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Theory of Antiferromagnetic-Ferromagnetic Transitions in Dilute Magnetic Alloys and in the Rare Earths*

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In a previous paper a theory of direct exchange and superexchange coupling between *d* or *f* electrons and conduction electrons was given. This led to the possibility of an antiferromagnetic-ferromagnetic transition. The present paper is devoted to a more complete treatment of this magnetic transition by way of examining a particular case. Both the molecular-field theory and a cluster theory due to Oguchi are applied. Each leads to a magnetic transition and both predict that for all such transitions the ferromagnetic state must have a lower free energy at 0°K than the antiferromagnetic state. The transition is found to be of second order. Expressions are given for the parallel and perpendicular susceptibility in the neighborhood of the Néel point. A discussion is given showing how the direct exchange interaction with the conduction electrons makes a magnetic transition possible. A comparison is made between the theory given here and recent experimental results in Cu-Mn alloys.

I. INTRODUCTION

IN dilute magnetic alloys and in the rare-earth metals one meets the interesting situation in which the usual Heisenberg mechanism for the coupling of the magnetic moments does not apply. For a sufficiently dilute alloy the average separation of magnetic atoms or ions will be so great that there will be no direct exchange interaction. Similarly, nearest-neighbor rare-earth atoms will have no direct exchange interaction between them because of the very small radial extension of the 4*f* orbitals. Therefore, the magnetic properties of these materials must arise from some new type of spin coupling whose primary feature must be the ability to produce a long-range interaction.

Two long-range exchange interactions were considered in a previous paper,[1] hereafter referred to as I. The first was the direct exchange interaction between localized singly occupied 3*d* or 4*f* atomic functions and the conduction electrons. The so-called *s-d* exchange interaction has been considered by a number of writers.[2–4] The second long-range interaction discussed in I was a superexchange interaction. Here one finds a coupling between the spins of widely separated atoms through excited states in which these atoms change their configurations by either gaining electrons from or giving electrons to the conduction band. Kasuya[4] has shown that a coupling will also appear as the result of including excited states in which the electronic configuration of the atoms is unchanged but where conduction electrons are excited to normally unoccupied *k* values.

It was assumed in I that the direct exchange between bound and conduction electrons was ferromagnetic, tending to align the spin of the magnetic atom with that of the conduction electron. The indirect or superexchange interaction, which is made up of contributions from all types of excited states, was assumed to be antiferromagnetic in character. A molecular-field treatment based on these assumptions was given in I and it was found to show the remarkable feature of allowing the possibility of an antiferromagnetic-ferromagnetic transition. That is, the strength of the exchange couplings could be chosen so that the material would first order antiferromagnetically on cooling from the paramagnetic state, and at some still lower temperature the material would order ferromagnetically and remain so down to 0°K. The molecular-field treatment as given in I did not allow the possibility of a transition from ferromagnetic to antiferromagnetic ordering with decreasing temperature.

The purpose of the present paper is to investigate more completely the antiferromagnetic-ferromagnetic transition. To this end, a particular example has been chosen which is defined by a fixed choice of the various exchange interactions, taking $S=\frac{1}{2}$ and assuming that the paramagnetic atoms can be ordered on a two sublattice structure. Two substantially different methods are used to examine the transition. Section III contains a molecular-field discussion of the problem. In Sec. IV a recent method due to Oguchi,[5] which is essentially a simplified Bethe-Peierls-Weiss theory, is employed. Since this method is based on an entirely different set of assumptions than those underlying the molecular-field theory, it serves as a good check on the physical predictions of the molecular-field approach. It is found here that both methods lead to an antiferromagnetic-ferromagnetic transition for the example chosen and are in qualitative agreement concerning the transition temperatures and the susceptibility.

Section II of the paper contains a discussion of the phenomenological Hamiltonian on which both methods are based. The results and conclusions of the paper are

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[1] G. W. Pratt, Jr., Phys. Rev. **106**, 53 (1957).

[2] S. Vonsovskii, J. Phys. (U.S.S.R.) **10**, 468 (1946).

[3] C. Zener, Phys. Rev. **81**, 440 (1951).

[4] T. Kasuya, Progr. Theoret. Phys. Japan **16**, 45 (1956); see also K. Yosida, Phys. Rev. **106**, 893 (1957).

[5] T. Oguchi, Progr. Theoret. Phys. Japan **13**, 148 (1955).

discussed in Sec. V. A physical explanation is given there of the mechanism responsible for the magnetic transition. Recent work on Cu-Mn alloys is also discussed.

II. PHENOMENOLOGICAL HAMILTONIAN

As pointed out in the Introduction, we are concerned here with the spin coupling problem where direct-exchange interactions between magnetic atoms are zero. The approach used to solve this problem was first given by Kramers[6] and later elaborated on by Löwdin.[7] A simple example using the method was given in I. One defines a set of ground states φ_i all of which correspond to the same electronic configuration but which cover all possible spin assignments to the one-electron orbitals such that every φ_i has the same total M_s. The ground configuration here consists of the collection of magnetic atoms with their normal configurations and all conduction electrons with a fixed set of k values doubly occupied and a fixed set singly occupied. In the particular example to be dealt with here each magnetic atom is assumed to have one electron outside closed shells. There will be no loss of generality by taking the M_s of each φ_i to be zero.

In general the true state of the system will be some linear combination of the φ_i's and of all possible excited states η_γ of the system. Kramers' idea was to treat the excited states η_γ as a perturbation on the ground states by setting up an effective Hamiltonian U_{km} which is to be diagonalized only with respect to the ground set φ_i. The form of U_{km} to second order is

$$U_{km}=H_{km}+\sum_\gamma \frac{H_{k\gamma}H_{\gamma m}}{E-H_{\gamma\gamma}}. \tag{2.1}$$

Here H_{km} is the matrix component of the actual many-electron Hamiltonian between φ_k and φ_m of the ground set; $H_{k\gamma}$ is the matrix component of H between φ_k and η_γ; E is the energy of the system, and $H_{\gamma\gamma}$ is the diagonal energy of the excited state η_γ.

The excited states η_γ are of four types. First, those in which conduction electrons are taken from the conduction band and put on the magnetic atoms. These states are similar to the excited states in MnO where an electron from the $O^=$ ion is transferred to a neighboring Mn^{++} ion. Second, those in which the magnetic centers retain their normal configurations but in which excitations in the conduction band take place. Third, those in which electrons are excited from the magnetic atoms into the conduction band. Fourth, those in which a combination of excitations takes place.

The net results of considering all possible types of states η_γ is that the effective Hamiltonian takes on the form

$$U=-\sum_{i<j} J(i,j)\mathbf{S}_i\cdot\mathbf{S}_j-\sum_i\sum_P J(i,P)\mathbf{S}_i\cdot\mathbf{S}_P -\sum_P\sum_Q J(P,Q)\mathbf{S}_P\cdot\mathbf{S}_Q. \tag{2.2}$$

The lower case letters refer to the conduction electrons and the upper case letters to the bound electrons.

We shall deal here with the simple case in which the magnetic atoms can be ordered on two sublattices. For a dilute magnetic alloy it is assumed that the magnetic atoms can be divided into two sets A and B such that on the average the nearest neighbor of an A atom is a B atom and on the average the next-nearest neighbor of an atom is another atom in the same set.

The interaction integral $J(P,Q)$ will be a function of the distance between P and Q. Let the value of $J(P,Q)$ for R_P-R_Q equal to the average nearest-neighbor distance be defined as I_1. The value of $J(P,Q)$ for R_P-R_Q at the average next-nearest neighbor distance is defined as I_3. In this treatment $J(P,Q)$ will be neglected for neighbors more distant than the next nearest.

