

A Generalization of the Theory of Ferromagnetism*

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The Weiss-Heisenberg theory of ferromagnetism is discussed and generalized in a plausible way. Whether this generalization is theoretically sound must be determined by a quantum-mechanical investigation. The proposed equations of state, however, may be regarded as an attempt to describe antiferromagnetism (i.e., the case in which oppositely directed spins on adjacent atoms have the lowest energy), pure metals having less than one spin per atom, and the magnetic properties of alloys. No attempt is made to compare the results with the properties of actual

alloys, but it is shown that the proposed equations do give systems in which the Curie temperature depends on composition and atomic order; in which nonmagnetic metals may combine to produce a ferromagnetic alloy; in which wasp waisted hysteresis loops occur; and in which heat treatment may radically affect magnetic properties. Large effects are predicted which should make it easy to verify experimentally whether or not the proposed approach to the problem is on the right track.

THE theory of ferromagnetism as developed by Weiss, Heisenberg, and others, has been used chiefly to interpret the magnetic properties of crystals of like atoms in which internal forces tend to make elementary magnetic moments point in the same direction. In this field even the simplest form of the theory has been quite successful in accounting for the dependence of spontaneous magnetization, magnetic susceptibility, and specific heat on temperature. The simple magnetic equation of state which gives these results is admittedly only approximate, but its success has been sufficient to give point to the question of how it might be generalized to include systems of unlike atoms and systems in which conflicting internal forces may be present. There is at present no hope of setting up such equations rigorously, and we shall consequently have to content ourselves with plausible guesses based on the theories of Weiss and Heisenberg, which we shall first briefly review. We shall assume systems containing dipoles that are either parallel or antiparallel to each other and to the externally applied field. In a system containing N such dipoles of which N_+ are pointing to the right and N_- are pointing to the left, the relative intensity of magnetization is defined as $i = (N_+ - N_-)/(N_+ + N_-)$, and the total intensity of magnetization is defined as $I = \mu N i$. The Langevin theory of paramagnetism states that

if these elementary dipoles do not interact with each other, the magnetization i , absolute temperature T , and magnetic field H are related by the equation $i = \tanh(\mu H/kT)$. The Weiss theory generalizes this by saying that if the dipoles do interact, this interaction may be represented as an additional field proportional and parallel to the intensity of magnetization and the equation of state becomes

$$i = \tanh [(Di + \mu H)/kT]. \quad (1)$$

From this equation of state one can calculate the physical properties of the system. The spontaneous magnetization (i as a function of T for $H=0$) and volume susceptibility ($K_0 = \mu N \partial i / \partial H$ for $H=0$) follow directly. If the equation has more than one solution, the most stable one is defined as that having the lowest free energy $f = u - \mu i H - T \varphi$, the internal energy u and entropy φ per atom being defined by¹

$$du = s_I dT - \left(T \frac{\partial H}{\partial T} - H \right) \frac{dI}{N}, \quad (2)$$

$$d\varphi = \frac{s_I dT}{T} - \frac{\partial H}{\partial T} \frac{dI}{N}, \quad (3)$$

where s_I is the atomic specific heat at constant magnetization. Substituting from the equation of state and integrating one finds that

$$u = -\frac{1}{2} D i^2, \quad (4)$$

$$\varphi = -\frac{1}{2} k [(1+i) \ln(1+i) + (1-i) \ln(1-i)], \quad (5)$$

¹ See F. Bitter, *Introduction to Ferromagnetism* (McGraw-Hill, 1937) Chapter IX.

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terms independent of i being omitted. s_I can be shown to be independent of i .

