

Application of the Bethe-Weiss Method to Ferrimagnetism

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The Bethe-Weiss theory of ferromagnetism is extended and applied to systems containing two nonequivalent sets of sites, designated by A and B , for the magnetic atoms. Each B atom has n_a nearest A neighbors and each A atom has n_b nearest B neighbors. In the theoretical development, the following restrictions are imposed: the spin per atom is $\frac{1}{2}$ and only nearest neighbor $A-B$ interactions are considered ($\alpha=\beta=0$, in Néel's notation). The $A-B$ interaction J may be either positive or negative, however, so that the sublattice magnetizations below the Curie temperature may be either parallel or antiparallel, respectively. Expressions are derived for the Curie temperature and for the susceptibility above the Curie temperature. If the two sublattices are made equivalent, our results for positive J reduce to Weiss' equations for the ferromagnetic case and our results for negative J reduce to Li's equations for the antiferromagnetic case.

A table of values of the ratio $kT_c/|J|$ as computed by the Néel, Ising-Bethe, and Bethe-Weiss theories is given for various values of n_a and n_b . For a given magnitude of J , the Bethe-Weiss Curie temperature for negative J is always greater than that for positive J . An empirical formula which approximates the Bethe-Weiss criterion for the existence of a ferrimagnetic transition is $n_a n_b > 5(n_a + n_b)/2$.

The Néel and Bethe-Weiss susceptibilities are calculated and compared for a ferrimagnet with $n_a=4$, $n_b=8$. The two general expressions for the susceptibility are found to agree quantitatively at extremely high temperatures. It is shown that for a ferrimagnet with $J<0$ the sublattice magnetizations in an external field become antiparallel not at the Curie temperature but considerably above.

I. INTRODUCTION

CRYSTALS that become spontaneously magnetized at low temperatures are usually divided into three classes: ferromagnetic, antiferromagnetic, and ferrimagnetic. At present, there are no universally accepted criteria for defining these three classes; however, one basis for classification is the division of the lattice of magnetic atoms into interpenetrating sublattices suggested by the chemical and crystallographic properties of the material. The principal points to be noted about this division are whether the sublattices are equivalent or nonequivalent, and whether the spontaneous magnetizations of individual sublattices are parallel or antiparallel to each other. In Table I, these ideas are illustrated for a system containing two sublattices.

In this paper, we shall discuss some of the magnetic properties of materials containing two nonequivalent sublattices. It turns out to be natural and convenient to carry out the calculations for parallel and antiparallel magnetizations simultaneously. In order to avoid an awkward terminology, we shall refer to systems with two nonequivalent sublattices as ferrimagnetic, regardless of the relative orientations of the sublattice magnetizations. Thus we are using the term ferrimagnetic in a sense which is more inclusive than the usual one.

The principal theoretical treatment of ferrimagnetism is Néel's molecular field theory.¹ In his 1948 paper, Néel deduced the various kinds of spontaneous magnetization-temperature curves that might occur and showed that the reciprocal susceptibility-temperature curve above the Curie temperature should have a hyperbolic form. He also pointed out that the ferrite compounds, which had been developed as commercial

magnetic materials by Snoek² and his co-workers at Eindhoven, were ferrimagnetic. The great amount of research devoted to ferrimagnetism since that time has been in part due to the intrinsic properties of such materials and in part to the commercial importance of the ferrites. In general, the Néel theory has been strikingly successful in predicting the qualitative features of the magnetic properties of the ferrites, especially considering the simplicity of the theory and the detailed nature of its predictions.

It seems likely that future improvements in the theory of ferrimagnetism will come from replacing the molecular field theory by more exact methods, rather than from refining Néel's model. Kaplan³ and Vonsovski and Seidov⁴ have used the spin-wave theory to treat the low temperature properties of ferrimagnets. We propose to discuss their high-temperature properties, particularly the location of the Curie temperature and the susceptibility above the Curie temperature. The method used is a generalization of the Weiss theory of ferromagnetism,⁵ which is in turn an extension of Bethe's

TABLE I. System with two sublattices.

	Sublattices equivalent	Sublattices nonequivalent
Sublattice magnetizations parallel	Ferro	Ferro? Ferri?
Sublattice magnetizations antiparallel	Antiferro	Ferri

² J. L. Snoek, *New Developments in Ferromagnetic Materials* (Elsevier Publishing Company, Inc., New York, 1947).

³ H. Kaplan, *Phys. Rev.* **86**, 121 (1952).

⁴ S. V. Vonsovski and Iu. M. Seidov, *Izvest. Akad. Nauk S.S.S.R. Ser. Fiz.* **3**, 319 (1954).

⁵ P. R. Weiss, *Phys. Rev.* **74**, 1493 (1948).

