the orders of magnitude of various forms of higher order anisotropic super-exchange couplings.

CRYSTAL SYMMETRY AND THE ANTISYMMETRIC SPIN COUPLING

In the preceding section a general theory of calculating the anisotropic superexchange interaction was developed. In an actual crystal, some components of the symmetric and antisymmetric coupling tensors vanish because of the crystal symmetry. Here we discuss the antisymmetric coupling (1.1) from the crystal symmetry point of view.

The coupling between two ions in the crystal is considered first. The two ions 1 and 2 are located at the points A and B, respectively, and the point bisecting the straight line AB is denoted by C. The following rules are obtained easily.

1. When a center of inversion is located at C,

$$\mathbf{D} = 0.$$

2. When a mirror plane perpendicular to AB passes through C,

$$\mathbf{D} \parallel \text{mirror plane or } \mathbf{D} \perp AB.$$

3. When there is a mirror plane including A and B,

$$\mathbf{D} \perp \text{mirror plane.}$$

_____

[7] This was first pointed out by P. W. Anderson.

4. When a two-fold rotation axis perpendicular to AB passes through C,

$$\mathbf{D} \perp \text{two-fold axis.}$$

5. When there is an n-fold axis ($n \geq 2$) along AB,

$$\mathbf{D} \parallel AB.$$

For example, for an $Fe^{3+}-Fe^{3+}$ pair in α-Fe_2O_3 oriented along the three-fold axis, $\mathbf{D}$ is parallel to the trigonal axis when the two ions are (1 or 4) and (2 or 3) in Fig. 1 and $\mathbf{D}$ is zero for the other pairs. For the rutile type iron group difluorides, $\mathbf{D}$ is not zero for the pairs of corner and body-center ions. $\mathbf{D}$ for the nearest neighbor interaction is given by the following table.

The Positions of the Ions		Direction	Magnitude
000 and	$\frac{1}{2},\ \frac{1}{2}, \pm\frac{1}{2}$	$[1\ \bar{1}\ 0]$	$\pm D$
000 and	$-\frac{1}{2},\ -\frac{1}{2}, \pm\frac{1}{2}$	$[1\ \bar{1}\ 0]$	$\pm D$
000 and	$-\frac{1}{2},\ \frac{1}{2}, \pm\frac{1}{2}$	$[1\ 1\ 0]$	$\pm D$
000 and	$\frac{1}{2},\ -\frac{1}{2}, \pm\frac{1}{2}$	$[1\ 1\ 0]$	$\pm D$

When the spins are ordered and form sublattices we are interested in the coupling between the sublattice magnetizations. In the case of iron group difluorides, we see from the above table that there is no anti-symmetric coupling of the form (1.1) between the two sublattice magnetizations. In α-Fe_2O_3, this coupling is not zero and $\mathbf{D}$ for the coupling between sublattice magnetizations is parallel to the trigonal axis. This was first shown by Dzialoshinski.[3]

Symmetry consideration on the transfer integrals is also useful in theoretical calculation of the anisotropic exchange. This will be discussed in the following section.

MAGNETIC ANISOTROPY IN THE ANTIFERRO-MAGNET CuCl$_2$·2H$_2$O

The magnetic anisotropy energy of $CuCl_2 \cdot 2H_2O$ which determines the spin orientation has been discussed by Yosida and the present author.[6] However, they neglected the antisymmetric coupling of the form (1.1). This interaction may be of particular importance in understanding the antiferromagnetic spin arrangement in this crystal as was briefly discussed in the reference 4. We shall show in this section how the coefficient $\mathbf{D}$ of the anisotropic exchange interaction can be calculated in $CuCl_2 \cdot 2H_2O$ as a typical example of the preceding section.

