ciably larger amounts of energy are not lost until the electronic energy is large enough to excite the molecular electrons. This conclusion is probably a correct one, though the results worked out here do not include the effects of polarization. Inclusion of polarization is unlikely to change the vibration-rotation cross sections unlikely to change the vibration-rotation cross sections

by a very large factor; it is more likely to affect the cross sections for electronic excitation, which appear for incident energies larger than those considered here. There is no indication of any sharp-peaked resonance effect in the energy region considered, nor, indeed, should one have been expected.

Magnetic Structure Transitions*†

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The problem of magnetic phase transitions between ferromagnetism and antiferromagnetism, or between two different kinds of antiferromagnetic arrangement, is treated by a molecular field approach. It is shown that such transitions may occur if the molecular field coefficients vary with temperature; if they do occur, they will be of first order. The theoretical results agree qualitatively with the experimental results of Guillaud and Serres on MnAs.

THE Weiss molecular field treatment of ferromagnetism and antiferromagnetism has recently modified to include both first and second nearest neighbor interactions with all four combinations of signs.[1-3] One of the results of these investigations is that there are, in general, at least three possible types of magnetic ordering for a given magnetic lattice. They are ferromagnetic ordering and two types of antiferromagnetic ordering, one favoring antiferromagnetic arrangement of nearest neighbors and the second favoring antiferromagnetic arrangement of second nearest neighbors. The type of ordering which will actually occur is that with the highest Curie temperature and is determined by the signs and relative magnitudes of the interactions. In some instances, there is a critical value for the ratio γ_2/γ_1 (the Weiss field coefficients for first and second nearest neighbor interactions) such that the orderings on either side of this critical value are of different kinds. This result suggests that, in addition to the usual Curie temperature transitions, there may sometimes occur transitions in which the magnetic ordering changes from one kind to another. Moreover, there is excellent experimental evidence, owing to Guillaud[4] and Serres,[5] that transitions from a ferromagnetic to an antiferromagnetic arrangement occur in MnAs and MnBi. The purpose of this paper is to develop a simple theoretical

model for such transitions. Garrett[6] and Ziman[7] have recently discussed the problem of phase transitions from an antiferromagnetic to a "ferromagnetic" state produced by a strong magnetic field. We shall discuss here, using a model similar to Garrett's, the possibility of changes in the type of magnetic ordering in zero applied field.

PROPERTIES OF A NORMAL FERROMAGNET OR ANTIFERROMAGNET

For simplicity, we consider a system of N atoms whose magnetic moments are due to a single unpaired spin on each atom. Let the atoms be arranged on a lattice which may be divided into n sublattices in such a way that a given atom has neither first nor second nearest neighbors on its own sublattice and only one kind of neighbors on any other sublattice. Let γ_1 and γ_2 be the Weiss field coefficients for first and second nearest neighbor interactions. If we assume, as is usual, that the molecular field is an approximation to the effects of exchange coupling, then the γ_i are given by

$$\gamma_i = 2Z_i |J_i|/g\beta, \quad i = 1, 2, \tag{1}$$

where Z_i is the number of ith nearest neighbors and J_i is the exchange interaction between electrons on ith neighbors; β is the Bohr magneton and g the gyromagnetic ratio of the electron. Then the molecular field $\mathbf{H}_{jk}$ acting on an atom on the jth sublattice due to its neighbors on the kth sublattice is

$$\mathbf{H}_{jk} = \epsilon_{jk}\gamma_{jk}\mathbf{S}_k, \tag{2}$$

where ϵ_{jk} is $+1$ or -1 depending on whether the $j-k$ interaction is ferromagnetic or antiferromagnetic, γ_{jk} is