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¹ L. Néel, *Ann. phys.* **3**, 137 (1948).

method of solving the problem of ordering in alloys.⁶ Li⁷ has previously applied the Weiss method to antiferromagnetism. Since the two kinds of ferrimagnetism reduce to ferro- and antiferromagnetism when the sublattices become equivalent, a useful check on our results is that they should reduce to the Weiss-Li results when the sublattices become equivalent.

In Part II of this paper, Weiss' theory and its results are reviewed; Part III shows how the theory can be generalized to systems containing nonequivalent sublattices. Appendix A gives, for comparison, some analogous formulas and results obtained by applying the Bethe method to the Ising model of a ferrimagnet. In Parts IV and V, the generalized Weiss theory is used to calculate Curie temperatures and susceptibilities of specific ferrimagnetic systems. The results are compared with the Néel theory predictions for the same system.

II. WEISS THEORY

In this section we briefly review the Weiss theory⁵ and some of its principal results. The notation and development have both been slightly changed, but we believe that the changes simplify the discussion of problems involving two or more sublattices.

In the Weiss theory, attention is focused on a particular cluster of atoms in the crystal. This cluster consists of a central atom (whose choice is arbitrary) and its shell of n nearest neighbors. The Hamiltonian for the cluster is assumed to have the form

$$\mathcal{H} = -2JS_0 \cdot S_1 - g\beta S_{0z}H_0 - g\beta S_{1z}H_1. \quad (1)$$

Here J is the exchange interaction, S_0 and S_1 are the spin operators for the central atom and the combined first shell, respectively. H_0 is the external applied field; H_1 is an effective field which acts on the shell atoms and includes the effect of the interaction with atoms outside the cluster as well as the external field. Both H_0 and H_1 are taken to be in the z -direction. We have assumed that there are no interactions within the first shell.

The eigenvalues of \mathcal{H} depend on m , the magnetic quantum number of the cluster; S_1 , the total spin of the first shell; and S , the total spin of the cluster. We shall consider only cases where the spin per atom is $\frac{1}{2}$; thus S , for given S_1 , has only two possible values, $S_1 \pm \frac{1}{2}$. In the following discussion, it will be convenient to designate these two values by the symbols \pm . The eigenvalues of \mathcal{H} are then

$$W(\pm, S_1, m) = \frac{1}{2}J[1 - 2mh_1 \mp [(2S_1 + 1)^2 - 4m(h_1 - h_0) + (h_1 - h_0)^2]^{\frac{1}{2}}], \quad (2)$$

where $h_{0,1} = g\beta H_{0,1}/J$. The occurrence of the square root makes numerical calculations of the partition function and thermodynamic functions very tedious. Consequently, Weiss expresses the eigenvalues by a series ex-

pansion in terms of $h = h_1 - h_0$. The use of this expansion means that the theory is valid only in regions where $h \ll 1$, i.e., at the Curie temperature and higher temperatures. We have

$$W(\pm, S_1, m) = J \left[\epsilon_{\pm} - mh_0 + \sum_{i=1}^{\infty} w_i(\pm, S_1, m) h^i \right], \quad (3)$$

with $\epsilon_+ = -S_1$, $\epsilon_- = S_1 + 1$. The first four $w_i(\pm, S_1, m)$ are:

$$w_1 = -m(1 \pm mR^{-1}), \quad (4a)$$

$$w_2 = \mp (1/4R)(1 - 4m^2R^{-2}), \quad (4b)$$

$$w_3 = \mp (m/2R^3)(1 - 4m^2R^{-2}), \quad (4c)$$

$$w_4 = \pm (1/16R^5)(1 - 24m^2R^{-2} + 80m^4R^{-4}), \quad (4d)$$

with $R = 2S_1 + 1$.

The notation for the succeeding sections can be much simplified if we define an operator \mathcal{S}_n by

$$\mathcal{S}_n f(\pm, S_1, m, j) = \sum_{S_1=0}^{n/2} \omega(n, S_1) \sum_{\pm} e^{-j\epsilon_{\pm}} \sum_{m=-(S_1 \pm \frac{1}{2})}^{S_1 \pm \frac{1}{2}} f(\pm, m, S_1, j), \quad (5)$$

where $j = J/kT$ and

$$\omega(n, S_1) = \frac{n!}{(\frac{1}{2}n + S_1)! (\frac{1}{2}n - S_1)!} \frac{n!}{(\frac{1}{2}n + S_1 + 1)! (\frac{1}{2}n - S_1 - 1)!}, \quad S_1 < \frac{1}{2}n \quad (6)$$

$$\omega(n, \frac{1}{2}n) = 1.$$

Then the partition function $P(j, h_0, h)$ may be written

$$P^{(n)}(j, h_0, h) = \mathcal{S}_n \exp \left[j \left(mh_0 - \sum_{i=1}^{\infty} w_i(\pm, S_1, m) h^i \right) \right]. \quad (7)$$