A Cu^{2+} ion has only one hole in the 3d shell. The crystal structure is orthorhombic and two Cu^{2+} ions are located at the corner and the base-center sites in a unit cell. The symmetry elements of the crystal are
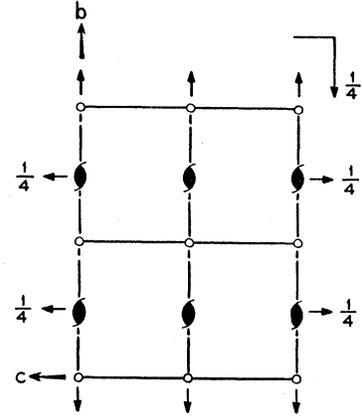

Fig. 2. Symmetry elements of $CuCl_2 \cdot 2H_2O$ crystal.

shown in Fig. 2. The principal axes of the crystalline electric field around the corner and the body-center sites are different. Only the b axis is a common principal axis. We denote it as the z axis. The two other principal axes at the corner site and those at the base-center sites are written as $\xi_1\eta_1$ and $\xi_2\eta_2$, respectively. Writing the a- and the c axes as y and x, respectively, we have a relation:

$$\xi_1 = x\cos\theta + y\sin\theta, \qquad \xi_2 = x\cos\theta - y\sin\theta,$$
$$\eta_1 = -x\sin\theta + y\cos\theta, \quad \eta_2 = x\sin\theta + y\cos\theta,$$

where the angle θ is constant but not known so far. The five localized $3d$ orbital states of a Cu^{2+} ion are nondegenerate in this crystalline field and have the following forms:

$$\psi_1 \propto C_0(3z^2 - r^2) + C_2(\xi^2 - \eta^2),$$
$$\psi_2 \propto C_0'(3z^2 - r^2) + C_2'(\xi^2 - \eta^2),$$
$$\psi_3 \propto \xi\eta, \qquad\qquad (4.1)$$
$$\psi_4 \propto \eta z,$$
$$\psi_5 \propto z\xi,$$

where the constants C_0, C_2, C_0', C_2' are in principle determined by the crystalline potential. We shall denote the transfer integral between the nth state of a corner ion and the mth state of its neighboring base-center ion by b_{nm}.

Then the following relations are obtained from symmetry considerations.

$$b_{13} = -b_{31}, \quad b_{23} = -b_{32}, \quad b_{45} = -b_{54};$$
$$b_{15} = -b_{51}, \quad b_{25} = -b_{52}, \quad b_{34} = -b_{43}; \qquad (4.2)$$
$$b_{14} = b_{41}, \quad b_{24} = b_{42}, \quad b_{35} = b_{53}.$$

All the nonvanishing matrix elements of $\mathbf{l}$ are listed below.

$$(3|l_z|1) = -i2C_2, \qquad (3|l_z|2) = -i2C_2', \qquad (4|l_z|5) = -i,$$
$$(1|l_\xi|5) = -i\sqrt{3}C_0 - iC_2, \quad (2|l_\xi|5) = -i\sqrt{3}C_0' - iC_2',$$
$$(3|l_\xi|4) = i,$$
$$(1|l_\eta|4) = i\sqrt{3}C_0 - iC_2, \quad (2|l_\eta|4) = i\sqrt{3}C_0' - iC_2',$$
$$(3|l_\eta|5) = -i.$$
$$(4.3)$$
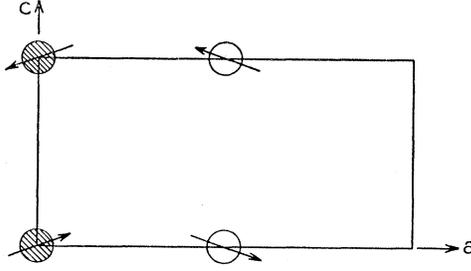
FIG. 3. Proposed spin arrangement in antiferromagnetic $CuCl_2 \cdot 2H_2O$. The spins are in the ac plane. The black and the open circles represent the ions at the positions 0, 0, 0 and $\frac{1}{2}$, $\frac{1}{2}$, 0, respectively.