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† A preliminary account of this work was given at the Washington Conference on Magnetism, September, 1952, and is being published in the Reviews of Modern Physics.
[1] L. Néel, Ann. phys. **3**, 137 (1948).
[2] P. W. Anderson, Phys. Rev. **79**, 705 (1950).
[3] J. S. Smart, Phys. Rev. **86**, 968 (1952).
[4] C. Guillaud, J. phys. et radium **12**, 223 (1951), and other references given there.
[5] A. Serres, J. phys. et radium **5**, 146 (1947).
[6] C. G. B. Garrett, J. Chem. Phys. **19**, 1154 (1951).
[7] J. M. Ziman, Proc. Phys. Soc. (London) A**64**, 1108 (1951).

either γ_1 or γ_2 (or some simple fraction thereof) and $\mathbf{S}_k$ is the average spin per atom on the kth sublattice.

We shall define a normal ferromagnet (or antiferromagnet) as one in which γ_1 and γ_2 are independent of temperature. The theoretical magnetic and thermodynamic properties of such a material are well known; the remainder of this section is devoted to listing some of these properties for comparison with results to be obtained later in this paper. First of all, the Weiss-Langevin equation of state for the material takes the form

$$\sigma_j = \sigma = \tanh(\sigma/\tau) \tag{3a}$$

and

$$\sigma_j = \eta_{jk}\sigma_k, \quad j, k = 1, 2, \cdots, n, \tag{3b}$$

where σ_j is the reduced magnetization of the jth sublattice and $\tau = T/T_c$. The η_{jk} are either $+1$ or -1; different sets of the η_{jk} obviously describe different kinds of magnetic ordering. The explicit expression for the Curie temperature corresponding to a given set of η_{jk} is

$$T_c = (g\beta/4k) \sum_{k \neq j}^{n} \eta_{jk}\epsilon_{jk}\gamma_{jk}. \tag{4}$$

Values of T_c for body-centered cubic and face-centered cubic lattices for various types of ordering are given in reference 3.

For a reduced magnetization σ_j, there are (N/n) $\times (1+\sigma_j)$ spins aligned in one direction and $(N/n)(1-\sigma_j)$ spins aligned in the other direction on the jth sublattice. Then the entropy of the entire sample is

$$S = k \ln \prod_{j=1}^{n} \frac{(N/n)!}{[(N/n)(1+\sigma_j)]![(N/n)(1-\sigma_j)]!}. \tag{5}$$

We note that this expression is an even function of σ_j; in other words, the entropy is unchanged if the directions of all the spins on a given sublattice are reversed. This result enables us to classify the types of transitions which may occur. If some of the sublattices merely reverse their directions of magnetization without changing σ, then the transition occurs without change in entropy and is a second order phase transition. On the other hand, if the reduced magnetizations of the sublattices are changed as well as their directions, the transition will in general be of the first order.

By use of Stirling's approximation and Eq. (3b), the expression for the entropy may be reduced to a form more convenient for calculation.

$$S = Nk[\ln 2 - \tfrac{1}{2}\ln(1-\sigma^2) - \sigma \tanh^{-1}\sigma]. \tag{6}$$

The Gibbs free energy in zero applied magnetic field may be obtained from the differential relation

$$dG = -SdT, \tag{7}$$

and we find, by integrating (7),

$$G(T) = Nk\left[-T \ln 2 + \tfrac{1}{2}T_c\left(\sigma^2 + \frac{\sigma \ln(1-\sigma^2)}{\tanh^{-1}\sigma} \right) \right], \tag{8}$$

if we set $G(T_c) = -NkT_c \ln 2$. (This is equivalent to setting the internal energy, U, equal to zero when $\sigma = 0$.) The function of σ in Eq. (8) is zero for $\sigma = 0$ and decreases monotonically for increasing σ (or decreasing T). Thus that type of ordering which has the highest Curie temperature will have the lowest Gibbs free energy for all temperatures below its Curie point. Consequently, there will be no transitions from one type of ordering to another for a normal material, or as long as the equations of state have the form of Eqs. (3).