Since we are considering only the case where $|h_{0,1}| \ll 1$, we may expand the exponential and keep only the first few terms. Thus

$$P^{(n)}(j, h_0, h) = \mathcal{S}_n \sum_{k+l} p_{kl}(m, w_i, j) h_0^k h^l, \quad (8a)$$

where the summation is taken over all pairs (k, l) consistent with $k, l = 0, 1, 2, \dots$ and $k+l = 0, 2, 4, \dots$. Terms which contain odd powers of m can be omitted since they vanish in the summation over m . We give below the functions p_{kl} which are needed to compute the Curie temperature, the susceptibility, and the specific heat discontinuity at the Curie temperature.

$$p_{00} = 1, \quad (9a)$$

$$p_{20} = \frac{1}{2}mj^2, \quad (9b)$$

$$p_{11} = -mw_1j^2, \quad (9c)$$

⁶ H. A. Bethe, Proc. Roy. Soc. (London) A150, 552 (1935).

⁷ Y.-Y. Li, Phys. Rev. 84, 721 (1951).

$$p_{02} = -w_2 j + \frac{1}{2} w_1^2 j^2, \quad (9d)$$

$$p_{13} = -m w_3 j^2 + m w_1 w_2 j^3 - \frac{1}{6} m w_1^3 j^4, \quad (9e)$$

$$p_{04} = -w_4 j + (w_1 w_3 + \frac{1}{2} w_2^2) j^2 - \frac{1}{2} w_1^2 w_2 j^3 + w_1^4 j^4 / 24. \quad (9f)$$

Finally, we let

$$\mathcal{S}_n p_{ki}(m, w_i, j) = P_{ki}^{(n)}(j), \quad (10)$$

so that

$$P^{(n)}(j, h_0, h) = \sum_{k+l} P_{ki}^{(n)}(j) h_0^k h^l. \quad (8b)$$

Some formulas useful in calculations involving the $P_{ki}^{(n)}(j)$ are given in Appendix B.

We are now ready to discuss the thermodynamic properties of the material. The average magnetic moments per atom for the central site and for a shell site are given by

$$\bar{m}_0 = (g\beta/j) \frac{\partial \ln P}{\partial h_0}; \quad \bar{m}_1 = (g\beta/nj) \frac{\partial \ln P}{\partial h_1}. \quad (11a, b)$$

(In the future, the superscript (n) will be omitted except when it is necessary to distinguish two functions.) Combining Eqs. (8) to (11) and keeping only terms of first order in the fields, we find

$$\bar{m}_0 = g\beta(jP_{00})^{-1} [(P_{11} - 2P_{02})h + (2P_{20} - P_{11})h_0], \quad (12a)$$

$$\bar{m}_1 = g\beta(njP_{00})^{-1} [2P_{02}h + P_{11}h_0]. \quad (12b)$$

Since the central atom and any one of the shell atoms are equivalent, we must have

$$\bar{m}_0 = \bar{m}_1, \quad (13)$$

or

$$[n(P_{11} - 2P_{02}) - 2P_{02}]h = [n(P_{11} - 2P_{20}) + P_{11}]h_0. \quad (14)$$

This consistency condition also determines the internal field h by giving a relation between h , h_0 , and j .

A principal point of interest is whether or not there is a Curie temperature, i.e., a temperature below which $h \neq 0$ when $h_0 = 0$. By setting $h_0 = 0$ in (14) we see that there is a solution $h = 0$ for all temperatures but that h need not vanish if

$$n(P_{11} - 2P_{02}) = 2P_{02}. \quad (15)$$

This condition determines the Curie temperature, if any.

The susceptibility above the Curie temperature may also be obtained by considering only terms linear in h_0 and h if we are not interested in saturation effects. Perhaps the simplest expression for χ is

$$J\chi = Ng\beta\bar{m}_1/h_0 = Ng^2\beta^2(njP_{00})^{-1}(P_{11} + 2P_{02}h/h_0), \quad (16)$$

where N is the number of atoms per unit volume. The ratio h/h_0 is found from Eq. (14).

The energy is given by

$$\frac{E}{J} = -\frac{N}{2} \frac{\partial \ln P}{\partial j} = \frac{N}{2P} \sum_{(k+l)} P_{ki}^{(n)}(j), \quad (17)$$

where the factor $\frac{1}{2}$ corrects for counting interactions twice. Here $P_{ki}^{(n)}(j)$ is defined by

$$P_{ki}^{(n)}(j) = \mathcal{S}_n [\partial p_{ki} / \partial j - \epsilon_{\pm} p_{ki}]. \quad (18)$$

III. APPLICATION TO FERRIMAGNETISM

We now wish to extend the methods described in the previous section to systems containing two nonequivalent sublattices of magnetic atoms. For simplicity, we consider the special case where all the magnetic atoms are identical (with spin $\frac{1}{2}$) but where there are two kinds of crystallographic sites on which the atoms are located. Let the kinds of sites be designated by A and B and let a unit volume of material contain λN A sites and μN B sites (where $\lambda + \mu = 1$). For such a system we must consider two types of clusters. One type consists of a central A atom and its shell of n_b B neighbors; the other type consists of a central B atom and its shell of n_a A neighbors. (Note that $\lambda n_b = \mu n_a$ so that λ and μ are determined when n_a and n_b are given.)