The direct exchange integral between the bound and conduction electrons $J(i,P)$ will in general be a function of $\mathbf{k}$. This dependence will be neglected here and the average value of $J(i,P)$ for all k defined as I_2 will be used to denote this interaction.

With the above qualifications, the effective Hamiltonian reduces to

$$\begin{aligned}U=-\sum_{i<j} J(i,j)\mathbf{S}_i\cdot\mathbf{S}_j-\sum_{Ai}^{\text{n.n.}}\sum_{Bj} I_1\mathbf{S}_{Ai}\cdot\mathbf{S}_{Bj} &-\sum_{Ai}\sum_{Bj} I_2(\mathbf{S}_{Ai}+\mathbf{S}_{Bj})\cdot\mathbf{S}_e\\ &-\sum_{i<j}^{\text{n.n.n.}} I_3(\mathbf{S}_{Ai}\cdot\mathbf{S}_{Aj}+\mathbf{S}_{Bi}\cdot\mathbf{S}_{Bj}).\end{aligned} \tag{2.3}$$

The first term in (2.3) is the exchange interaction between conduction electrons which will be assumed to be of negligible importance in the following. The second term is the indirect exchange coupling of the A sublattice and B sublattice, the summation being taken over nearest neighbors (n.n.). I_1 can in general have either sign but is taken negative here so as to represent an antiferromagnetic coupling. The third term represents the direct exchange between the bound and the conduction electrons and it is ferromagnetic as I_2 is positive definite. The last term is the interaction of the A sublattice with itself and the B sublattice with itself. The summation is taken only over next-nearest neighbor (n.n.n.) pairs ij and I_3 can have either sign. With the first term of (2.3) omitted, the effective Hamiltonian becomes identical with (73) of I.

III. MOLECULAR-FIELD (M.F.) THEORY

As shown in I, the Hamiltonian (2.3) may be written as

$$H=A\mathbf{M}_A\cdot\mathbf{M}_B+\tfrac{1}{2}\Gamma(\mathbf{M}_A\cdot\mathbf{M}_A+\mathbf{M}_B\cdot\mathbf{M}_B) -\eta(\mathbf{M}_A+\mathbf{M}_B)\cdot\mathbf{M}_e. \tag{3.1}$$

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[6] H. A. Kramers, Physica 1, 182 (1934).

[7] P. O. Löwdin, J. Chem. Phys. 19, 1396 (1951).

The constants are given by

$$-A=2I_1Z_{AB}/N(g\mu_B)^2,\quad -\Gamma=4I_3Z_{AA}/N(g\mu_B)^2,$$
$$\eta=I_2/2g\mu_B{}^2. \tag{3.2}$$

Here Z_{AB} is the number of nearest neighbors lying on one sublattice to an atom on the other sublattice; N is the total number of magnetic atoms; Z_{AA} is the number of nearest A atoms to a given A atom and is taken equal to Z_{BB} here.

The internal magnetic field acting on the atoms of the A sublattice is

$$\mathbf{H}_A=-A\mathbf{M}_B+\eta\mathbf{M}_e-\Gamma\mathbf{M}_A. \tag{3.3}$$

That acting on the B sublattice is

$$\mathbf{H}_B=-A\mathbf{M}_A+\eta\mathbf{M}_e-\Gamma\mathbf{M}_B. \tag{3.4}$$

The field acting on the conduction electrons is

$$\mathbf{H}_e=\eta(\mathbf{M}_A+\mathbf{M}_B). \tag{3.5}$$

Suppose first that the material is ferromagnetically ordered. Then $M_A=M_B$ and the molecular-field equation for M_A is

$$M_A=\tfrac{1}{2}(Ng\mu_BS)B_S\left(\frac{(\eta M_e-AM_B-\Gamma M_A)g\mu_BS}{kT}\right). \tag{3.6}$$

M_e can be eliminated from (3.6) by the relation

$$\mathbf{M}_e=\eta\chi_C(\mathbf{M}_A+\mathbf{M}_B). \tag{3.7}$$

Thus, (3.6) becomes

$$M_A=\tfrac{1}{2}(Ng\mu_BS)B_S\left(\frac{(2\eta^2\chi_C-A-\Gamma)g\mu_BSM_A}{kT}\right). \tag{3.8}$$

The ferromagnetic Curie temperature is readily found from (3.8) to be

$$T_C=C\{\eta^2\chi_C-\tfrac{1}{2}(A+\Gamma)\}, \tag{3.9}$$

where C is $Ng^2\mu_B{}^2S(S+1)/3k$.

The general expression for the free energy is given by[8]

$$\begin{aligned}F=&A\mathbf{M}_A\cdot\mathbf{M}_B+\tfrac{1}{2}\Gamma(\mathbf{M}_A\cdot\mathbf{M}_A+\mathbf{M}_B\cdot\mathbf{M}_B)\\&-\eta^2\chi_C(\mathbf{M}_A+\mathbf{M}_B)\cdot(\mathbf{M}_A+\mathbf{M}_B)\\&-kT\ln g(\mathbf{M}_A\cdot\mathbf{M}_B)\end{aligned} \tag{3.10}$$

where $g(\mathbf{M}_A\cdot\mathbf{M}_B)$ is the number of arrangements of the spins on the A and B sublattices corresponding to a given M_A and M_B. The case of particular interest here is for $S=\frac{1}{2}$ and with the aid of Sterling's approximation (3.10) becomes

$$\begin{aligned}-F/N=&\{\tfrac{1}{8}I_1Z_{AB}+I_2{}^2N\chi_C/4g^2\mu_B{}^2+\tfrac{1}{4}I_3Z_{AA}\}y^2\\&+kT\ln2-\tfrac{1}{2}kT[(1+y)\ln(1+y)\\&+(1-y)\ln(1-y)].\end{aligned} \tag{3.11}$$

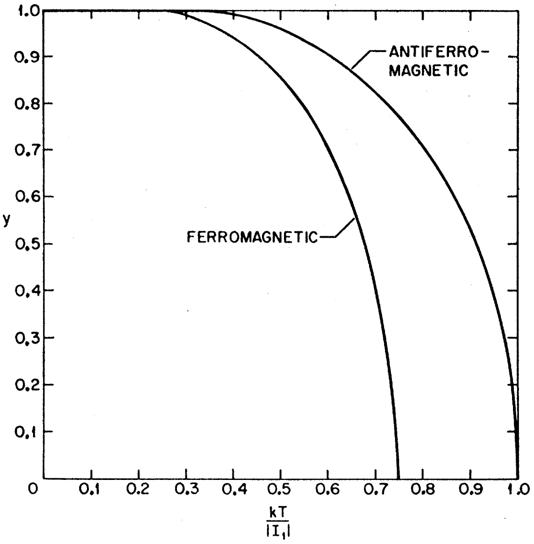

FIG. 1. Relative magnetization as a function of $kT/|I_1|$ for ferromagnetic and antiferromagnetic ordering.

Here y is the relative sublattice magnetization $2M_A/Ng\mu_BS$.