The Heisenberg theory is the quantum-mechanical counterpart of an earlier theory due to Ising² which was first developed for the case of linear chains of atoms, but which we shall run through in a more general way. The magnetic moments are assumed to be distributed on the lattice points of a crystal, and each dipole has z nearest neighbors. It is assumed that only nearest neighbors interact, and that the total energy of the crystal may be taken as the sum of the mutual energies of all pairs of nearest neighbors

$$Nu = \epsilon_{++}\nu_{++} + \epsilon_{+-}\nu_{+-} + \epsilon_{--}\nu_{--}$$

ϵ_{++} is the interaction energy of a pair of positive dipoles, ν_{++} is the number of these present in some particular configuration of the crystal, and it is assumed for simplicity that the total volume of the crystal is one cubic centimeter. It can be shown that this expression can be rewritten in terms of a new parameter σ , sometimes called the short range order, defined by

$$\nu_{+-} = \frac{1}{4}Nz(1-\sigma).$$

From this definition it follows that

$$\begin{aligned} \nu_{++} &= \frac{1}{4}Nz\{1+i-\frac{1}{2}(1-\sigma)\}, \\ \nu_{--} &= \frac{1}{4}Nz\{1-i-\frac{1}{2}(1-\sigma)\}, \\ u &= -\frac{1}{2}D\sigma \end{aligned} \quad (6)$$

where D is a constant derived from the interaction energies. The variables i and σ define the state of the crystal. Unfortunately it is not possible to write the entropy as a function of i and σ except for the case of a linear chain of atoms, because we do not know how to estimate the number of configurations corresponding to given values of i and σ . We do know, however, that there are far more configurations for $\sigma = \bar{\sigma}$ than for any other configuration; in fact that the total number of configurations for all values of σ with a fixed i is very nearly equal to the number of configurations for $\sigma = \bar{\sigma}$ and the same value of i . It can easily be shown that the mean value³ of σ is

$$\bar{\sigma} = i^2$$

² E. Ising, *Zeits. f. Physik* **31**, 253 (1925).

³ Let x_k be a number which is +1 when the k th lattice point is occupied by a positive moment, and -1 when occupied by a negative moment. $\sum_{k=1}^N x_k = N_+ - N_- = Ni$;

and that if we neglect states with values of $\sigma \neq \bar{\sigma}$, the entropy must have the forms given in Eq. (5). With these assumptions one can readily obtain the equation of state (1) by minimizing the free energy.

Heisenberg's theory differs from the above form of Ising's theory in two respects. First, if electronic spins are responsible for the magnetization i , the mean value of σ must be found by calculating the mean value⁴ of the product of two spin operators $\langle s_j \cdot s_k \rangle_{AV}$ instead of the mean value of the product two numbers $\langle x_j x_k \rangle_{AV}$. For the case of a pure ferromagnetic metal, however, this calculation gives $\bar{\sigma} = i^2$ as in Ising's theory, and to this approximation the two theories give the same result. Heisenberg, however, goes on to assume a Gaussian distribution of states about the mean value, and adjusts the spread of this assumed distribution, so that the quantity $\bar{\sigma}^2 - \bar{\sigma}^2$ has its correct value. In this approximation the two theories give different results. Ising's approximation is⁵

$$i = \tanh \left\{ \frac{\mu H}{kT} + \frac{Di}{kT} \left[1 - \frac{D}{kT} \frac{(1-i^2)}{z} \right] \right\}, \quad (7)$$

which behaves "sensibly" at all temperatures, while Heisenberg's more correct treatment gives

$$i = \tanh \left\{ \frac{\mu H}{kT} + \frac{Di}{kT} \left[1 - \frac{D}{kT} \frac{(2-i^2)}{z} \right] \right\}, \quad (8)$$

which breaks down at low temperatures. The physical properties derived by means of these equations differ only slightly from those obtained from the simpler equation of state (1).

This is the foundation on which we shall proceed with our generalization. The inclusion of fluctuations⁶ adds so much to the complexity of the work, and so little to the physical content of the equations, that we shall omit them here. Eq. (1) is consequently our starting point. In

$\sum_{k=1}^N x_k^2 = N$; $\frac{1}{2} \sum_{\text{all pairs}} (1 - x_j x_k) = \nu_{AB}$; $\sum_{\text{all pairs}} x_j x_k = Nz\sigma/2$;
 $\langle x_j x_k \rangle_{AV} = \bar{\sigma}$; $\sum x_j \sum x_k = i^2 N^2 = \sum x_k^2 + N(N-1)\bar{\sigma}$;
 $\bar{\sigma} = N(N-1)\bar{\sigma}$; and for large values of N therefore $\bar{\sigma} = i^2$.