In Néel's treatment of ferrimagnetism, he introduces three phenomenological interactions, J_{ab} , J_{aa} , and J_{bb} . In order to avoid complicating our problem with interactions within the shells, we shall restrict ourselves to the case where $J_{aa} = J_{bb} = 0$ ($\alpha = \beta = 0$, in Néel's notation). This restriction does not eliminate any basic ferrimagnetic properties of the model as long as $\lambda \neq \mu$, and it greatly simplifies the calculations involved. The eigenvalues for the two types of clusters are then given by (2) with $J_{ab} = J$ and with h_1 replaced by h_1^b and h_1^a , respectively. Also, there will be two summation operators \mathcal{S}_b and \mathcal{S}_a and two partition functions $P^b(j, h_0, h_b)$ and $P^a(j, h_0, h_a)$. In each case the superscripts and subscripts a and b refer to the kinds of sites in the shell.

The average magnetic moments for central and shell atoms in A and B sites are given by

$$\bar{m}_0^b = (g\beta/j) \frac{\partial \ln P^b}{\partial h_0}, \quad (19a)$$

$$\bar{m}_1^b = (g\beta/n_b j) \frac{\partial \ln P^b}{\partial h_1^b}. \quad (19b)$$

$$\bar{m}_0^a = (g\beta/j) \frac{\partial \ln P^a}{\partial h_0}, \quad (19c)$$

$$\bar{m}_1^a = (g\beta/n_a j) \frac{\partial \ln P^a}{\partial h_1^a}. \quad (19d)$$

There are two consistency conditions corresponding to (13), i.e., the average magnetic moments of all A atoms must be the same and the average magnetic moments of all B atoms must be the same.

$$\bar{m}_0^b = \bar{m}_1^a, \quad (20a)$$

$$\bar{m}_0^a = \bar{m}_1^b. \quad (20b)$$

If only first powers in the h 's are retained, the conditions are

$$-2P_{00}^b P_{02}^a h_a + n_a P_{00}^a (P_{11}^b - 2P_{02}^b) h_b = [n_a P_{00}^a (P_{11}^b - 2P_{02}^b) + P_{00}^b P_{11}^a] h_0, \quad (21a)$$

$$n_b P_{00}^b (P_{11}^a - 2P_{02}^a) h_a - 2P_{00}^a P_{02}^b h_b = [n_b P_{00}^b (P_{11}^a - 2P_{02}^a) + P_{00}^a P_{11}^b] h_0. \quad (21b)$$

The Curie temperature is determined by the condition that the determinant of the coefficients of h_a and h_b in (21) must vanish.

$$n_a n_b (P_{11}^a - 2P_{02}^a) (P_{11}^b - 2P_{02}^b) = 4P_{02}^a P_{02}^b. \quad (22)$$

In general, numerical methods must be used to find the values of j which satisfy (22). The results of actual calculations indicate that solutions will normally occur in pairs. The members of a given pair have opposite signs but approximately the same magnitudes. (If more than one pair of solutions occur for a particular equation the pair of lowest magnitude should be chosen, in order to avoid the anti-Curie points mentioned by Anderson.⁸) By resubstituting in (21) we find that h_a and h_b have the same sign when the solution j_c is positive (i.e., $J > 0$) and opposite signs when j_c is negative. These results, of course, merely confirm our intuitive ideas that the spontaneous magnetizations of the sublattices should be parallel or antiparallel according to whether J is positive or negative. The result that the Curie temperatures for parallel and antiparallel orientation are not exactly equal is characteristic of the Bethe-Weiss method.

If the sublattices are equivalent ($n_a = n_b$), the condition for the Curie temperature reduces to

$$n(P_{11} - 2P_{02}) = \pm 2P_{02}. \quad (23)$$

It can be readily shown that the plus and minus signs give Weiss' condition for the ferromagnetic Curie temperature and Li's condition for the antiferromagnetic Curie temperature, respectively.

The susceptibility above the Curie temperature is given by a formula analogous to (16).

$$(J\chi/kC) = 4j^{-1} (n_a + n_b)^{-1} \{ (P_{00}^a)^{-1} [P_{11}^a + 2P_{02}^a h_a/h_0] + (P_{00}^b)^{-1} [P_{11}^b + 2P_{02}^b h_b/h_0] \}. \quad (24)$$

Here C is the Curie constant, $Ng^2\beta^2/4k$. The ratios h_a/h_0 and h_b/h_0 are obtained by solving Eqs. (21).