The special case to be examined here is defined by the following choice of parameters:

$$Z_{AB}=6,\quad Z_{AA}=Z_{BB}=6,\quad I_3=\tfrac{1}{6}I_1,$$

and

$$I_2{}^2\chi_CN/4\mu_B{}^2=11|I_1|. \tag{3.12}$$

Using the relations in (3.2) and in (3.12), we find for the Curie temperature

$$kT_C=0.75|I_1|. \tag{3.13}$$

The equation for the relative magnetization y is found from (3.8) to be

$$y=\tanh\left\{\frac{y}{2kT}\left(\frac{I_2{}^2\chi_CN}{2g^2\mu_B{}^2}+I_3Z_{AA}+\frac{I_1Z_{AB}}{2}\right)\right\}, \tag{3.14}$$

which is, in view of (3.12),

$$y=\tanh\left(\frac{3|I_1|}{4kT}y\right). \tag{3.15}$$

The free energy is given in terms of y for the ferromagnetic case, when one uses the values of the parameters given in (3.12), as

$$\begin{aligned}-F/N=&(7/4)|I_1|y^2+kT\ln2\\&-\tfrac{1}{2}kT[(1+y)\ln(1+y)+(1-y)\ln(1-y)].\end{aligned} \tag{3.16}$$

In Fig. 1, y is plotted as a function of T, and in Fig. 2 $-[F+NkT\ln2]/N|I_1|$ is plotted as a function of T.

In the antiferromagnetic case $\mathbf{M}_A=-\mathbf{M}_B$ and, according to (3.7), $\mathbf{M}_e$ is zero. The molecular-field equation for M_A is

$$M_A=\tfrac{1}{2}(Ng\mu_BS)B_S\left(\frac{\{-AM_B-\Gamma M_A\}g\mu_BS}{kT}\right). \tag{3.17}$$

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[8] See for example P. W. Kasteleijn and J. van Kranendonk, Physica 22, 367 (1956).

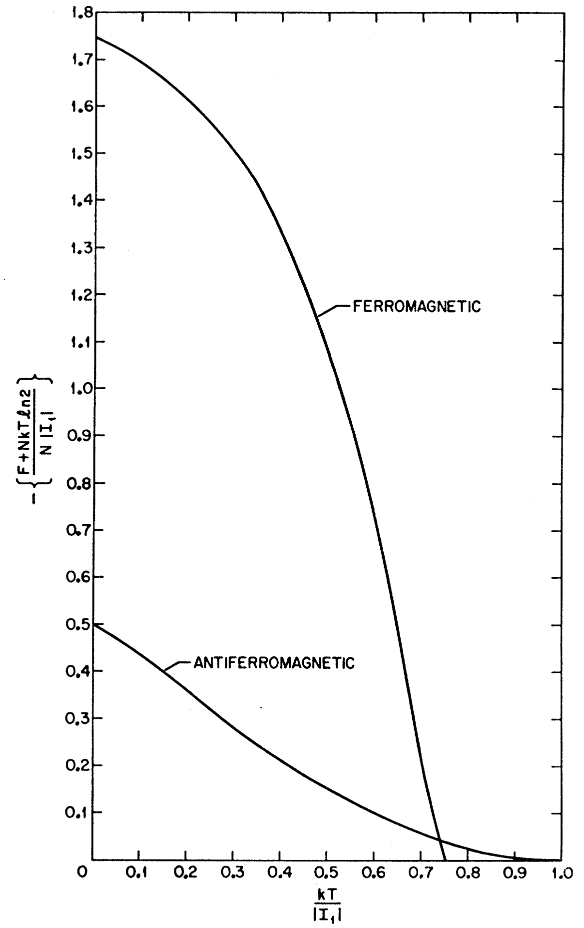

FIG. 2. Plot of $-[F+NkT\ln 2]/N|I_1|$ as a function of $kT/|I_1|$ for ferromagnetic and antiferromagnetic ordering. The intersection indicates the presence of a magnetic transition.

The Néel temperature is

$$T_N=\tfrac{1}{2}C(A-\Gamma)=|I_1|/k. \qquad (3.18)$$

Equation (3.17) becomes for the specific example considered here

$$y=\tanh(|I_1|y/kT). \qquad (3.19)$$

The free energy is

$$-F/N=\tfrac{1}{2}|I_1|y^2+kT\ln 2-\tfrac{1}{2}kT[(1+y)\ln(1+y)+(1-y)\ln(1-y)]. \qquad (3.20)$$

A plot of y as a function of T for the antiferromagnetic case is given in Fig. 1, and $-(+F+NkT\ln 2)/N|I_1|$ for this ordering is shown in Fig. 2.

As it stands, Fig. 2 indicates that a first-order antiferromagnetic-ferromagnetic transition occurs at the intersection of the two free-energy curves. However, it is possible that there could be states intermediate between ferromagnetic and antiferromagnetic order in which the angle between $\mathbf{M}_A$ and $\mathbf{M}_B$ lies between 0 and π. Such states could have the property that the phase change would be of second order. The molecular-field treatment of the intermediate states will be considered next.

Let there be a fixed angle θ between $\mathbf{M}_A$ and $\mathbf{M}_B$ with the spins on the A sublattice quantized in the direction of $\mathbf{M}_A$ and those on the B sublattice in the direction of $\mathbf{M}_B$. Then

$$\mathbf{M}_A\cdot\mathbf{H}_A=(\eta^2\chi_C-\Gamma)M_0^2+(\eta^2\chi_C-A)M_0^2\cos\theta, \qquad (3.21)$$

where $M_0=|\mathbf{M}_A|=|\mathbf{M}_B|$. Thus,

$$M_0=\tfrac{1}{2}Ng\mu_B SB_S\left(\frac{M_0g\mu_BS}{kT}[\eta^2\chi_C-\Gamma+(\eta^2\chi_C-A)\cos\theta]\right). \qquad (3.22)$$

For the example being considered here, the relative sublattice magnetization as a function of θ is given by

$$y=\tanh\left(\frac{y|I_1|}{8kT}\{7-\cos\theta\}\right). \qquad (3.23)$$

The Curie temperature of the state of fixed θ is

$$T_C=\tfrac{1}{2}C\{\eta^2\chi_C-\Gamma+(\eta^2\chi_C-A)\cos\theta\}. \qquad (3.24)$$

If $A>\eta^2\chi_C$, T_C steadily increases as θ goes from zero to π.

The free energy as a function of θ is given by

$$\begin{aligned}-F/N=&(I_1Z_{AB}/8+I_2^2\chi_CN/8g^2\mu_B^2)y^2\cos\theta\\&+(I_3Z_{AA}/4+I_2^2\chi_CN/8g^2\mu_B^2)y^2\\&+kT\ln 2-\tfrac{1}{2}kT[(1+y)\ln(1+y)\\&+(1-y)\ln(1-y)]. \qquad (3.25)\end{aligned}$$

It would be desirable to know at any temperature the value of θ which minimizes the free energy. Since y is a function of θ, as can be seen from (3.23), finding the maximum of (3.25) as a function of θ would lead to a very complicated transcendental equation. However, the significant details can easily be found graphically. At 0°K, where y is unity, the extremes of (3.25) occur for $\theta=0$ or $\theta=\pi$. Thus the free energy of an intermediate state of fixed θ will lie between that of the ferromagnetic and the antiferromagnetic states.

In Fig. 3 the quantity $-[(F+NkT\ln 2)/N|I_1|]$ is plotted as a function of T for $\theta=0$, $\theta=\pi/4$, $\theta=\pi/2$, $\theta=3\pi/4$, and $\theta=\pi$. It can be seen from the figure that the antiferromagnetic-ferromagnetic transition is of second order with the system following the envelope of curves of the intermediate states. It was pointed out in I that the molecular-field theory does not allow the possibility of a magnetic transition in the opposite order.