⁴ See Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford, 1932) Chapter XII.

⁵ A similar equation has been obtained by J. G. Kirkwood, *J. Chem. Phys.* **6**, 73 (1938) for the order-disorder problem.

⁶ L. Néel has attempted to include the effects of fluctuations in a different way. *Ann. de physique* **17**, 1 (1932).

discussing it we may use the language of any of the three derivations given above, which we shall refer to briefly by the names of Weiss, Ising, and Heisenberg. Of these we shall choose the method of Weiss because it is best suited to discussing the physical ideas in words with a minimum of calculation. The same results follow from the theory of Ising if we limit ourselves to the mean values of the energy, but it seems hardly worth while to go through the calculations in print. Whether or not the Heisenberg theory gives the same result to this approximation has not been determined.

Equation (1) applied to pure ferromagnetic media for which $D > 0$ gives a spontaneous magnetization which vanishes for $T > D/k = T_c$; a specific heat having a discontinuity for $T = T_c$; and an initial susceptibility given by the formula

$$K_0 = \frac{N\mu^2/k}{T/(1-i^2) - T_c}. \quad (9)$$

This quantity is $\partial I/\partial H$ for $H=0$ as calculated from Eq. (1). Below the Curie point it represents the small increase in the spontaneous magnetization which can be produced by strong fields. This has not yet been measured. Above the Curie temperature there is no spontaneous magnetization, $i=0$, and the behavior of actual materials is fairly well described by Eq. (9). The internal field in Eq. (1) is assumed to be proportional to the intensity of magnetization. This statement should be made more precise by saying, instead, that the field acting on any one atom is proportional to the intensity of magnetization of that group of atoms with which it interacts. It can be shown that for the case under discussion the positive and negative spins are randomly arranged among each other, and that, therefore, the intensity of magnetization of all groups of atoms within a region of spontaneous magnetization will be the same. The question of the range of the interatomic forces is, therefore, irrelevant, and Eq. (1) will hold whether we assume short range forces as in the Ising and Heisenberg treatments, or arbitrarily long range forces.

The question of the range of the forces,⁶ however, becomes important when we consider antiferromagnetism, or the case in which the

internal forces are such as to make interacting spins antiparallel to each other. To illustrate this, we shall consider two limiting cases. If the range of the forces is sufficiently large, we may assume as before that the internal field is proportional to the spontaneous magnetization, since the average magnetization of a sufficiently large group of atoms is likely to be equal to the spontaneous magnetization. The equation of state is then Eq. (1), with $D/k = T_c < 0$. The spontaneous magnetization is now zero for all temperatures, the specific heat is constant, and the initial susceptibility is given by

$$K_0 = \frac{N\mu^2/k}{T - T_c}. \quad (10)$$

This formula predicts a finite susceptibility at the absolute zero, continuously decreasing with rising temperature, and with small values of N and large negative values of T_c its contribution to the total susceptibility is of the same order of magnitude as that observed for some metals.

If the range of the internal forces is exceedingly short, we may neglect the interaction of all but nearest neighbors. In this case we must consider the possibility of orderly arrangements of magnetic moments in such a way that the average intensity of magnetization of the nearest neighbors of an atom is not equal to the total average intensity of magnetization of nearby atoms. In the case of a body-centered cubic lattice, for instance, it is convenient to break the lattice up into two simple cubic lattices which have the property that any atom on one of these sublattices has its eight nearest neighbors on the other sublattice. In the absence of interactions between next nearest neighbors⁷ we may assume the magnetization of these sublattices to be uniform. Denoting the relative intensity of magnetization of these sublattices by i_1 and i_2 , we may write

$$i_1 = \tanh \frac{Di_2 + \mu H}{kT}, \quad (11)$$

$$i_2 = \tanh \frac{Di_1 + \mu H}{kT}, \quad (12)$$

⁷ For a suggestion as to how these and more remote interactions may be taken into account, see a note by the author to appear shortly in J. Chem. Phys. and footnote 12 below.