Using (4.2) and (4.3) we can calculate D from (2.4b) and (2.5). Though we do not know which of the five states (4.1) the ground state is, the following formulas are valid, regardless of the ground state:

$$D_z^{(2)} = D_b^{(2)} = \frac{8i\lambda}{U} \sum_m \frac{(l_z)_{mn}}{\epsilon_m - \epsilon_n} b_{nm} b_{nn},$$

$$D_x^{(2)} = D_a^{(2)} = \frac{8i\lambda}{U} \sum_m \frac{(l_\xi \cos\theta - l_\eta \sin\theta)_{mn}}{\epsilon_m - \epsilon_n} b_{nm} b_{nn},$$

$$D_y^{(2)} = D_c^{(2)} = 0,$$

where n denotes the ground orbital state and m the excited states. There is no reason why any one of the transfer integrals should vanish and therefore we see from (4.3) and (4.4) that the a and b components of D are nonzero regardless of which the ground state may be. D_z or D_x in (4.4) consists of only one term when the ground state is other than ψ_3 and two terms when the ground state is ψ_3. Similarly the direct exchange contribution is calculated as follows.

$$D_z^{ex} = 4i\lambda \sum_m \frac{(l_z)_{mn}}{\epsilon_m - \epsilon_n} J(nmmn),$$

$$D_x^{ex} = 4i\lambda \sum_m \frac{(l_\xi \cos\theta - l_\eta \sin\theta)_{mn}}{\epsilon_m - \epsilon_n} J(nmmn), \quad (4.5)$$

$$D_y^{ex} = 0,$$

where $J(nmmn)$ is defined by (2.9). These expressions are also valid regardless of what the ground state may be.

Quantitative calculation of the transfer integrals b_{mn} and the direct exchange integrals $J(nmmn)$ is necessary to get D. However, we may expect that b_{mn} and $J(nmmn)$ are of the same order of magnitude as b_{nn} and $J(nnnn)$, respectively, because of the low symmetry at the positions of Cu^{2+}. The magnitude of D may be about $(\Delta g/g)$ times the isotropic superexchange interaction.

In the antiferromagnetic $CuCl_2 \cdot 2H_2O$, a magnetic unit cell is considered to consist of two chemical unit

cells oriented in the c direction. A four sublattice model may be reasonable. In this case, D_x for the interaction between the corner and the base-center sublattice magnetizations vanishes. However, non-vanishing D_y is very important in determining the spin arrangement. The spin arrangement which is accepted at present is the ferromagnetic layers parallel to the ab plane with the spins pointing in the $+a$ and $-a$ directions alternatingly.[8] When D_y is not zero this arrangement cannot be stable. We propose instead the spin arrangement shown in Fig. 3. The c component of a spin is expected to be $(\Delta g/g)$ times, i.e., about 10% of, the a component. We expect that this spin arrangement may give a more consistent understanding of the proton resonance data both above and below the Néel temperature[8,9] and the neutron diffraction data[10] for the positions of the protons. Neutron diffraction experiment below the Néel temperature is highly desirable.

WEAK FERROMAGNETISM OF SOME TRIGONAL CRYSTALS

The following trigonal crystals are known to be weak ferromagnets: α-Fe_2O_3, $MnCO_3$, $CoCO_3$, CrF_3, and possibly FeF_3. α-Fe_2O_3 has a corundum type crystal structure and $MnCO_3$ and $CoCO_3$ are of $NaNO_3$ type. The crystal structures of CrF_3 and FeF_3 have recently been determined.[11] All of these crystals have the same space group $D_{3d}^6 - R\bar{3}C$. The spin superstructure of α-Fe_2O_3[12] gives rise to a nonvanishing antisymmetric spin coupling of the form (1.1) between the sublattice magnetizations and D is parallel to the trigonal axis as was first shown by Dzialoshinski.[3] For the remaining crystals, the carbonates and the trifluorides, non-vanishing D parallel to the trigonal axis exists when the magnetic unit cell is just the same as the chemical unit cell (with two molecular units) as may actually be the case.

When the spins are perpendicular to the trigonal axis in the ordered state, a net magnetic moment is induced by this interaction. The magnitude of this net moment at $0°K$ may be estimated by

$$\frac{M}{Ng\mu_B S} \sim \frac{D}{2J} \sim \left(\frac{\Delta g}{g}\right). \quad (5.1)$$

Comparison of the value estimated by (5.1) with the measured moments is shown in Table I. The agreement is generally reasonable. In $CoCO_3$, the orbital moment

[8] N. J. Poulis and G. E. G. Hardeman, Physica 18, 201 (1952).