The susceptibility just below the Néel temperature, where $\mathbf{M}_A$ is very nearly opposite to $\mathbf{M}_B$, is readily found by using Van Vleck's approach.[9] If $\mathbf{H}_A^{(0)}$ and

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[9] J. H. Van Vleck, J. Chem. Phys. 9, 85 (1941).

$\mathbf{H}_B^{(0)}$ are the molecular fields acting on the A and B sublattices in the absence of an external field $\mathbf{H}_0$, and $\mathbf{H}_A$ and $\mathbf{H}_B$ are the molecular fields in the presence of $\mathbf{H}_0$, then the magnetization in the direction of $\mathbf{H}_0$ is given by

$$M=\frac{N}{2}g\mu_BS\left\{\cos(\mathbf{H}_A,\mathbf{H}_0)\left[B_S\left(\frac{H_A{}^{(0)}g\mu_BS}{kT}\right)+\frac{g\mu_BS}{kT}B_S'\left(\frac{H_A{}^{(0)}g\mu_BS}{kT}\right)d\mathbf{H}_A\right]+\cos(\mathbf{H}_B,\mathbf{H}_0)\left[B_S\left(\frac{H_B{}^{(0)}g\mu_BS}{kT}\right)+\frac{g\mu_BS}{kT}B_S'\left(\frac{H_B{}^{(0)}g\mu_BS}{kT}\right)d\mathbf{H}_B\right]\right\}. \quad (3.26)$$

Let $\mathbf{H}_0$ be in the z direction making equal angles with $\mathbf{H}_A$ and $\mathbf{H}_B$. Then

$$M=2M_0\cos(H_A,H_0)+\frac{Ng^2\mu_B{}^2S^2}{2kT}\times\cos(\mathbf{H}_A,\mathbf{H}_0)B_S'(y_0)\{d\mathbf{H}_A+d\mathbf{H}_B\}, \quad (3.27)$$

where $M_0=|M_A|=|M_B|$ and $y_0=|H_A{}^{(0)}|g\mu_BS/kT$. Following Van Vleck, we take

$$\cos(H_A,H_0)=(H_{Az}{}^{(0)}+dH_{Az})/|H_A|. \quad (3.28)$$

If $H_{Az}{}^{(0)}$ is neglected in (3.28) and only the first term taken in (3.27), we have

$$M=2M_0dH_{Az}/|H_A|. \quad (3.29)$$

Eliminating $\mathbf{M}_e$ from (3.3) and using the fact that $d\mathbf{M}_A$ and $d\mathbf{M}_B$ are equal and are in the z direction, we find

$$d\mathbf{H}_{Az}=\mathbf{H}_0+(2\eta^2\chi_C-A-\Gamma)d\mathbf{M}_A. \quad (3.30)$$

The absolute value of $\mathbf{H}_A$ is found by (3.21) and on taking $\theta=\pi$, becomes

$$|H_A|=M_0(A-\Gamma). \quad (3.31)$$

Thus, (3.29) is

$$\mathbf{M}=\frac{2}{(A-\Gamma)}\{\mathbf{H}_0+(2\eta^2\chi_C-A-\Gamma)d\mathbf{M}_A\}. \quad (3.32)$$

Since $\mathbf{M}=d\mathbf{M}_A+d\mathbf{M}_B$ or $2d\mathbf{M}_A$, the perpendicular susceptibility just below T_N is

$$\chi_\perp=1/(A-\eta^2\chi_C). \quad (3.33)$$

If $\mathbf{M}_A$, $\mathbf{M}_B$, and $\mathbf{H}_0$ are taken to lie in the zx plane with $\mathbf{M}_A$ and $\mathbf{M}_B$ making a small angle φ with the positive and negative x axis, respectively, then $H_{Az}{}^{(0)}$ is approximately $M_0(A-\Gamma)\varphi$. $\chi_\perp$ is then given by

$$\chi_\perp=\frac{1}{A-\eta^2\chi_C}+\frac{2M_0\varphi}{H_0}. \quad (3.34)$$

For $\mathbf{H}_0$ parallel to $\mathbf{M}_A$ we have $\cos(H_A,H_0)\sim 1$ and $\cos(H_B,H_0)\sim -1$ just below T_N. Substituting in (3.30) gives

$$\mathbf{M}=\frac{Ng^2\mu_B{}^2S}{2kT}B_S'(y_0)\{d\mathbf{H}_A+d\mathbf{H}_B\}. \quad (3.35)$$

The value of $d\mathbf{H}_A$ is given by (3.30) and here it is a vector in the x direction. Thus,

$$M\left\{1-(2\eta^2\chi_C-A-\Gamma)\frac{Ng^2\mu_B{}^2S^2}{2kT}B_S'(y_0)\right\}=\frac{Ng^2\mu_B{}^2S^2}{kT}B_S'(y_0)H_0. \quad (3.36)$$

Using (3.9) we find

$$\chi_\parallel=C\bigg/\left(\frac{T}{B_S'(y_0)}-T_C\right). \quad (3.37)$$

The susceptibility for random orientation of the internal field with respect to the external field will be $\chi_R=\frac{1}{3}\chi_\parallel+\frac{2}{3}\chi_\perp$. As the temperature decreases from T_N,

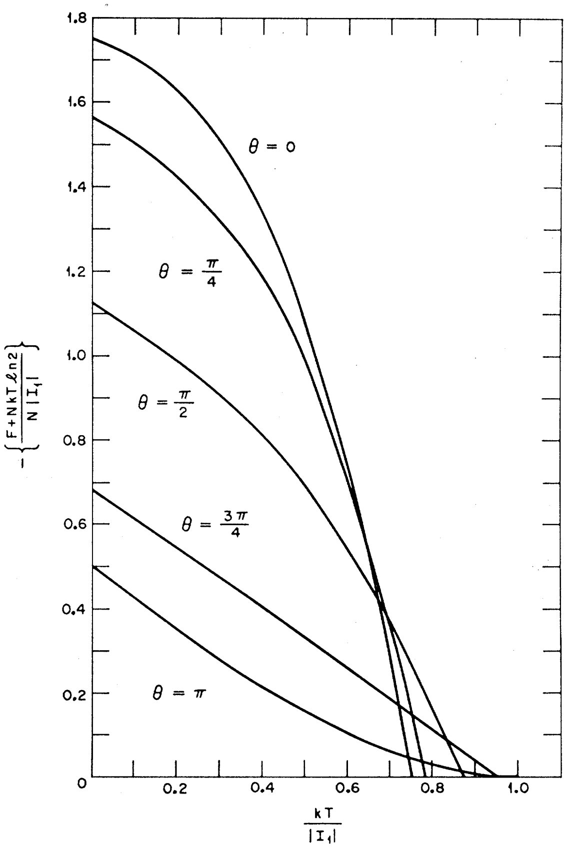

FIG. 3. Plot of $-[F+NkT\ln2]/N|I_1|$ as a function of $kT/|I_1|$ for various fixed angles between sublattice magnetizations M_A and M_B. This represents a second-order magnetic transition with the system following the envelope of the curves.

a net magnetization will appear spontaneously and χ_R will rise rapidly. The form of χ_R is shown in Fig. 4.

IV. APPLICATION OF OGUCHI'S THEORY

Oguchi[5] has recently developed a very simple theory of ferromagnetism and of antiferromagnetism analogous to the Bethe-Peierls-Weiss (B.P.W.) method. Instead of treating a central atom and all of its nearest neighbors exactly as in the B.P.W. scheme, Oguchi deals only with a single pair of neighboring atoms. It can be shown that Oguchi's theory is a special case of the constant-coupling method of Kasteleijn and van Kranendonk.[10] By carrying out this independent analysis of the problem it will be possible to check the results of the molecular-field treatment. In particuar, we wish to know whether a condition can be foulnd where T_N exceeds T_C but in which the free energy at 0°K is lower for the ferromagnetic case than for the antiferromagnetic case.