since the internal field acting on the atoms of one sublattice is proportional to the intensity of magnetization of the atoms on the other sublattice. It is convenient to replace these variables by the total relative intensity of magnetization $i = (i_1 + i_2)/2$ and an order parameter $p = (i_1 - i_2)/2$ similar to the order parameter S in the theory of order-disorder in alloys. In terms of these variables Eqs. (11) and (12) may be written

$$\frac{1}{4} \ln \frac{(1+i+p)(1+i-p)}{(1-i-p)(1-i+p)} = \frac{Di + \mu H}{kT}, \quad (13)$$

$$\frac{1}{4} \ln \frac{(1+i+p)(1-i+p)}{(1-i-p)(1+i-p)} = -\frac{Dp}{kT} \quad (14)$$

and the expression for the internal energy becomes

$$u = -\frac{1}{2}D(i^2 - p^2). \quad (15)$$

For ferromagnetic substances $D > 0$, and the solution of the above equations is $p = 0$, and i satisfies Eq. (1). For antiferromagnetic substances $D < 0$, and in the absence of a magnetic field the solution of (13) and (14) is

$$i = 0, \quad (16)$$

$$p = \tanh(-T_c p/T).$$

$$K_0 = \frac{N\mu^2/k}{T/(1-p^2) - T_c}. \quad (17)$$

The specific heat has an anomaly for $T = -T_c$ identical with that of a ferromagnetic at the Curie temperature, and the susceptibility has the form shown in Fig. 1. No material exhibiting such properties is known.

Néel⁸ has pointed out that manganese probably is an antiferromagnetic substance in the above sense, as it has an anomaly in the specific heat near 350°C. Its magnetic susceptibility, however, is constant below the critical temperature and falls off slightly above it. Our considerations were based on the assumption that the elementary magnetic moments were parallel or antiparallel to the applied field. Néel⁹ shows that if this assumption is dropped, it seems

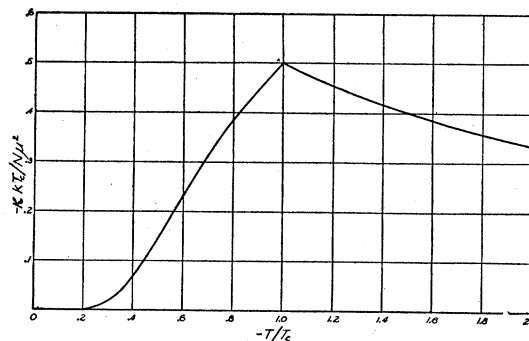


FIG. 1. Susceptibility of an antiferromagnetic substance as a function of temperature.

quite reasonable to expect susceptibilities for $T=0$ of the same order of magnitude as for $T=T_c$, because of the rotation of individual magnetic moments.

Hulthen¹⁰ has also calculated the susceptibility of antiferromagnetic materials at low temperatures, using a method due to Heller and Kramers.¹¹ He finds that in small fields the magnetic moments tend to set themselves at right angles to the applied field and antiparallel to their nearest neighbors. At low temperatures the susceptibility has the form $A - BT^2$. In actual materials the behavior will be complicated by crystalline fields tending to orient magnetic moments with reference to the crystallographic axes. If anomalies of the type shown in Fig. 1 do actually occur, they will be superimposed on other effects due to causes which have not been considered in this article.

The results obtainable for alloys⁶ are very complicated, and we shall attempt here only to indicate the general outlines of a theory. If it is assumed that we may neglect the interactions of all but nearest neighbors, it is at once apparent that the ordering tendency of different types of atoms in an alloy will play an important part in determining magnetic properties. Furthermore, the internal fields responsible for ferromagnetism will influence the degree of order at any particular temperature, and these effects may be large, as the critical temperatures for ferromagnetism are of the same order of magni-

¹⁰ L. Hulthen, Proc. Roy. Acad. Amsterdam **39**, 190 (1936).

¹¹ G. Heller and H. A. Kramers, Proc. Roy. Acad. Amsterdam **37**, 378 (1934).

⁸ L. Néel, Comptes rendus **203**, 304 (1936).