[9] J. Itoh, R. Kusaka, Y. Yamagata, R. Kiriyama, and H. Ibamoto, Physica 19, 415 (1953).

[10] S. W. Peterson and H. A. Levy, J. Chem. Phys. 26, 220 (1957).

[11] For CrF_3 see K. H. Jack and R. Maitland, Proc. Chem. Soc. (London) 232 (1957); K. Knox has also obtained the same result (private communication). For FeF_3 see M. A. Hepworth, Acta. Cryst. 10, 345 (1957).

[12] C. G. Shull, W. A. Strauser, and E. O. Wollan, Phys. Rev. 83, 333 (1951).

may be of particular importance. Though the g values are not available. we may naturally expect a comparatively large D and therefore a large moment, in qualitative agreement with the experiment. In α-Fe_2O_3, CrF_3, and FeF_3, we have neutron diffraction data[12,13] which show that the spins are perpendicular to the [111] axis below the Néel temperature. For $MnCO_3$ neutron data[14] suggest the spin directions are between the [111] axis and the (111) plane while a magnetic susceptibility measurement[15] seems to show that the spins are almost perpendicular to the [111] axis.

Various magnetic properties of α-Fe_2O_3 have been discussed by Dzialoshinski[3] from phenomenological grounds with the essential use of an interaction of the form (1.1) with **D** as a parameter. We have now provided the mechanism for this interaction, thus giving a firmer ground to his theory. We shall here remark one property of these weak ferromagnets which has not been discussed. The paramagnetic susceptibility of these weak ferromagnets shows a very sharp increase near the Néel temperature. A simple model to show this may be the following Hamiltonian:

$$H=J\sum_{\langle i,j\rangle} (\mathbf{S}_i,\mathbf{S}_j)+B\sum_i S_{jz}^2$$
$$+D\sum_{\langle i,j\rangle} (S_{ix}S_{jy}-S_{iy}S_{jx})+g\mu_B\mathbf{H}\cdot\sum_j \mathbf{S}_j, \quad (5.2)$$

where summations are taken over nearest neighboring pairs. We assume that B is positive, i.e., the easy direction is perpendicular to the z axis. By a molecular field approximation we can easily show that $\chi_{\parallel}$ (z component) obeys the Curie-Weiss law fairly well down to T_N while $\chi_{\perp}$ is given by

$$\chi_{\perp}=\frac{Ng^2\mu_B^2 S(S+1)}{3k(T+T_N)}\frac{T-T_0}{T-T_N}, \quad (5.3)$$

with

$$T_N=\frac{JZS(S+1)}{3k}\left[1+\left(\frac{D}{J}\right)^2\right]^{\frac{1}{2}},$$
$$\quad (5.4)$$
$$T_0=\frac{JZS(S+1)}{3k},$$

where Z is the number of nearest neighbors. As (T_N-T_0) is small and positive, $\chi_{\perp}$ increases very sharply near T_N. A measure of the sharpness may be given by

$$(T_N-T_0)/T_N\sim\frac{1}{2}\left(\frac{D}{J}\right)^2\sim 2\left(\frac{M}{Ng\mu_B S}\right)^2. \quad (5.5)$$

The smaller the net moment below T_N the sharper is

[13] E. O. Wollan, H. R. Child, W. C. Koehler, and M. K. Willsinson, Phys. Rev. **112**, 1132 (1958).
[14] S. J. Pickart, Bull. Am. Phys. Soc. **5**, 59 (1960).
[15] A. S. Borovik-Romanov, J. Exptl. Theoret. Phys. (U.S.S.R.) **36**, 766 (1959) [translation: Soviet Phys.—JETP **36** (9), 539 (1959)].

