

# Ferro- and Antiferromagnetism in a Simple Cubic Lattice

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(Received April 3, 1962)

The properties of the ferro- and antiferromagnetic state in a simple cubic lattice are calculated using a model based on the exact solution to a cluster of eight spins. The model which is considered is that of a simple cubic lattice with spin  $1/2$  at each lattice site, the spins being coupled via the Heisenberg exchange Hamiltonian. First-, second-, and third-neighbor interactions are included. The free energy is calculated by means of a perturbation expansion. For the ferromagnetic state, this calculation gives the Curie temperature  $T_C$ , saturation magnetization, paramagnetic susceptibility, spin correlation functions, and heat capacity. For the antiferromagnetic state, no long-range order is obtained. The paramagnetic susceptibility, spin correlation functions, and heat capacity are calculated. For the low-temperature region, qualitative statements are made about the effect of second- and third-neighbor interactions on the antiferromagnetic state.

## I. INTRODUCTION

IT is known both experimentally and theoretically that the magnetic properties of an infinite ferromagnetic or antiferromagnetic lattice depend strongly on the range of the Heisenberg exchange interaction. The theoretical approach to the quantum mechanical problem which is based on the solution to a small cluster (the Bethe-Peierls-Weiss or BPW method) is not easy to extend to the case of distant-neighbor interactions, because the basic cluster which has been used contains only nearest-neighbor interactions. This paper is an extension of the BPW method in that the cluster itself contains first-, second-, and third-neighbor interactions, and hence is more convenient for calculation of the effect of more distant interactions on the magnetic properties.

A previous publication<sup>1</sup> has given the general solution to the cubic array of eight spins, each with spin  $1/2$ , interacting by means of the Heisenberg exchange Hamiltonian. This paper considers the infinite simple cubic (sc) lattice as a collection of eight-spin cubes with interactions between cubes treated as a perturbation. First-, second-, and third-neighbor interactions are considered between spins. Crystalline anisotropy effects are not included.<sup>1a</sup>

Thermodynamic perturbation theory is used to calculate the free energy to first order. The approach taken here is to treat to first order a Hamiltonian which includes second- and third-neighbor interactions, rather than a simpler Hamiltonian to higher order in perturbation theory.

In the case of ferromagnetism, a molecular field is introduced in order to obtain convergence of the perturbation expansion, i.e., long-range order is introduced by means of a local field. For the calculation of

the antiferromagnetic state, no such molecular field is used, and only short-range order is obtained. The customary method for introducing long-range order into the antiferromagnetic problem is to consider the lattice as a superposition of a number of sublattices each with ferromagnetic interactions within the sublattice and antiferromagnetic interactions between the sublattices. This has not been done here for several reasons. Firstly, it seemed desirable to treat both ferro- and antiferromagnetism on the same footing using the same expression for the free energy with the only difference being the sign of the exchange integral. Secondly, one of the goals for this calculation was to allow for the inclusion of second- and third-neighbor exchange interactions. It is known from the classical calculation that for some values of the interactions spiral configurations occur. A sublattice model does not allow for this possibility.

The free energy is used to obtain the magnetization, magnetic susceptibility, spin correlation function (i.e., the thermal average of the scalar product between two spins), and the heat capacity. The existence of a spontaneous magnetization in zero external field below a certain temperature is used to define a ferromagnetic Curie temperature  $T_C$ . The antiferromagnetic transition temperature  $T_N$  is not given unambiguously by this calculation.

This calculation yields short-range order in the paramagnetic state. The susceptibility in this region is given approximately by the Curie-Weiss law. The dependence of the Curie-Weiss law parameters on the strength of the first- and second-neighbor interaction is indicated.

The body-centered cubic and face-centered cubic lattice though not considered here could be approximated using the results of reference 1 and the method due to Smart<sup>2</sup> and Oguchi,<sup>3</sup> the bcc being two interpenetrating sc and the fcc four interpenetrating sc lattices.

\* Operated with support from the U. S. Army, Navy, and Air Force.