In the same way, the energy is given by a straightforward generalization of (17). The formula is not given explicitly since no use is made of it in this paper. We note that the energy and susceptibility formulas are valid for both positive and negative j , and that they reduce to the corresponding Weiss-Li relations if the sublattices are equivalent.

IV. CURIE TEMPERATURES

The first questions to be resolved in studying a particular system are whether or not a transition occurs,

⁸ P. W. Anderson, Phys. Rev. 80, 922 (1950).

and, if so, where the Curie temperature is located. As might be expected, the Néel, Ising-Bethe, and Bethe-Weiss methods give different criteria for the occurrence of a ferrimagnetic transition. For the Néel theory, the formal condition is simply $n_a n_b > 0$, and for the Ising-Bethe theory, it is $n_a n_b > n_a + n_b$ (see Appendix A). Because of the algebraic complexity of Eq. (22), we have not been able to derive any comparable simple condition for the Bethe-Weiss method. However, numerical calculations have been carried out for various values of n_a and n_b ; the results can be seen in Table II. An empirical relationship which approximates the Bethe-Weiss criterion for a transition is $n_a n_b > (5/2)(n_a + n_b)$.

The numbers in Table II give the ratio $kT_c/|J|$ as determined by the three methods. The two principal features of the table are that the ratio diminishes as we go from the molecular field theory to the more exact theories and that the Bethe-Weiss Curie temperature for negative J is slightly greater than that for positive J . These results are in agreement with and extend Li's comparison of the ferromagnetic and antiferromagnetic cases.⁷

It should be kept in mind that the results obtained here are valid only when there are no interactions within the first shell. Thus, as an example, the figures quoted

TABLE II. Values of $kT_c/|J|$ for ferrimagnets. The four entries in each position represent, respectively, the values obtained by the Néel method, the Ising-Bethe method, the Bethe-Weiss method with $J < 0$, and the Bethe-Weiss method with $J > 0$. $S_0 = \frac{1}{2}$. No first shell interactions.

$n_a \backslash n_b$	2	4	6	8	10	12
2	1.00 ... ^a	1.41 0.76	1.73 0.96	2.00 1.26	2.23 1.44	2.45 1.61
4		2.00 1.44	2.45 1.90	2.83 2.25 1.65 1.59	3.16 2.56 2.08 1.91	3.47 2.84 2.39 2.19
6			3.00 2.46 2.00 1.85	3.47 2.92 2.56 2.34	3.87 3.33 2.99 2.75	4.25 ^b 3.68 3.36 3.10
8				4.00 3.48 3.18 2.90	4.47 3.95 3.66 3.39	4.90 4.37 4.12 3.81
10					5.00 4.48 4.24 3.94	5.48 4.95 4.72 4.41
12						6.00 5.48 5.26 4.95

^a Dashes mean no transition occurs.

^b Results were obtained graphically, and values of $kT_c/|J| > 4$ may be in error as much as 1%.

for $n_a=n_b=12$ do not properly apply to the face-centered cubic lattice. Actually many, and perhaps most, of the pairs (n_a, n_b) for which Curie temperatures are given in Fig. 2 cannot be associated with any real crystals. These extra values are given merely as an aid in seeing how the Curie temperature depends on n_a and n_b .

V. SUSCEPTIBILITY ABOVE THE CURIE TEMPERATURE

The Néel expression for the susceptibility is, in our notation,

$$\frac{J\chi}{kC} = j \frac{1+n_a n_b (n_a+n_b)^{-1j}}{1-\frac{1}{4}n_a n_b j^2}, \quad (25)$$

while the Bethe-Weiss expression was given in Eq. (24). Of the two formulas, the Bethe-Weiss result is presumably more nearly correct. However, since both theories are expected to become more reliable with increasing temperature, it is of interest to compare Eq. (25) with a high-temperature approximation of Eq. (24). If the Bethe-Weiss expression is expanded about the point $j=0$ with the aid of Appendix B and only the

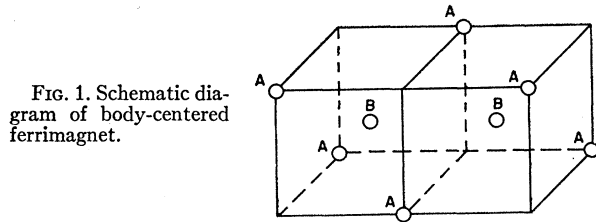


FIG. 1. Schematic diagram of body-centered ferrimagnet.

lowest terms are kept, the exact Néel formula is obtained. Thus, at very high temperatures, the two theories are in quantitative, as well as qualitative, agreement.