We derive here the cluster Hamiltonian for a nearest-neighbor pair of magnetic atoms, one on each of two sublattices. The Hamiltonian for the entire system is taken as the last three terms of (2.3). By using (3.7) the net spin of the conduction electrons S_e which appears in (2.3) can be eliminated leading to the result

$$U=\sum_{i,j}\left\{-I_1\mathbf{S}_{Ai}\cdot\mathbf{S}_{Bj}-\frac{I_2^2N\chi_C}{2g^2\mu_B^2}(\mathbf{S}_{Ai}+\mathbf{S}_{Bj})\cdot(\mathbf{S}_A+\mathbf{S}_B)\right.$$
$$\left.-I_3(\mathbf{S}_{Ai}\cdot\mathbf{S}_{Aj}+\mathbf{S}_{Bi}\cdot\mathbf{S}_{Bj})\right\},\quad(4.1)$$

where $\mathbf{S}_A$ and $\mathbf{S}_B$ represent the average spin per atom on the indicated sublattice. If the pair of atoms which comprises our cluster is Ai and Bj, the cluster Hamiltonian is

$$H_{\mathrm{cl}}=-I_1\mathbf{S}_{Ai}\cdot\mathbf{S}_{Bj}-\mathbf{S}_{Ai}\cdot\{K_1\mathbf{S}_B+K_2\mathbf{S}_A\}$$
$$-\mathbf{S}_{Bj}\cdot\{K_1\mathbf{S}_A+K_2\mathbf{S}_B\}.\quad(4.2)$$

The constants K_1 and K_2 are given by

$$K_1=I_1(Z_{AB}-1)+\frac{I_2^2N\chi_C}{2g^2\mu_B^2},$$
$$K_2=\frac{I_2^2N\chi_C}{2g^2\mu_B^2}+I_3Z_{AA}.\quad(4.3)$$

The total Hamiltonian (4.1) commutes with the z component of the total spin. Therefore, the average value of S_{Ax}, S_{Bx}, S_{Ay}, and S_{By} are zero. This reduces (4.2) to

$$H_{\mathrm{cl}}=-I_1\mathbf{S}_{Ai}\cdot\mathbf{S}_{Bj}-S_{Aiz}\{K_1S_{Bz}+K_2S_{Az}\}$$
$$-S_{Bjz}\{K_1S_{Az}+K_2S_{Bz}\}.\quad(4.4)$$

Because of the presence of the last two terms in (4.4), the square of the total spin of the cluster does not commute with (4.4). Consequently the eigenvectors of H_{cl} will be linear combinations of the following four states

$$\psi_1^1=\varphi_i(1)\varphi_j(2)\alpha(1)\alpha(2),\quad(4.5)$$
$$\psi_1^{-1}=\varphi_i(1)\varphi_j(2)\beta(1)\beta(2),\quad(4.6)$$
$$\psi_1^0=\varphi_i(1)\varphi_j(2)[\alpha(1)\beta(2)+\beta(1)\alpha(2)]/\surd 2,\quad(4.7)$$
$$\psi_0^0=\varphi_i(1)\varphi_j(2)[\alpha(1)\beta(2)-\beta(1)\alpha(2)]/\surd 2.\quad(4.8)$$

The secular equation corresponding to this representation has the form

$$\begin{vmatrix}-\frac{1}{4}I_1+(a+b)-\lambda & 0 & 0 & 0\\ 0 & -\frac{1}{4}I_1-(a+b)-\lambda & 0 & 0\\ 0 & 0 & -\frac{1}{4}I_1-\lambda & a-b\\ 0 & 0 & a-b & (7/4)I_1-\lambda\end{vmatrix}=0,\quad(4.9)$$

where the rows and columns are ordered as are the states in (4.5) through (4.8) and a and b are given by

$$2a=-(K_1S_{Az}+K_2S_{Bz}),\quad(4.10)$$
$$2b=-(K_1S_{Bz}+K_2S_{Az}).\quad(4.11)$$

The eigenvalues of (4.9) are

$$\lambda_1=-\tfrac{1}{4}I_1-\tfrac{1}{2}\{K_1S_{Bz}+K_2S_{Az}\}-\tfrac{1}{2}\{K_1S_{Az}+K_2S_{Bz}\},$$
$$\lambda_2=-\tfrac{1}{4}I_1+\tfrac{1}{2}\{K_1S_{Bz}+K_2S_{Az}\}+\tfrac{1}{2}\{K_1S_{Az}+K_2S_{Bz}\},$$
$$\lambda_3=+\tfrac{1}{4}I_1+\tfrac{1}{2}Q,\quad\lambda_4=+\tfrac{1}{4}I_1-\tfrac{1}{2}Q,\quad(4.12)$$

where Q is defined as

$$Q=\{I_1^2+(K_1-K_2)^2(S_{Az}-S_{Bz})^2\}^{\frac{1}{2}}.\quad(4.13)$$

The cluster partition function $Z=\mathrm{Tr}\,e^{-H/kT}$ is given by

$$\mathrm{Tr}\,e^{-H/kT}=2e^{I_1/4kT}\cosh[(K_1+K_2)(S_{Az}+S_{Bz})/2kT]$$
$$+e^{-I_1/2kT}\cosh(Q/2kT).\quad(4.14)$$

Self-consistency is introduced through the condition that

$$S_{Az}=\mathrm{Tr}(S_{Aiz}e^{-H/kT})/\mathrm{Tr}(e^{-H/kT}).\quad(4.15)$$

In order to evaluate the numerator of (4.15), it is necessary to find the eigenvectors of the 2×2 part of (4.9). The four eigenvectors of the cluster are

$$\Phi_1=\psi_1^1,$$
$$\Phi_2=\psi_1^{-1},$$
$$\Phi_3=\left(\frac{Q-I_1}{2Q}\right)^{\frac{1}{2}}\psi_1^0+\left(\frac{Q+I_1}{2Q}\right)^{\frac{1}{2}}\psi_0^0,\quad(4.16)$$
$$\Phi_4=\left(\frac{Q+I_1}{2Q}\right)^{\frac{1}{2}}\psi_1^0-\left(\frac{Q-I_1}{2Q}\right)^{\frac{1}{2}}\psi_0^0.$$

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[10] P. W. Kasteleijn and J. van Kranendonk, Physica **22**, 317 (1956).

The self-consistency constraint becomes

$$S_{Az}=\frac{\sinh[(K_1+K_2)(S_{Az}+S_{Bz})/2kT]+[(K_1-K_2)(S_{Az}-S_{Bz})/Q]e^{-I_1/2kT}\sinh Q/(2kT)}{2\cosh[(K_1+K_2)(S_{Az}+S_{Bz})/2kT]+2e^{-I_1/2kT}\cosh(Q/2kT)}. \tag{4.17}$$

If the ordering is ferromagnetic, $S_{Az}=S_{Bz}$ and (4.17) reduces to

$$S_{Az}=\frac{\sinh[(K_1+K_2)S_{Az}/kT]}{2\cosh[(K_1+K_2)S_{Az}/kT]+2e^{-I_1/2kT}\cosh(I_1/2kT)}. \tag{4.18}$$

The Curie temperature is found from (4.18) to be the solution of the following equation

$$kT_C=\frac{K_1+K_2}{3+e^{-I_1/kT_C}}. \tag{4.19}$$

Since I_1 is negative here, $T_C=0$ is always a solution of (4.19). A necessary condition for a ferromagnetic state is that K_1+K_2 be positive. If this condition is satisfied, there will always be a nonzero solution of (4.19) which gives the actual Curie point. Using the values for the various parameters given in (3.12) in (4.19) leads to a Curie temperature of

$$kT_C=0.68|I_1|, \tag{4.20}$$

as compared with $kT_C=0.75|I_1|$ as determined by the molecular-field treatment.