⁹ L. Néel, Ann. de physique **17**, 63 (1932).

tude as the critical temperatures for the order-disorder transitions. One ought really to build up a theory on the assumption that atoms of two kinds, A and B , each having a magnetic moment μ_A or μ_B , can interact in several ways, and that the total energy of any configuration of the alloy is the sum of the energies of pairs of nearest neighbors. This would give different values to parallel and antiparallel pairs of types $A-A$, $A-B$, and $B-B$. One ought then to calculate the equilibrium degree of order and magnetization for every temperature. The equations defining such equilibrium may be readily set up in a nice symmetrical form, but their solution is so laborious that we shall simply treat the order parameter and the concentration as independent variables, and omit the question of determining the conditions that homogeneous phases of given composition and order may exist.¹²

¹² The formulation of this problem may be undertaken quite generally as follows: Suppose we have an arbitrary number of kinds of atoms, arranged on the lattice points of a crystal. Among the various kinds of atoms we may distinguish between atoms of the same chemical species, but in different states. Our calculations are based on the assumptions that the energy of interaction of any two atoms is independent of the arrangement of the remaining atoms of the lattice. With this assumption interactions over arbitrarily large distances may be included. To do this, break up the lattice into a set of interpenetrating sublattices such that the nearest neighbors on each sublattice are a distance apart greater than some arbitrarily chosen distance, R_0 , which we define as the range of the atomic interactions. The atoms of any one sublattice may then be considered to have no interaction with each other. Consider now any two sublattices in their mutually correct positions. It will always be possible to break up the original lattice into a sufficient number of sublattices such that each atom of one of any pair of sublattices j and k has a certain number of neighbors on the other sublattice a distance $R_{jk} < R_0$ away, and that in this pair of sublattices there are no other neighbors at distances less than R_0 . If n_j represents the total number of lattice points on the j th sublattice, and n_{jA} the number of these lattice points occupied by atoms of type A , we may define any configuration of the lattice in terms of the concentration variables $x_{jA} = n_{jA}/n_j$. The entropy may be written as a sum of terms of the form $-x_{jA} \ln x_{jA}$. Numerical factors will appear in some of these terms if the number of atomic sites is not the same for all the sublattices. The energy may be expressed as a sum of terms of the form $\epsilon_{jkAB} \nu_{jkAB}$ where the first factor represents the energy of interaction of two atoms A and B a distance R_{jk} apart, and the second factor represents the number of such pairs on the j and k sublattices in any particular configuration. If, as above, we replace the energy distribution by its mean value, we must calculate the mean values of the quantities ν_{jkAB} . These can readily be calculated by the following device. Let ν_{jk} be the total number of pairs of nearest neighbors on sublattices j and k . Let $\delta_{ij}^{(\alpha)}$ be a number equal to unity if the i th lattice point on the j th sublattice in some particular configuration

For simplicity we shall again consider a body-centered cubic lattice which may be broken up into two sublattices having the property that any atom of one interacts only with atoms on the other, if we consider nearest neighbor interaction only. If N_{A1+} are the number of atoms of type A on sublattice one whose magnetic moments point to the right, and other similar symbols are used for the number of atoms of other types we have

$$\begin{aligned} N_{A1+} + N_{A1-} &= N_{A1}, \\ N_{A1} + N_{B1} &= N_1, \\ N_{A1} + N_{A2} &= N_A \end{aligned}$$

and similarly for atoms of type B and sublattice two. The concentration of atoms of types A and B on one sublattice is defined by

$$\begin{aligned} y_1 &= (N_{A1} - N_{B1})/N_1, \\ N_{A1}/N_1 &= \frac{1}{2}(1 + y_1); \quad N_{B1}/N_1 = \frac{1}{2}(1 - y_1). \end{aligned}$$

The total mean concentration is

$$y = (N_A - N_B)/N = \frac{1}{2}(y_1 + y_2)$$

and the long range order is defined by

$$S = \frac{1}{2}(y_1 - y_2).$$

The relative intensity of magnetization is defined by

$$i_{A1} = (N_{A1+} - N_{A1-})/N_{A1}$$

with similar variables for both types of atoms on either lattice. If we assume that the internal field acting on any one atom is made up of two parts, one due to the atoms of the same type, and one due to atoms of the opposite type, and that either of these fields is proportional to the

designated by (α) is an atom of type A , otherwise $\delta = 0$. Similarly let $\gamma_{ij}^{(\alpha)}$ be unity if the site is occupied by an atom of type B , otherwise $\gamma = 0$.