For lower temperatures, it is not easy to make an analytical comparison of the two formulas, so we shall instead show their results for a specific system. In looking for a suitable system, the ferrites naturally come to mind first. However, the numerical computations, which are lengthy in any case, are especially tedious for the spinel structure because of the relatively large number of nearest neighbors ($n_a=6, n_b=12$). Consequently, we have preferred to discuss a simpler structure which is based on the body-centered cubic lattice. We begin with a body-centered cubic lattice, divide it into the usual two sublattices, and then remove half the atoms on one sublattice as shown in Fig. 1. This structure, which will be called a "body-centered ferrimagnet," is characterized by $n_a=4, n_b=8$. There are no actual materials known in which the lattice of magnetic atoms has such an arrangement. However, the properties of the body-centered ferrimagnet are still of interest since it should exhibit all of the distinguishing characteristics of ferrimagnetism and

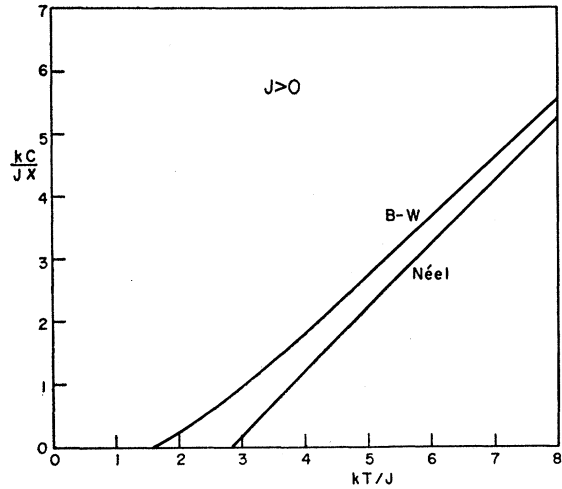


FIG. 2. Reduced reciprocal susceptibility vs reduced temperature for the body-centered ferrimagnet. $J > 0$. The Néel curve is actually a section of a hyperbola, (25), although the curvature is too small to show on this scale.

since we can use it for a quantitative comparison of the Néel and Bethe-Weiss predictions.

Figures 2 and 3 show the reduced reciprocal susceptibility for the body-centered ferrimagnet for positive and negative J . The curves marked Néel and B-W are calculated from Eqs. (25) and (24), respectively. The approach of the two curves at high temperatures can be clearly seen. On the other hand, there is still a difference of several percent in magnitude at a temperature of $T=4T_c$.

In the temperature region where many of the experimental measurements of susceptibility are made, i.e., at two or three times the Curie temperature, the slopes of the B-W and Néel curves differ appreciably. Now the Néel theory predicts that at high temperatures the slope of the $1/\chi-T$ curve should be $1/C$; many of the

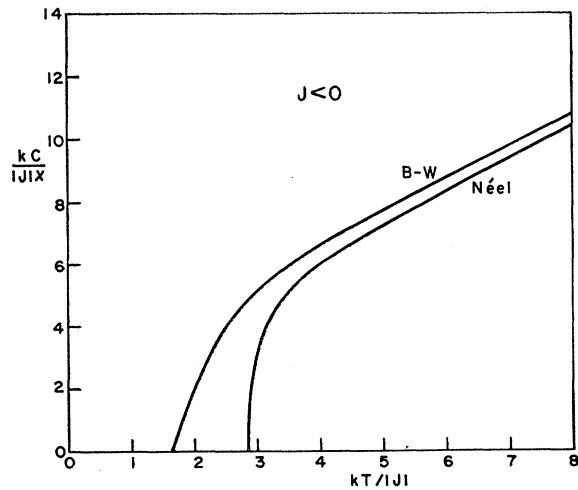


FIG. 3. Reduced reciprocal susceptibility vs reduced temperature for the body-centered ferrimagnet. $J < 0$.

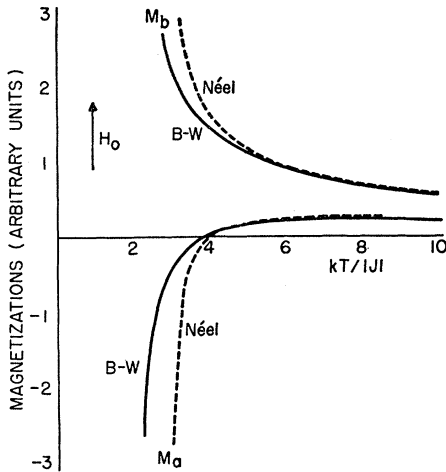


FIG. 4. Sublattice magnetizations for the body-centered ferrimagnet in an external magnetic field ($J < 0$). Although the magnetizations are given in arbitrary units, their relative magnitudes are significant.