EFFECTS OF TEMPERATURE VARIATION OF THE WEISS FIELD COEFFICIENTS

We have seen that magnetic structure transitions do not occur in a normal ferromagnet or antiferromagnet. A possible explanation of the fact that such transitions apparently do occur in nature is that the Weiss field coefficients, γ_1 and γ_2, actually vary with temperature. Thus, if a material has a value of γ_2/γ_1 near the critical ratio for some given temperature, a change in temperature may shift the ratio across the critical value and thus produce a transition. There are a number of reasons why γ_1 and γ_2 may be expected to be temperature-dependent but perhaps the simplest is that the exchange integrals, J_i, are expected to depend sensitively on the interatomic separation which of course varies with temperature. This point has been especially emphasized by Néel.[8] We shall assume a simple linear variation of the form

$$\gamma_i = \gamma_{i0}(1+\alpha_i T), \quad i = 1, 2. \tag{9}$$

Thus the molecular fields, as defined by Eq. (2), now have a temperature variation over and above that resulting from the spontaneous magnetization. This leads to a new form for the equation of state:

$$\sigma_j = \sigma = \tanh\left(\frac{1+\lambda\tau}{\tau}\sigma \right), \tag{10}$$

with $\sigma_j = \eta_{jk}\sigma_k$ as before. In this equation $\tau = T/T_c^0$, where T_c^0 is the Curie temperature for $\alpha_1 = \alpha_2 = 0$. The temperature coefficient λ is a function of the γ_{i0} and α_i whose exact form depends on both the type of lattice and the type of ordering occurring. We have

$$\lambda = (g\beta/4k) \sum_{k \neq j}^{n} \eta_{jk}\epsilon_{jk}\gamma_{jk0}\alpha_{jk}. \tag{11}$$

One effect of the temperature dependence of the γ_i is to distort the normal $\sigma - \tau$ curve obtained for $\alpha_1 = \alpha_2 = 0$. An example of this distortion is shown in Fig. 1 for the special case $\lambda = -0.23$. The new Curie temperature is given by

$$T_c = T_c^0/(1-\lambda). \tag{12}$$

The entropy is of course the same function of σ as it was for the normal case. The calculation of the Gibbs

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[8] L. Néel, Ann. phys. 8, 237 (1937).

free energy from the differential relation is somewhat more difficult than for the normal case because of the more complicated relationship between σ and τ. We were unable to integrate the expression exactly; however, it can be written as

$$G(T)=Nk\left[-T\ln 2+\tfrac{1}{2}T_c{}^0\left\{\frac{\sigma^2\tanh^{-1}\sigma+\sigma\ln(1-\sigma^2)}{\tanh^{-1}\sigma-\lambda\sigma}\right.\right.$$

$$\left.\left.+\lambda\int_{\tau_c}^{\tau}\sigma^2 d\tau\right\}\right], \quad (13)$$

with $\tau_c=T_c/T_c{}^0$.

Now let us consider two possible types of magnetic ordering, which we designate by A and B, for a particular system. First of all, it is important to note that though γ_{10}, γ_{20}, α_1, and α_2 are the same for the A and B states, the temperature coefficients λ_A and λ_B are unequal since they are different functions of the first four quantities. It is this difference which makes the ordering transitions possible.

We assume that the A state has the highest actual Curie temperature. Then for temperatures just below T_{CA}, $G_A<G_B$, and the A ordering will obtain. Evidently the condition that a magnetic structure transition occurs is

$$G_B(0)<G_A(0), \quad (14a)$$

or, with the use of Eq. (11),

$$\lambda_A T_{CA}{}^0\int_0^{\tau_{CA}}\sigma_A{}^2 d\tau_A-\lambda_B T_{CB}{}^0\int_0^{\tau_{CB}}\sigma_B{}^2 d\tau_B$$

$$<T_{CB}{}^0-T_{CA}{}^0, \quad (14b)$$

where $\tau_A=T/T_{CA}{}^0$ and $\tau_B=T/T_{CB}{}^0$.