Substance	$(M/Ng\beta\mu S)$	$(\Delta g/g)$
α-Fe_2O_3	1.4×10^{-3}	$\sim 1\times10^{-3}$
$MnCO_3$	$2\sim 6\times10^{-3}$	$\sim 1\times10^{-3}$
$CoCO_3$	$2\sim 6\times10^{-2}$	
CrF_3	1×10^{-2}	$\sim 1\times10^{-2}$
FeF_3		$\sim 1\times10^{-3}$

the increase of $\chi_{\perp}$ near T_N. This behavior seems to be observed in CrF_3.[16] For $MnCO_3$ there is some sign of this behavior but it is not yet clear.[15] Similar behavior has been expected theoretically[17] and was observed in NiF_2.[18] This behavior of the paramagnetic susceptibility may be one of the distinctive features of weak ferromagnets.

Our next discussion is on the possible other mechanisms of weak ferromagnetism. Interactions between two spins have been fully discussed in 2 and the higher order interactions are more than two orders of magnitude smaller than the bilinear term discussed above. We shall consider the anisotropy energy of single spin nature which comes from the spin-orbit coupling under the crystalline electric field. This interaction does not depend on the superexchange mechanism and therefore is more important in substances with low Néel temperatures. In NiF_2 this kind of interaction is responsible for its weak ferromagnetism.[17] In the trigonal crystals which we are discussing now the fourth order terms of trigonal symmetry are the lowest order terms which may give rise to a net magnetization of the crystals. This is possible because there are essentially two kinds of positions for the magnetic ions and the crystalline fields around them are different. They are written as

$$K\left[\sum_i^{(1)} S_{ix}S_{iy}(S_{iy}^2-3S_{ix}^2)\right.$$
$$\left.-\sum_j^{(2)} S_{jx}S_{jy}(S_{jy}^2-3S_{jx}^2)\right], \quad (5.6)$$

where the first and the second summations are taken over one and the other kinds of ions, respectively. This interaction is effective in producing weak ferromagnetism only when the equilibrium spin orientation is somewhere between the trigonal axis and the plane perpendicular to it. This is possible when the total effect of the second order and the other fourth order anisotropy energies and the dipolar and pseudodipolar interactions favor it. In α-Fe_2O_3, CrF_3, FeF_3 this does not seem to be the case.[12,13] Moreover, the estimated values of K for α-Fe_2O_3 and $MnCO_3$ are more than one

[16] W. N. Hansen and M. Griffel, J. Chem. Phys. **30**, 913 (1959).
[17] T. Moriya, Phys. Rev. **117**, 635 (1960).
[18] R. G. Shulman, NMR measurement in NiF_2 (to be published); A. H. Cooke, $\chi_{\perp}$ of NiF_2 (private communication); J. C. Burgiel, V. Jaccarino, and A. L. Schawlow, χ of powdered NiF_2 and $Ni(IO_3)_2\cdot 2H_2O$ [Bull. Am. Phys. Soc. **4**, 424 (1959)].

order of magnitude smaller than D. We may fairly safely conclude that this interaction is not of primary importance in the weak ferromagnetism of α-Fe_2O_3, $MnCO_3$, CrF_3, and FeF_3. The sixth order anisotropy energy is probably negligibly small as compared with D.

CONCLUDING REMARKS

It should be emphasized here that now a firm ground has been given to the mechanism of weak ferromagnetism first proposed by Dzialoshinski. It is no longer a phenomenological model but is a real effect established theoretically. Though there may be some impurity effects (chemical or structural), this mechanism always exists as an intrinsic property of the crystal.

At present we have many weak ferromagnets and we know two types of interactions which can be the origin of weak ferromagnetism. One is a coupling between the spins such as the antisymmetric part of the anisotropic superexchange interaction, and the other is the single spin anisotropy energy. In α-Fe_2O_3, etc., the first mechanism and in NiF_2 the second one are the origins of their weak ferromagnetism. There may be substances in which both of these types of interactions are important. Generally speaking, there is a tendency that when the Néel temperature is high the first type of interaction is more important and when the Néel temperature is low, the second mechanism is more important. This is because the first is approximately proportional to the exchange interaction while the second is independent of the exchange interaction. When the single spin anisotropy energy is comparable with the exchange energy, as may be possible for some substances with low Néel temperature, or when $(\Delta g/g)$ is not small, the magnetic moment may not necessarily be small. This may be the case in ludlamite where $T_N = 20°K$ and the magnetic moment is $0.8 \mu_B$ per ion of divalent iron.[19]

The antisymmetric spin coupling treated here is important not only as an origin of weak ferromagnetism but also in determining the spin arrangement in antiferromagnets as was illustrated in the case of $CuCl_2 \cdot 2H_2O$.