$$\nu_{jkAB}^{(\alpha)} = \sum_{ii^*} (\delta_{ij}^{(\alpha)} \gamma_{ik}^{(\alpha)} + \gamma_{ij}^{(\alpha)} \delta_{ik}^{(\alpha)}),$$

$$\langle \nu_{jkAB} \rangle_{Av} = \frac{\sum_{(\alpha)} \nu_{jkAB}^{(\alpha)}}{\frac{n_j!}{n_{jA}! n_{jB}!} \cdots \frac{n_k!}{n_{kA}! n_{kB}!} \cdots}$$

\sum_{ii^*} means sum over all pairs of nearest neighbors, and $\sum_{(\alpha)}$ means sum over all configurations of the system. Substituting the first expression in the second, and summing first over (α) keeping i and l fixed, one finds that

$$\langle \nu_{jkAB} \rangle_{Av} = \nu_{jk} (x_{jA} x_{kB} + x_{jB} x_{kA}).$$

These expressions define the system thermodynamically. In many cases the number of independent variables can be reduced by arguments concerning the symmetry of the equations defining equilibrium.

concentration of the type of atom in question and to its intensity of magnetization, then the equations of state can be written directly in the following form

$$\begin{aligned} i_{A1} &= \tanh \frac{Di_{A2}(1+y_2) + Gi_{B2}(1-y_2) + \mu_A H}{kT}, \\ i_{B1} &= \tanh \frac{Gi_{A2}(1+y_2) + Fi_{B2}(1-y_2) + \mu_B H}{kT}, \\ i_{A2} &= \tanh \frac{Di_{A1}(1+y_1) + Gi_{B1}(1-y_1) + \mu_A H}{kT}, \\ i_{B2} &= \tanh \frac{Gi_{A1}(1+y_1) + Fi_{B1}(1-y_1) + \mu_B H}{kT}. \end{aligned} \quad (17A)$$

D , F , and G are constants. D and F determine the behavior of pure A and pure B , respectively. μ_A and μ_B are the dipole moments of an atom of A or B , and G determines the interactions of dipoles of A and B with each other. Even with all the above simplifications these equations are quite formidable, and we shall discuss only a few special cases.

It is well known that ferromagnetic metals do not in general have an absolute saturation corresponding to one magnetic moment per atom, but that only some fraction of the atoms contribute to the ferromagnetism. A way of introducing such a feature into the above theory is to let A represent those atoms having a magnetic moment, and to let B represent atoms with no moment. The equations then reduce to

$$\begin{aligned} i_{A1} &= \tanh \frac{Di_{A2}(1+y_2) + \mu_A H}{kT}, \\ i_{A2} &= \tanh \frac{Di_{A1}(1+y_1) + \mu_A H}{kT}. \end{aligned} \quad (18)$$

The solutions of these equations are determined to a large extent by assumptions which we must make concerning the arrangement of the nonmagnetic atoms in the lattice. If they are arranged at random, we may put $y_1 = y_2 = y$. Since the substance is ferromagnetic $D > 0$, and hence, $i_{A1} = i_{A2}$. The equations reduce to the form of Eq. (1), and the nonmagnetic atoms have no influence on the properties of the system.

If, on the other hand, the nonmagnetic atoms tend to arrange themselves in an orderly fashion, then $y_1 \neq y_2$, and the equation of state is modified. If we measure the mean concentration of nonmagnetic atoms by the parameter $y = \frac{1}{2}(y_1 + y_2)$, and the long range order by $s = \frac{1}{2}(y_1 - y_2)$, the Curie temperature can be written in the form