It is not immediately obvious whether such transitions would be first or second order. However, we note that the temperature at which $\sigma_A=\sigma_B$ is given by

$$(1+\lambda_A\tau_A)\tau_A{}^{-1}=(1+\lambda_B\tau_B)\tau_B{}^{-1},$$

or

$$T_\sigma=(T_{CA}{}^0-T_{CB}{}^0)/(\lambda_B-\lambda_A). \quad (15)$$

Inspection of Eq. (13) shows that in general $G_A(T_\sigma) \neq G_B(T_\sigma)$. Consequently if Eq. (14) is satisfied and a transition does occur it will be a first-order transition.

So far all of the discussion has been for zero applied field. The effect of an external magnetic field is twofold; first, it adds a term of the order of magnitude of $-MH$ to the Gibbs free energy where M is the total magnetization of the sample; second, it alters the σ_j so that $\sigma_j=\eta_{jk}\sigma_k$ no longer holds and thus changes the form of Eq. (13). For materials with Curie temperatures of 100°K or above, these effects are relatively small, except for ferromagnetic states where the $-MH$ term may make an appreciable contribution to the Gibbs free energy. In particular, without attempting any detailed calculations, it can be said that an external magnetic field may produce an appreciable shift in transi-
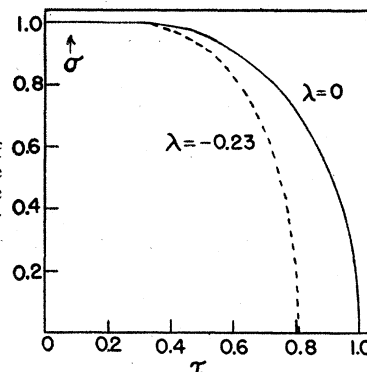

FIG. 1. Distortion of the normal $\sigma-\tau$ curve owing to temperature variation of the molecular field coefficients.

tion temperatures in cases where one of the states is ferromagnetic.

The other changes in the Gibbs free energy produced by application of an external field will be important in cases where the Curie temperatures are extremely low. We shall not, however, discuss these effects any further here.

COMPARISON WITH EXPERIMENTAL DATA

In this section we first review briefly the experimental data on the compounds MnAs and MnBi, most of which is due to Guillaud[4] and Serres.[5] MnAs and MnBi both crystallize in the NiAs structure; the magnetic lattice is a hexagonal layer arrangement. Both compounds are ferromagnetic at low temperatures with saturation magnetizations corresponding to about 3.5β per Mn atom. When MnAs is heated to about 318°K, its magnetization drops suddenly from $0.64 M_0$ to zero; when the material is cooled, the magnetization reappears at 305°K. Above 350°K the paramagnetic susceptibility increases gradually with temperature to 395°K; above this latter temperature, the susceptibility begins to fall off, following the relation $\chi=C/(T-\theta)$ with $\theta=+285$°K and C corresponding to a moment of 3.7β per Mn atom. The interpretation of these results, which are shown in Fig. 2, is that MnAs undergoes a transition from a ferromagnetic to an antiferromagnetic state at 318°K and that the antiferromagnetic Curie temperature is at 395°K. No susceptibility data has been obtained on MnBi but it has a similar discontinuity in the magnetization at 630°K; Guillaud has reported a specific heat anomaly at 720°K which might indicate an antiferromagnetic Curie temperature.

In both compounds, the low temperature transition seems to be of first order as there is a latent heat observed in each case along with a volume change of 3 percent for MnAs and 4.5 percent for MnBi. MnAs contracts along the a axis and MnBi along the c axis upon being heated through the transition temperature. If the suggestions of Smart and Greenwald[9] concerning crystal structure changes in other antiferromagnetic

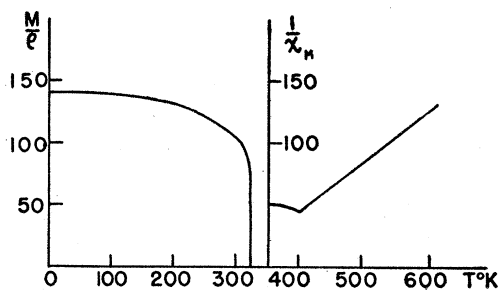[9] J. S. Smart and S. Greenwald, Phys. Rev. 82, 113 (1951).