<sup>1</sup> G. Dresselhaus, Phys. Rev. **126**, 1664 (1962); the wave functions are contained in G. Dresselhaus, Lincoln Laboratory Technical Report 254 (unpublished).

<sup>1a</sup> Note added in proof. Dr. S. Katsura has kindly informed the author that the solution to the eight-spin eigenvalue problem was given previously by R. Serber [J. Chem. Phys. **2**, 697 (1934)].

<sup>2</sup> J. S. Smart, J. Phys. Chem. Solids **20**, 41 (1961).

<sup>3</sup> T. Oguchi, Progr. Theoret. Phys. (Kyoto) **13**, 148 (1955).

## II. CALCULATION

The Heisenberg Hamiltonian for an infinite array of cubes is

$$\mathcal{H} = - \sum (\alpha, \beta, p, q) J(\alpha p, \beta q) \mathbf{S}(\alpha p) \cdot \mathbf{S}(\beta q) + g\mu_B H_0 \sum S^z(\alpha p), \quad (1)$$

in which the indices  $\alpha, \beta$  label the cubes and  $p, q$  label the sites within the cube,  $H_0$  is the external magnetic field directed along the  $z$  direction,  $g$  is the spectroscopic splitting factor,  $\mu_B$  is the Bohr magneton,  $\mathbf{S}(\alpha p)$  is spin operator for the electron at site  $\alpha p$ , and  $J(\alpha p, \beta q)$  is the exchange constant between sites  $\alpha p$  and  $\beta q$ . The summation in Eq. (1) is unrestricted, so that each term occurs twice. The cluster Hamiltonian for a single cube which was solved in reference 1 is

$$\mathcal{H}_{cl}^{(\alpha)} = - \sum_{p, q} J(\alpha p, \alpha q) \mathbf{S}(\alpha p) \cdot \mathbf{S}(\alpha q) + g\mu_B (H_0 + H_W) \sum_p S^z(\alpha p). \quad (2)$$

The effect on a particular cube of the neighboring cubes is treated by introducing a Weiss molecular field  $H_W$  which remains to be determined. The perturbation Hamiltonian is defined as

$$\mathcal{H}' = \mathcal{H} - \sum_{\alpha} \mathcal{H}_{cl}^{(\alpha)} = \mathcal{H} - \mathcal{H}_0 \quad (3)$$

or

$$\mathcal{H}' = - \sum' (\alpha, \beta, p, q) J(\alpha p, \beta q) \mathbf{S}(\alpha p) \cdot \mathbf{S}(\beta q) - g\mu_B H_W \sum S^z(\alpha p), \quad (4)$$

in which the prime on the first summation indicates that  $\alpha \neq \beta$ . The free energy is calculated using thermodynamic perturbation theory and is given by<sup>4</sup>

$$F = F_0 + F_1 + F_2 + \dots \quad (5)$$

in which

$$F_0 = -\beta^{-1} \text{tr} \exp(-\beta \mathcal{H}_0) = -\beta^{-1} \sum \exp(-\beta E_n^{(0)}), \quad (6)$$

$$F_1 = \sum w_n(\mathbf{n}) |\mathcal{H}'| \mathbf{n} \rangle \langle \mathcal{H}'| \mathbf{n} \rangle = \langle \mathcal{H}'_{nn} \rangle, \quad (7)$$

$$F_2 = -\frac{1}{2} \sum'_{n, m} | \langle \mathbf{n} | \mathcal{H}' | \mathbf{m} \rangle |^2 \times [(w_m - w_n) / (E_n^{(0)} - E_m^{(0)})] - \frac{1}{2} \beta \langle (\mathcal{H}'_{nn} - \langle \mathcal{H}'_{nn} \rangle)^2 \rangle, \quad (8)$$

$\beta = 1/kT$ ,  $E_n^{(0)}$  is the energy eigenvalue of  $\mathcal{H}_0$  for the state  $\mathbf{n}$ , and  $w_n = \exp[\beta(F_0 - E_n^{(0)})]$ .