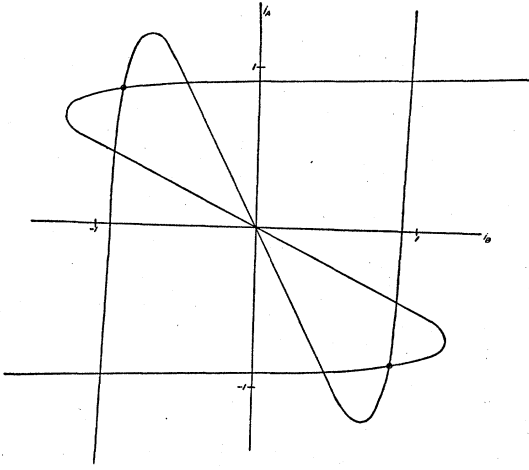
$$T_c = (D/k)[(1+y)^2 - s^2]^{\frac{1}{2}}.$$

It can be shown that $0 \leq s^2 \leq (1-|y|)^2$; that for $0 \geq y \geq -1$, or for concentrations involving fewer magnetic atoms A than nonmagnetic atoms B , the metal may become paramagnetic simply because the magnetic atoms may be completely surrounded by nonmagnetic atoms; and that for $0 \leq y \leq 1$ there is a real Curie temperature which rises as the degree of order diminishes. Under these circumstances, one should expect additional anomalies in the specific heat due to the changes of order.

The topics discussed so far have had to do with the possibilities of long range order in the electronic states of similar atoms in a pure metal, and the results obtained do not seem to indicate that such a behavior actually exists except possibly in Mn. In discussing alloys, we shall therefore concern ourselves with ferromagnetic metals, as in this case the antiparallel moments will be arranged at random, and we shall discuss metals with one magnetic moment per atom only, so as to avoid assumptions as to how nonmagnetic atoms are arranged in the lattice.

If the pure metals A and B used for the alloy described in Eq. (17A) are ferromagnetic, then D and F must be positive. To illustrate the effect of order-disorder on the magnetic properties, we shall consider the case of an alloy having A and B in equal proportions, but in one case fully disordered $y_1 = y_2 = y$, $s = 0$; and again fully ordered $y_1 = -y_2 = 1$, $y = 0$, $s = 1$. For the disordered case it can be shown that the two sublattices are identical, $i_{A1} = i_{A2}$, $i_{B1} = i_{B2}$, and the equations reduce to

$$\begin{aligned} i_A &= \tanh \frac{Di_A + Gi_B + \mu_A H}{kT}, \\ i_B &= \tanh \frac{Gi_A + Fi_B + \mu_B H}{kT}. \end{aligned} \quad (19)$$

FIG. 2. Plot of Eqs. (21) as functions of i_A and i_B .

For the completely ordered case, on the other hand $i_{A2}=i_{B1}=0$ because there are no atoms of B on lattice 1 or atoms of A on lattice 2, and the equations reduce to

$$\begin{aligned} i_A &= \tanh \frac{2Gi_B + \mu_A H}{kT}, \\ i_B &= \tanh \frac{2Gi_A + \mu_B H}{kT}. \end{aligned} \quad (20)$$

If, for instance, $D=F=0$ but $G>0$, it is easily seen that the Curie temperature is G/k for the disordered alloys, but $2G/k$ for the ordered alloy. The main point which it is desired to emphasize is that equations of this sort can give radical changes of properties with heat treatment and can make understandable, in principle at least, the appearance of ferromagnetism in alloys of nonmagnetic elements.¹³ Whether a more detailed comparison with the behavior of actual systems is possible remains to be seen.

In order to demonstrate somewhat more fully the predictions of Eqs. (17A) we shall discuss them for the case of an alloy of two ferromagnetic elements in any proportions in which the atoms are arranged at random. In this case the two sublattices are identical, and we may put $y_1=y_2=y$, and $i_{A1}=i_{A2}$, $i_{B1}=i_{B2}$, and the equa-

tions become

$$\begin{aligned} i_A &= \tanh \frac{Di_A(1+y) + Gi_B(1-y) + \mu_A H}{kT}, \\ i_B &= \tanh \frac{Gi_A(1+y) + Fi_B(1-y) + \mu_B H}{kT}. \end{aligned} \quad (21)$$