FIG. 2. Magnetization and reciprocal susceptibility of MnAs as a
function of temperature (from Guillaud and Serres).

materials are used as a guide, these results indicate
that the antiferromagnetic ordering in MnBi consists
in having the spin directions alternate from layer to
layer in the hexagonal layer arrangement. On the other
hand, the change in a axes for MnAs suggests that its
magnetic structure may be an arrangement whereby
the spin direction alternate in planes parallel to the
c axis. In this case, the symmetry should be deformed
to something lower than that of the hexagonal layer
structure, but this effect might not be detectable unless
an apparatus of high resolution was used. Figure 3
shows the two types of magnetic ordering suggested
above.

The theoretical model used here is much too simple
to try to obtain any quantitative agreement between
calculated and observed magnetic and thermal changes
in MnAs. For example, the theory would never allow
any changes in volume, since we have assumed only a
pure magnetic material. Also, the crystal structure in-
dicates that third nearest neighbor interactions may be
as important as first and second; if this were so, it would
complicate the analysis considerably.

However, there seems to be good qualitative agree-
ment between the theory and the experimental results.
First of all, the transitions are first-order transitions,
as has been mentioned previously. Second, numerical
calculations show that the values of α_1 and α_2 required
to give the observed transitions is of the order of magni-
tude of $10^{-4}/°K$. This value is in good agreement with
estimates (made by Néel[8]) based on other considera-
tions. Also, Guillaud's data[4] shows a variation of

transition temperature with applied field which seems
to be of the right order of magnitude.

Finally, there is some supporting evidence from the
magnetic susceptibility data. The θ/T_c ratio for MnAs
is $+0.7$, all other known antiferromagnets have a
negative θ/T_c. This unique behavior can be understood
however if it is assumed that the transition from ferro-
magnetism to antiferromagnetism is caused by tempera-
ture variation of the molecular field coefficients. First
of all, in the ferromagnetic state, the material will have
$\theta/T_c = +1$. If the Curie temperature of the antiferro-
magnetic state now becomes slightly higher because of
changes in γ_1 and γ_2 and a transition occurs, the corre-
sponding θ/T_c should be slightly less than $+1$ as is
observed.

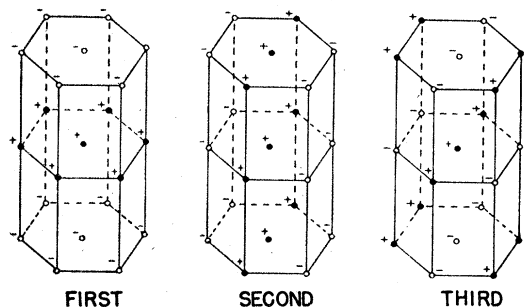FIRST   SECOND   THIRD

FIG. 3. Possible types of magnetic ordering for the
hexagonal layer lattice.

We may also expect that transitions between two
different kinds of antiferromagnetic ordering will occur
in some cases. There is no definite experimental evi-
dence for such transitions, although the susceptibility
and crystal structure anomalies observed[10] in FeS sug-
gest something of the sort. Neutron diffraction experi-
ments would probably be required to determine whether
the low temperature transition in FeS is really a mag-
netic structure transition or whether it is some other
effect such as a change in direction of the antiferro-
magnetic axes.

The author is greatly indebted to various members of
the Solid State Division for discussions of this problem.

[10] H. Haraldsen, Z. anorg. u. allgem. Chem. 246, 169, 175 (1941).