The limit of S_{Az} as T approaches zero for the ferromagnetic case is found from (4.18) to be

$$\frac{1}{2}\left\{\frac{1}{1+\exp[-(K_1+K_2)S_{Az}-I_1/kT]}\right\}. \tag{4.21}$$

If $(K_1+K_2)S_{Az}$ is greater than $|I_1|$, the limiting value is $\frac{1}{2}$. Otherwise it is zero. Therefore, we have the condition that (K_1+K_2) be greater than $2|I_1|$ in order that Oguchi's method give a ferromagnetic state at 0°K.

If the ordering is antiferromagnetic, $S_{Az}=-S_{Bz}$ and (4.17) reduces to

$$S_{Az}=\frac{[(K_1+K_2)S_{Az}/Q]e^{-I_1/2kT}\sinh(Q/2kT)}{1+e^{-I_1/2kT}\cosh(Q/2kT)}. \tag{4.22}$$

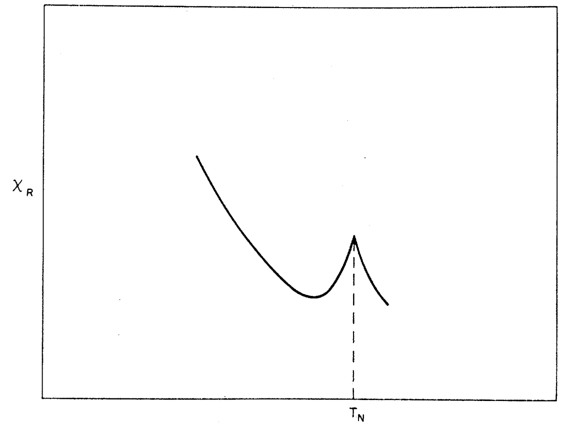

FIG. 4. Sketch of the susceptibility for random orientation of the internal fields with respect to an external magnetic field.

The Néel temperature is given by

$$kT_N=|I_1|\Big/\ln\left(\frac{K_1-K_2+3I_1}{K_1-K_2-I_1}\right), \tag{4.23}$$

or equivalently as

$$kT_N=|I_1|\Big/\ln\left(\frac{I_1(Z_{AB}+2)-I_3Z_{AA}}{I_1(Z_{AB}-2)-I_3Z_{AA}}\right). \tag{4.24}$$

Substituting from (3.12), we find that $kT_N=1.33|I_1|$ as compared with $|I_1|$ as determined from the molecular-field method.

As T approaches 0°K the limiting value of S_{Az} for the antiferromagnetic case is

$$S_{Az}=\left[\frac{(K_1-K_2)^2-I_1^2}{4(K_1-K_2)^2}\right]^{\frac{1}{2}}. \tag{4.25}$$

Although there is no antiCurie point, S_{Az} does not reach $\frac{1}{2}$ at 0°K.

Our purpose in discussing Oguchi's theory is to compare it with the molecular-field results. The transition temperatures for the ferromagnetic and antiferromagnetic cases agree quite well for the specific example chosen here. It remains to find out whether Oguchi's formulation also leads to the possibility of an antiferromagnetic-ferromagnetic transition. The summations in the total effective Hamiltonian (4.1) can be carried out approximately to give

$$\begin{aligned}U=\{-NI_1Z_{AB}/2-I_2^2\chi_CN^2/2g^2\mu_B^2\}\mathbf{S}_A\cdot\mathbf{S}_B\\-\{I_2^2\chi_CN^2/4g^2\mu_B^2+NI_3Z_{AA}/2\}\\\times(\mathbf{S}_A\cdot\mathbf{S}_A+\mathbf{S}_B\cdot\mathbf{S}_B),\end{aligned} \tag{4.26}$$

where A_A and S_B are the average spins per atom on the A and B sublattices. The condition that the ferromagnetic state be stable at 0°K is given from (4.26) as

$$I_1Z_{AB}+\frac{I_2^2\chi_CN}{g^2\mu_B^2}>0. \tag{4.27}$$

Unfortunately the complexity of the expressions for the

Curie point (4.19) and the Néel temperature (4.23) do not lead to a simple expression for the requirement that T_N exceed T_C. However, for the example chosen here (4.27) is $5|I_1|$ so that the ferromagnetic state lies lowest at 0°K and it has already been found that $T_N > T_C$. Therefore, Oguchi's method also admits the possibility of a magnetic transition.

It remains to be determined whether Oguchi's method allows a transition in the reverse order where the stable phase at 0°K is antiferromagnetic and with $T_C > T_N$. For this to occur, (4.27) is replaced by

$$I_1 Z_{AB} + I_2^2 \chi_C N / g\mu_B^2 < 0. \tag{4.28}$$

However, in order that kT_C be positive, we have from (4.19) that K_1+K_2 exceed zero. This becomes on substitution

$$I_1(Z_{AB}-1) + I_2^2 \chi_C N / g\mu_B^2 + I_3 Z_{AA} > 0. \tag{4.29}$$

First let $I_3=0$. Then the largest possible value of kT_C is $\frac{1}{4}(K_1+K_2)$ as can be seen from (4.19), since I_1 is negative. The largest value of K_1+K_2 consistent with (4.28) is $|I_1|$. Thus,

$$(kT_C)_{\max} = \tfrac{1}{4}|I_1|. \tag{4.30}$$

With $I_3=0$, kT_N becomes

$$kT_N = |I_1| \bigg/ \ln\left(\frac{Z_{AB}+2}{Z_{AB}-2}\right). \tag{4.31}$$

In order that $T_C > T_N$, it must be that $\ln[(Z_{AB}+2)/(Z_{AB}-2)] > 4$. Except for the case of $Z_{AB}=2$, which is not ordinarily realized, we see that for I_3 zero T_C will never exceed T_N with (4.28) holding at the same time.

If I_3 is positive, it can be seen from (4.24) that the minimum value of kT_N occurs for $I_3=0$. But it has already been established that for $I_3=0$ the minimum T_N cannot be less than the maximum value of T_C in view of (4.28). Therefore, under these conditions the desired magnetic transition cannot occur.

If I_3 is negative, $|I_3 Z_{AA}|$ must be less than $|I_1|$ in order that T_C be positive. The largest possible value of kT_C is given by (4.30). For $Z_{AB} \geq 4$, the smallest possible value of kT_N is $|I_1|/\ln 5$. Therefore, for I_3 negative and $Z_{AB} \geq 4$, the reverse transition is impossible. If $Z_{AB}=3$, kT_N goes to zero when $|I_3 Z_{AA}| = |I_1|$. However, T_C also goes to zero at that point and can readily be shown to be less than kT_N for $0 < |I_3 Z_{AA}| < |I_1|$.

Thus Oguchi's method does permit a transition from the antiferromagnetic state to the ferromagnetic state with decreasing temperature but, in agreement with the molecular-field theory, does not allow a transition from ferromagnetic to antiferromagnetic order with decreasing temperature. This result is in accord with the behavior of all antiferromagnetic-ferromagnetic transitions observed so far.