experimental results on ferrimagnetic materials show considerable deviation from this prediction. Our comparison of the Néel and B-W theories suggests that the $1/C$ value for the slope should not be expected until temperatures very high compared to T_c are attained and that most experimental measurements reported have been made at much lower temperatures. Moreover, values of C determined from the slopes at lower temperatures will be too high. It should be pointed out, however, that other factors may also contribute to the discrepancy between the measured and theoretical values of C . One is lack of knowledge of the actual value C because of uncertainties about the orbital contributions to the magnetic moment. Another possibility is that J may vary with temperature.⁹

Figure 4 shows how the individual sublattice magnetizations of the body-centered ferrimagnet with $J < 0$ vary with temperature when an external field is applied. (They are, of course, zero for $T > T_c$ when $H_0 = 0$.) Though this behavior has a very simple interpretation, it has apparently not been previously noted or explained. According to the Néel model, the explanation is as follows. At very high temperatures, both M_a and M_b are parallel to H_0 . However, the molecular field acting on each sublattice tends to turn it antiparallel to H_0 . As the temperature is decreased the molecular field acting on the A sublattice becomes larger in magnitude than H_0 . Then M_a reverses direction and remains antiparallel to H_0 and M_b to and through the Curie temperature. The Bethe-Weiss explanation gives essentially the same physical picture but with emphasis on the short-range order. The change in sign of M_a apparently occurs near the knee of the $1/\chi$ - T curve.

This result was obtained for a specific ferrimagnetic system. However, one can show by Néel theory calcula-

tions that it is quite general and that such an effect should occur in any ferrimagnetic system with $J < 0$. There seems to be no reason to believe that calculations based on the Bethe-Weiss theory, although tedious, would not show the same thing. Thus, in a ferrimagnet with negative A - B interactions, the sublattice magnetizations in the presence of an external field become antiparallel not at the Curie temperature but considerably above.¹⁰ This behavior is to be contrasted with that of an antiferromagnet where the change from parallel to antiparallel orientation occurs at the Curie temperature.

ACKNOWLEDGMENTS

I am indebted to Mr. Benjamin Muckenhoupt for the derivation of Eqs. (B8) and (B9).

APPENDIX A. ISING-BETHE METHOD

For convenience we refer to the method described herein as the Ising-Bethe Method, because it utilizes the Ising Hamiltonian and the Bethe method of solution.¹¹ However, the principal contributions to the magnetic problem were made by Peierls,¹² Firkau,¹³ Weiss,⁵ and Ziman.¹⁴

The Hamiltonian for a cluster is assumed to be

$$3\mathcal{C}' = -2JS_{0z}S_{1z} - g\beta S_{0z}H_0 - g\beta S_{1z}H_0. \quad (A1)$$

If we set

$$x_0 = \exp(-\frac{1}{2}jh_0); \quad x_1 = \exp(-\frac{1}{2}jh_1); \quad y = \exp(\frac{1}{2}j). \quad (A2)$$

the partition function can be shown to be⁵

$$P(x_0, x_1, y) = \frac{1}{x_0} \left[\frac{x_1^2 + y^2}{x_1 y} \right]^n + x_0 \left[\frac{x_1^2 y^2 + 1}{x_1 y} \right]^n. \quad (A3)$$

In the application to ferrimagnetism, we proceed as in the Bethe-Weiss method by considering both types of clusters, defining two partition functions, and computing the average magnetic moments of center and shell atoms. The consistency conditions analogous to Eqs. (21) are

$$\begin{aligned} [n_a y^4 - 2(n_a - 2)y^2 + n_a]h_a + n_b(1 - y^4)h_b &= 2(1 + y^2)h_0, \\ n_a(1 - y^4)h_a + [n_b y^4 - 2(n_b - 2)y^2 + n_b]h_b &= 2(1 + y^2)h_0. \end{aligned} \quad (A4)$$

The Curie temperature is defined by

$$j_c = \ln\{1 + 2[1 + (1 + z)^{\frac{1}{2}}]z^{-1}\}, \quad (A5)$$

where

$$z = n_a n_b - n_a - n_b. \quad (A6)$$

¹⁰ In the Néel theory, the ratio of the "reversal" temperature to the Curie temperature is $(n_b/n_a)^{\frac{1}{2}}$.

¹¹ I. Syozi and H. Nakano, Progr. Theoret. Phys. (Japan) **13**, 69 (1955), have given exact solutions for some two-dimensional Ising ferrimagnets.

¹² R. Peierls, Proc. Cambridge Phil. Soc. **32**, 477 (1936).

¹³ U. Firkau, Ann. Physik **40**, 295 (1941).

¹⁴ J. M. Ziman, Proc. Phys. Soc. (London) **64**, 1108 (1951).

⁹ L. Néel, J. phys. radium **12**, 238 (1951).

The Curie temperatures for parallel and antiparallel orientation are the same.