These equations may be plotted as functions of i_A and i_B as in Fig. 2. They have the form of an S , and may have as many as nine solutions. The solutions for the largest absolute values of i_A and i_B have the lowest free energy, and are, therefore, the most stable. For this solution i_A and i_B will have the same sign if $G>0$, or opposite signs if $G<0$. If there are nine solutions, then, in addition to the two mentioned, there will be two solutions corresponding to subsidiary minima of the free energy at the points indicated by circles in the figure. None of the other solutions correspond to minima of the free energy, and are, therefore, not stable solutions. For high temperatures the curves cross only at the origin, if there is no applied magnetic field. The condition for the appearance of spontaneous magnetization is that the slope of the two curves at the origin shall be equal. This may occur for two temperatures, but the higher one of the two is, of course, the Curie point. The subsidiary minima of the free energy appear at temperatures below the lower of the above-mentioned temperatures. The Curie temperature is given by¹⁴

$$\begin{aligned} T_c &= (1/2k)[D(1+y) + F(1-y) \\ &+ \{[D(1+y) - F(1-y)]^2 + 4G^2(1-y^2)\}^{1/2}]. \end{aligned} \quad (22)$$

If G is small, the behavior of the alloy will be almost that of two coexisting pure ferromagnetic metals; the Curie point of each will be proportional to its concentration in the alloy. At the Curie point one of these will become ferromagnetic. As the temperature is lowered the magnetization of this component will increase until at some point the second component becomes magnetized. The magnetization of this component will be parallel or antiparallel to that of the first depending on whether G is greater than or less than zero, and the mag-

¹³ Experimental work in this connection is summarized by F. C. Nix and W. Shockley, *Rev. Mod. Phys.* **10**, 59 (1938).

¹⁴ Expressions similar to (22) and (23) were first obtained by L. Néel, reference 6.

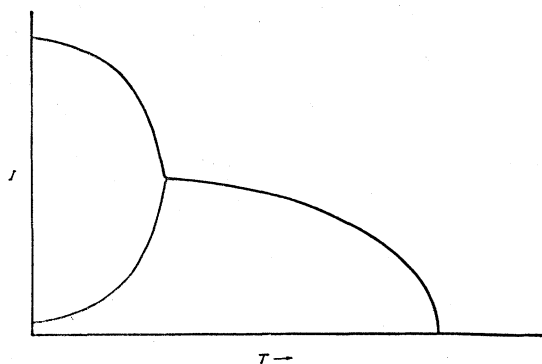


FIG. 3. Intensity of magnetization of an alloy.

netization of the alloy will either increase or decrease with the temperature, as shown in Fig. 3. In the latter case the magnetization can be shifted from the lower to the upper of the two curves in Fig. 3 by the application of a sufficiently strong magnetic field. Hysteresis effects are to be expected in the neighborhood of this field strength because of the presence of two minima in the free energy of almost equal depth. This behavior is similar to that found in the so-called "wasp waisted" hysteresis loops of certain iron-nickel-cobalt alloys.¹⁵ Further experiments on the less complex alloys of this type over wide ranges of field and temperature are greatly to be desired.

¹⁵ Such loops are briefly described by T. D. Yensen in F. Bitter, *Introduction to Ferromagnetism* (McGraw-Hill, 1937).

For other values of G one may expect a behavior of the spontaneous magnetization ranging from that shown in Fig. 3 to that of a pure substance. If $G^2 = DF$, the Curie temperature is a linear function of the concentration, and if in addition $D = F$ all alloys behave like either pure substance.

The anomalies in the spontaneous magnetization will, of course, be reflected in the behavior of the specific heats. Also the initial susceptibility above the Curie point will no longer be given by the simple formula, Eq. (9) with $i=0$, but by the expression

$$K_0 = \frac{N\mu^2 T + (1/2k)(2G - D - F)(1 - y^2)}{k(T - T_1)(T - T_2)}, \quad (23)$$

T_1 being the Curie temperature as defined in Eq. (22), and T_2 a lower temperature defined by this same expression with a negative sign in front of the square root. It is assumed that $\mu_A = \mu_B = \mu$.

The behavior of an alloy in the neighborhood of its Curie point is not completely determined by Eqs. (17A). For a range of temperatures near the critical temperature the alloy may break up into a paramagnetic and a ferromagnetic phase having different compositions. This behavior is influenced by interaction energies which do not appear in the magnetic equation of state, and will, therefore, not be discussed further at this point.