Finally, we compare the susceptibility as found by the Oguchi method with that from the molecular-field theory. This is done in the immediate neighborhood of the Néel temperature where the spontaneous moment of the system can be neglected. Since the parallel and perpendicular susceptibilities are equal at T_N, only $\chi_{\parallel}$ is derived below.

Let the external field H_0 be in the direction of the magnetization of the A sublattice which is taken along the positive z axis here. The cluster Hamiltonian in the presence of H_0 is

$$\begin{aligned} H_{\mathrm{cl}} = -I_1 \mathbf{S}_{Ai}\cdot\mathbf{S}_{Bj} - S_{Aiz}\{K_1 S_{Bz} + K_2 S_{Az} - g\mu_B H_0\} \\ - S_{Bjz}\{K_1 S_{Az} + K_2 S_{Bz} - g\mu_B H_0\}. \end{aligned} \tag{4.32}$$

The energy levels (4.13) are modified in that the term $g\mu_B H_0$ is subtracted from λ_1 and added to λ_2 with λ_3 and λ_4 unchanged. It is readily found that $\mathrm{Tr}(S_{Aiz}e^{-H/kT})$ is

$$\begin{aligned} \mathrm{Tr}(S_{Aiz}e^{-H/kT}) = e^{I_1/4kT}\Bigg[\sinh\left(\frac{(K_1+K_2)(S_{Az}+S_{Bz})-2g\mu_B H_0}{2kT}\right) \\ + \frac{e^{-I_1/2kT}(K_1-K_2)(S_{Az}-S_{Bz})}{Q}\sinh\left(\frac{Q}{2kT}\right)\Bigg]. \end{aligned} \tag{4.33}$$

If one takes $S_{Az} = S_{Az}^{(0)} + \delta S_{Az}$ and $S_{Bz} = S_{Bz}^{(0)} - \delta S_z$, the self-consistency condition (4.15) in the presence of H_0 becomes

$$\begin{aligned} S_{Az}^{(0)} + \delta S_z \sim \frac{Q^{-1}(K_1-K_2)S_{Az}^{(0)}e^{-I_1/2kT}\sinh(Q/2kT)}{1+e^{-I_1/2kT}\cosh(Q/2kT)} \\ + \frac{[(K_1+K_2)\delta S_z - g\mu_B H_0]/kT}{2+2e^{-I_1/2kT}\cosh(Q/2kT)}. \end{aligned} \tag{4.34}$$

From (4.22) we see that the first term of (4.34) is just $S_{Az}^{(0)}$. Thus,

$$\delta S_z = \frac{(K_1+K_2)\delta S_z - g\mu_B H_0}{kT[2+2e^{-I_1/2kT}\cosh(Q/2kT)]}. \tag{4.35}$$

The parallel susceptibility is found to be

$$\chi_{\parallel} = \frac{Ng^2\mu_B^2}{kT(3+e^{-I_1/kT}) - kT_C(3+e^{-I_1/kT_C})}, \tag{4.36}$$

where Q has been taken as I_1 since S_{Az} is small near T_N. Comparing (4.36) at T_N with (3.37) or (3.41) at T_N, we find

$$\chi_{\parallel}(T_N)_{\mathrm{Oguchi}} = 0.538\,\chi_{\parallel}(T_N)_{\mathrm{M.F.}}.$$

Apparently this large difference comes from the exponential dependence of $\chi_{\parallel}$ in (4.37) on T_N and T_C, and from the differences in the transition temperatures as found by the two methods.

V. RESULTS AND CONCLUSIONS

Both the molecular-field theory and Oguchi's theory as applied to the particular example discussed here lead to an antiferromagnetic-ferromagnetic transition. The two approaches only allow the possibility of going from the antiferromagnetic state to the ferromagnetic state with decreasing temperature. Furthermore, we have seen from the molecular-field theory that the magnetic transition is of second order.

One cannot write down directly the free energy for the entire system from Oguchi's theory which deals only with a pair of neighboring atoms. However, connection can be made between the properties of the pair and those of the crystal by use of the formalism developed by Kasteleijn and van Kranendonk in their constant-coupling method.[10] In fact, it is readily shown that Oguchi's cluster Hamiltonian for a neighboring pair given in Eq. (2.2) of his paper is identical with the effective Hamiltonian for a neighboring pair given in Eq. (19) of reference 10 since A_3 is $\frac{1}{2}(Z-1)JS/\mu_B$ as it is shown there to be in the limit of high temperatures. Oguchi's cluster Hamiltonian for the antiferromagnetic case can also be shown to be the same as the pair Hamiltonian of the constant-coupling method given by Eq. (24) of reference 8 in the high-temperature limit. The work of Kasteleijn and van Kranendonk appears to be the proper generalization of Oguchi's theory.

It is of interest to have a physical picture of the mechanism underlying the antiferromagnetic-ferromagnetic transition. Therefore, consider the A set of atoms. The agency which produces their net magnetization in the molecular-field theory is H_A. The temperature to which the system must be raised in order to destroy M_A is seen from (3.21) and (3.24) to be

$$T_C=\frac{C|H_A(T=0)|}{Ng\mu_B S_0}. \tag{5.1}$$

If the free energy of the system at 0°K were for both the antiferromagnetic and ferromagnetic cases

$$F(T=0)=-\tfrac{1}{2}(\mathbf{H}_A\cdot\mathbf{M}_A+\mathbf{H}_B\cdot\mathbf{M}_B), \tag{5.2}$$

as it ordinarily is, then using (5.1) and taking $M_A=M_B=\frac{1}{2}(Ng\mu_B S_0)$ at 0°K, one finds

$$F(T=0)=-\frac{3NS_0}{2(S_0+1)}kT_C. \tag{5.3}$$

This shows that if (5.2) holds for all types of ordering, that ordering with the highest transition temperature T_C is stable at 0°K with respect to any other type. This result has been obtained in a somewhat different manner for $S_0=\frac{1}{2}$ by Smart.[11]

The reason why this prohibition of magnetic transitions does not apply in the present case is that (5.2) does not hold for both the ferromagnetic and antiferromagnetic cases. The direct-exchange interaction of the paramagnetic atoms with the conduction electrons contributes a term to $F(T=0)$ which is seen from (2.3) to be

$$-\textstyle\sum_{Ai}\sum_{Bj}I_2(\mathbf{S}_{A1}+\mathbf{S}_{Bj})\cdot\mathbf{S}_e. \tag{5.4}$$

Here

$$\mathbf{S}_e=\textstyle\sum_i\mathbf{S}_i, \tag{5.5}$$

the sum over i going over all of the conduction electrons. From (3.5) and (3.7) we have that $\mathbf{S}_e$ is directly proportional to $\mathbf{M}_A+\mathbf{M}_B$. This result is also derived on the basis of the Hartree-Fock equations in I. Thus, $\mathbf{S}_e$ is zero in the antiferromagnetic case and (5.2) does represent the situation. However, in the ferromagnetic case $\mathbf{S}_e\neq0$ and (5.4) must be added to the free energy. Hence (5.2) does not describe both types of ordering here and (5.3) is consequently invalid. Thus, even though $H_A(T=0)$ or equivalently T_C is greater for the antiferromagnetic case, the interaction with the conduction electrons can make the ferromagnetic state that of lowest free energy.