The susceptibility above the Curie temperature is given by

$$J\chi/kc = j(n_a + n_b)^{-1} \{ n_a(1 - (1 + y^2)^{-2}(n_a - (n_a - 2)y^2 + n_a y^4)h_a/h_0) + n_b(1 - (1 + y^2)^{-2}(n_b - (n_b - 2)y^2 + n_b y^4)h_b/h_0) \}. \quad (A7)$$

APPENDIX B. SUMMATION FORMULAS

Let

$$S' f(m) = \sum_{\pm} e^{-i\epsilon_{\pm}} \sum_{m=(S_1 \pm \frac{1}{2})}^{S_1 \pm \frac{1}{2}} f(m). \quad (B1)$$

Then

$$S'(1) = 2e^{-i/2} [\sinh x + R \cosh x], \quad (B2)$$

$$S'(\pm 1) = 2e^{-i/2} [R \sinh x + \cosh x], \quad (B3)$$

$$S'(m^2) = \frac{1}{6} R e^{-i/2} [3R \sinh x + (R^2 + 2) \cosh x], \quad (B4)$$

$$S'(\pm m^2) = \frac{1}{6} R e^{-i/2} [(R^2 + 2) \sinh x + 3R \cosh x], \quad (B5)$$

$$S'(m^4) = R e^{-i/2} [15R^3 \sinh x + (3R^4 + 20R^2 - 8) \cosh x] / 120, \quad (B6)$$

$$S'(\pm m^4) = R e^{-i/2} [(3R^4 + 20R^2 - 8) \sinh x + 15R^3 \cosh x] / 120, \quad (B7)$$

where $x = Rj/2$. These formulae are especially useful in computing numerical values of $P_{kl}^{(n)}(j)$ for both positive and negative values of j .

To obtain approximate expressions for the $P_{kl}^{(n)}(j)$ which are valid in the region $|j| \ll 1$, we need

$$\sum_{S_1=0}^{n/2} \omega(n, S_1) R = 2^n, \quad (B8)$$

$$\sum_{S_1=0}^{n/2} \omega(n, S_1) R^3 = (3n + 1) 2^n. \quad (B9)$$

L X-Ray Energies of Np, Pu, and Am

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Five Np, eight Pu, and five Am *L* x-ray transitions have been observed in conventional x-ray fluorescence from 200-mg amounts of Np²³⁷, Pu²³⁹, and Am²⁴¹ using a Cauchois type curved crystal transmission spectrometer. The energies of these transitions have been determined, with reference to *Kα*₁ lines of the elements from ³⁷Rb through ⁴⁷Ag, to an accuracy of 3 to 8 ev. Disagreement with previous measurements by Barton, Robinson, and Perlman; Jaffe, Passell, Browne, and Perlman; and Day has been found while excellent agreement with the Pu measurements of Cauchois, Manescu, and Le Berquier was obtained.

I. INTRODUCTION

THE electromagnetic spectra (gamma rays and x-rays) of transuranium nuclides have been previously investigated using bent crystal spectrometers of moderate resolution. In these studies, the x-rays resulted from either internal conversion of gamma rays which accompanied alpha decay or by fluorescence from the gamma rays. Barton, Robinson, and Perlman,¹ in this manner, first observed Np and Pu *L* x-rays. The *L* x-rays of Np resulted from the radioactive decay of Am²⁴¹ and those of Pu from the decay of Cm²⁴². Jaffe, Passell, Browne, and Perlman² and Day³ recently re-

investigated the electromagnetic spectrum of Am²⁴¹ and recorded many *L* lines of Np and Am. In another study, Cauchois, Manescu, and Le Berquier,⁴ using conventional x-ray fluorescence, have examined the radiation from 10 mg of Pu with a curved crystal spectrometer of high resolution and have observed four Pu *L* lines.

We have recorded five Np *L* x-ray lines, eight Pu *L* lines, and five Am *L* lines, all observed in conventional x-ray fluorescence from approximately 200 mg of each element. The energies of these transuranium x-rays have been precisely determined and our results disagree with those of Barton *et al.*, Jaffe *et al.*, and Day. However, our Pu results are in excellent agreement with those of Cauchois *et al.* We also find that the extrapolated values of Hill, Church, and Mihelich⁵ are in better agreement with our measurements than the previous determinations.

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¹ Barton, Robinson, and Perlman, *Phys. Rev.* **81**, 208 (1951).

² Jaffe, Passell, Browne, and Perlman, *Phys. Rev.* **97**, 142 (1955).

³ Paul P. Day, *Phys. Rev.* **97**, 689 (1955).

⁴ Cauchois, Manescu, and Le Berquier, *Compt. rend.* **25**, 1782 (1954).

⁵ Hill, Church, and Mihelich, *Rev. Sci. Instr.* **23**, 523 (1952).