ACKNOWLEDGMENT

The writer is very much indebted to Dr. P. W. Anderson for his continuous interest and kind advice on this work.

[19] R. M. Bozorth and V. Kramer, *Colloque International de magnetisme, Grenoble*, 1959 [J. phys. radium **20**, 393 (1959)].

APPENDIX

We shall show here an alternative derivation of the interaction of the form (1.1). We start from the localized electron orbital states and consider the spin-orbit coupling as a perturbation. The unperturbed states of the ions 1 and 2 are specified by $(n, m, \cdots)$ and $(n', m', \cdots)$, respectively, n and n' being their ground states. The second order perturbation energy bilinear with respect to the spin-orbit coupling and the exchange interaction is given as follows:

$$E_{1,2} = \sum_m \left(\frac{(n|\lambda \mathbf{l}_1 \cdot \mathbf{S}_1|m)2J(mn'n'n)\mathbf{S}_1 \cdot \mathbf{S}_2}{\epsilon_n - \epsilon_m} \right.$$
$$+ \frac{2J(nn'n'm)(\mathbf{S}_1 \cdot \mathbf{S}_2)(m|\lambda \mathbf{l}_1 \cdot \mathbf{S}_1|n)}{\epsilon_n - \epsilon_m} \right)$$
$$+ \sum_{m'} \left(\frac{(n'|\lambda \mathbf{l}_2 \cdot \mathbf{S}_2|m')2J(m'nnn')(\mathbf{S}_1 \cdot \mathbf{S}_2)}{\epsilon_{n'} - \epsilon_{m'}} \right.$$
$$+ \frac{2J(n'nnm')(\mathbf{S}_1 \cdot \mathbf{S}_2)(m'|\lambda \mathbf{l}_2 \cdot \mathbf{S}_2|n')}{\epsilon_{n'} - \epsilon_{m'}} \right), \quad (A.1)$$

where J's are the exchange integrals given by (2.9) in the text. When the orbital state is nondegenerate, the matrix elements of $\mathbf{l}$ are purely imaginary and we can rewrite (A.1) as follows:

$$E_{1,2} = 2\lambda \sum_m \frac{J(nn'n'm)}{\epsilon_n - \epsilon_m}(n|\mathbf{l}_1|m) \cdot [\mathbf{S}_1, (\mathbf{S}_1 \cdot \mathbf{S}_2)]$$
$$+ 2\lambda \sum_{m'} \frac{J(nn'm'n)}{\epsilon_{n'} - \epsilon_{m'}}(n'|\mathbf{l}_2|m') \cdot [\mathbf{S}_2, (\mathbf{S}_1 \cdot \mathbf{S}_2)]$$
$$= 2i\lambda \left(\sum_m \frac{J(nn'n'm)(n|\mathbf{l}_1|m)}{\epsilon_n - \epsilon_m} \right.$$
$$\left. - \sum_{m'} \frac{J(nn'm'n)(n'|\mathbf{l}_2|m')}{\epsilon_{n'} - \epsilon_{m'}} \right) \cdot [\mathbf{S}_1 \times \mathbf{S}_2]. \quad (A.2)$$

This is equivalent to (2.8). If we replace $J(nn'm'n)$ by the effective superexchange integral: $b_{nn'}b_{m'n}/U$, etc., we get the expression equivalent to (2.4b) and (2.5).

Though this derivation is more elementary, the one given in the text is superior for the systematic study of the anisotropic superexchange interaction.

Note added in proof.—It has been shown by Professor K. W. H. Stevens [Revs. Modern Phys. **25**, 166 (1953)] that there can exist anisotropic terms of the exchange interaction which are linear in the spin-orbit coupling.