The fact that a magnetic transition would be impossible without the exchange coupling with the conduction electrons and that their inclusion leads to a long-range interaction of the spins is strong support for the claim that the theory developed here and in I does apply to the rare earths where magnetic transitions have been observed in dysprosium[12] and erbium.[13] Furthermore, these transitions are in the order predicted here. It can be argued correctly that temperature-dependent molecular-field constants could lead to a magnetic transition. However, this does not answer the question as to the source of the long-range spin coupling necessary in the rare earths. The treatment given in this paper would have to be modified in order to apply it properly to the rare earths by making allowance for the orbital contribution to the magnetic moment and for the effects of anisotropy.

An interesting comparison between the theory given here and in I and with experiment can be made in the case of dilute alloys of Mn in Cu. A comprehensive investigation of the magnetic properties of this alloy is reported in two papers.[14,15] Of particular interest here are the results of reference 15. Alloys of 1.4 and 5.6 atomic percent Mn were investigated at low temperatures for ferromagnetism. In both alloys a small spontaneous magnetization was observed at 4°K which decreased rapidly on heating and vanished at the antiferromagnetic transition temperature. According to the results of Secs. III and IV this is precisely what would be expected of a material which undergoes an antiferromagnetic-ferromagnetic transition.

Owen *et al.*[15] carried out electron spin resonance measurements on the alloys and interpreted the results as indicating that the strength of the *s-d* direct exchange

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[11] J. S. Smart, Revs. Modern Phys. **25**, 327 (1953).

[12] Elliott, Legvold, and Spedding, Phys. Rev. **94**, 1143 (1954).

[13] Elliott, Legvold, and Spedding, Phys. Rev. **100**, 1595 (1955).

[14] Owen, Browne, Knight, and Kittel, Phys. Rev. **102**, 1501 (1956).

[15] Owen, Browne, Arp, and Kip, J. Phys. Chem. Solids **2**, 85 (1957).

coupling, measured by η defined in (3.2), was 1/10 to 1/20 of that expected from the free-ion value. Although an entirely different molecular-field treatment was used in reference 14, it led to a similar sharply reduced value of η.

In order that the results obtained here and in I describe the antiferromagnetic and ferromagnetic properties found in reference 15, it is necessary to assume that the strength of the direct *s-d* coupling is comparable to that of the antiferromagnetic coupling. In particular, from Eq. (88) of I, the condition for an antiferromagnetic-ferromagnetic transition is

$$2\eta^2\chi_c > A > \eta^2\chi_c. \tag{5.6}$$

In the opinion of the writer the experimental results obtained in references 14 and 15 can be explained without assuming a very weak direct-exchange coupling and that (5.6) may be satisfied. If the Mn goes into the alloy as an Mn^{++} ion, it presents an extra positive charge to the conduction electrons. The induced screening charge is made up of conduction electrons of both spins. Those of spin parallel to the Mn^{++}-ion spin are favored by an exchange interaction while those of opposite spin have the exclusive ability to spend part of their time trapped on the Mn ion. This latter possibility is embodied in the superexchange interaction. The net result of these two effects can be that the net spin of the screening charge will be very small. It was concluded in I that a very small value of η may have been found in reference 14 as a result of not including the superexchange interaction in the theory given there.

As indicated above, the interpretation of the electron spin resonance results in reference 15 indicated a small value of η. If one assumes that the model on which this conclusion is based is essentially correct, it seems that a legitimate objection can be raised concerning the treatment of the *s-d* coupling. If the alloy were in the antiferromagnetic state, then according to (3.7), M_e is zero. Thus, the first-order theory would imply that the conduction electrons play no role in the antiferromagnetic state.[16] This cancellation would not be complete in a higher order theory and one would be led to a molecular field due to the conduction electrons acting on a Mn ion, say in the A set, of the form

$$(\eta_0^2-\eta^2)\chi_c M_0, \tag{5.7}$$

where η_0 is related to the exchange coupling of conduction electrons interacting more strongly with the A set than the B set, and η is related to the exchange interaction with this atom in the A set of conduction electrons interacting more strongly with the B set. In reference 15 η was neglected as compared with η_0 and on comparing the results with experiment a small value of η_0 resulted. According to the picture developed in Sec. III, the fact that T_N and T_C are not widely different in the CuMn alloys and in particular that an antiferromagnetic-ferromagnetic transition appears to take place, leads to the conclusion that the screening charge is made up nearly equally of conduction electrons of each spin. This means that η_0^2 and η^2 in (5.7) must be nearly equal. If one assumes that the resonance theory of reference 15 is valid, it is the difference between η_0 and η which is measured. A small value of this quantity is consistent with the theory given here. Furthermore, it is consistent with the small electronic g shift found in the electron spin resonance of these alloys for $T \gg T_N$.

V. ACKNOWLEDGMENT

It is a pleasure for the writer to acknowledge helpful discussions with his colleagues and in particular with Dr. H. J. Zeiger.

Note added in proof.—Yosida[17] has raised an important point concerning the treatment given here. Our results are based on the Hamiltonian (2.3) which is derived from Kramers' method for solving the spin degeneracy problem arising from all possible spin assignments to a fixed set of orbitals. Hence in this theory there are as many singly occupied Bloch functions in the conduction band in the antiferromagnetic case where M_e is zero as in the ferromagnetic case where M_e is not zero. Thus the conduction electron kinetic energy is unnecessarily high for antiferromagnetic ordering of the A and B sets. Yosida suggests that this situation be remedied by adding the conduction electron kinetic energy to the Hamiltonian as $M_e^2/2\chi_c$. To discuss the antiferromagnetic case we would use a ground configuration in Kramers' method with no singly occupied levels in the conduction band. In the ferromagnetic case we would use a ground configuration with $M_e/g\mu_B$ unpaired spins where M_e is determined by setting the variation of (2.3) plus $M_e^2/2\chi_c$ with respect to M_e equal to zero. However, in addition to this suggestion one must include the dependence of the number of excited states η_γ, which can couple two states ϕ_i and ϕ_j in the ground set, on the number of singly occupied Bloch functions in the conduction band. In general this dependence can be expressed by expanding I_1 and I_3 of (2.3) in power series in M_e the first terms of which must go as the square of M_e. Hence the Hamiltonian to be used for the molecular field case becomes in place of (3.1)

$$H=(A_0+A_1M_e^2)\mathbf{M}_A\cdot\mathbf{M}_B+\frac{(\Gamma_0+\Gamma_1M_e^2)}{2}(\mathbf{M}_A\cdot\mathbf{M}_A+\mathbf{M}_B\cdot\mathbf{M}_B)$$
$$-\eta(\mathbf{M}_A+\mathbf{M}_B)\cdot\mathbf{M}_e+\frac{M_e^2}{2\chi_c}.$$

The molecular fields acting on the A and B sets are still given by (3.3) and (3.4), respectively, but M_e is found by setting $\partial H/\partial M_e$ equal to zero instead of from (3.7). One finds that T_C and T_N are unaltered from (3.9) and (3.18) but that the condition for the antiferromagnetic-ferromagnetic transition becomes

$$\eta^2\chi_c > A_0(1+K) > \eta^2\chi_c(1+K)$$

where K is

$$\frac{N^2g^2\mu_B^2S^2(A_1+\Gamma_1)}{2}.$$

This can only hold if $A_1+\Gamma_1$ is negative and it becomes the same condition as that found by the unmodified theory if K is $-\frac{1}{2}$. A magnetic transition is possible here only because the strength of the superexchange coupling changes with the conduction electron magnetization. The qualitative nature of the transition as given by the generalized theory is the same as that described in Secs. III and IV.

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[16] The appearance of a contribution from direct exchange in the expression for the Néel temperature, Eq. (7) of reference 15, is incorrect.

[17] K. Yosida (private communication).