The magnetization  $\mathcal{M}$ , paramagnetic susceptibility  $\chi$ , heat capacity  $C_V$ , and spin correlation functions  $\tau(lmn)$  are found from the free energy and are given by

$$\mathcal{M} = -\partial F / \partial H_0, \quad (9)$$

$$\chi = \partial \mathcal{M} / \partial H_0 = -(\partial^2 F / \partial H_0^2)_{H_0=0}, \quad (10)$$

$$C_V = -T(\partial^2 F / \partial T^2)_V, \quad (11)$$

and

$$\tau(lmn) = \langle \mathbf{S}(\alpha p) \cdot \mathbf{S}(\beta q) \rangle = -\partial F / \partial J(\alpha p, \beta q), \quad (12)$$

in which  $(l, m, n)a = \alpha p - \beta q$ ,  $a$  being the lattice constant.

<sup>4</sup> L. D. Landau and E. Lifshitz, *Statistical Physics* (Pergamon Press, New York, 1958), p. 93.

Consider now an sc lattice consisting of  $N$  spins ( $N/8$  cubes). The exchange constants are taken as  $J$  for nearest neighbors,  $xJ$  for second neighbors,  $yJ$  for third neighbors, and all others are assumed to be zero. The calculation which corresponds to considering non-interacting cubes involves no molecular field, so that  $\mathcal{H}' = 0$ . This case is treated in reference 1. The evaluation of Eq. (6) for interacting cubes yields

$$F_0 = \frac{1}{8} N f_0, \quad (13)$$

in which the free energy for a cluster is given by

$$f_0 = - \frac{1}{\beta} \sum_i \omega_i e^{-U \lambda_i} \frac{\sinh[\frac{1}{2} \beta g \mu_B (2S_i + 1)(H_0 + H_W)]}{\sinh[\frac{1}{2} \beta g \mu_B (H_0 + H_W)]}. \quad (14)$$

The temperature-dependent parameter which expresses the coupling strength is  $U = 2J/kT$ , and the properly normalized eigenvalues  $\lambda_i$  are listed in Table I of reference 1. The degeneracy of a state in the cluster is denoted by  $\omega_i$ , and  $S_i$  represents the spin of cluster eigenfunction  $i$ .

It is convenient to express the molecular field in terms of an effective spin  $S_0$  which obeys the relation

$$-g\mu_B H_W = J(3 + 9x + 7y)S_0. \quad (15)$$

Then Eq. (7) assumes the form

$$F_1 = (N/8)J(3 + 9x + 7y)[\langle M_S \rangle_{cl} S_0 - \frac{1}{8} \langle M_S \rangle_{cl}^2], \quad (16)$$

in which the thermal average of the magnetic quantum number for a cluster  $M_S$  is

$$\langle M_S \rangle_{cl} = \text{tr} M_S \exp[-\beta(\mathcal{H}_{cl}^{(\alpha)} - f_0)]. \quad (17)$$

The condition which is used to determine the Weiss field or the effective spin  $S_0$  is that the mean spin is the

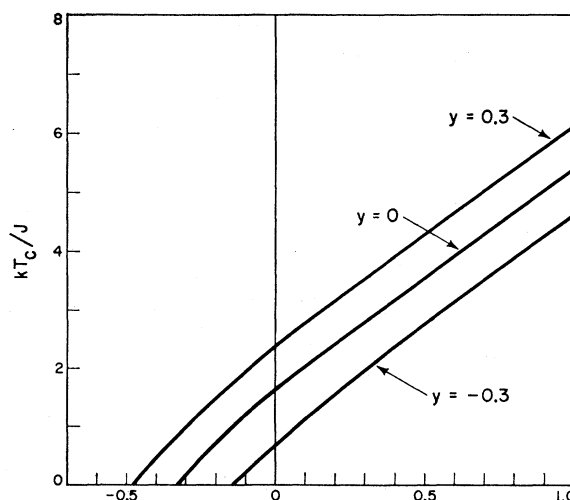


FIG. 1. The Curie temperature as a function of second-nearest-neighbor exchange interaction  $xJ$  with the third-neighbor interaction  $yJ$  as a parameter. Nearest-neighbor interactions correspond to  $x = y = 0.0$ .

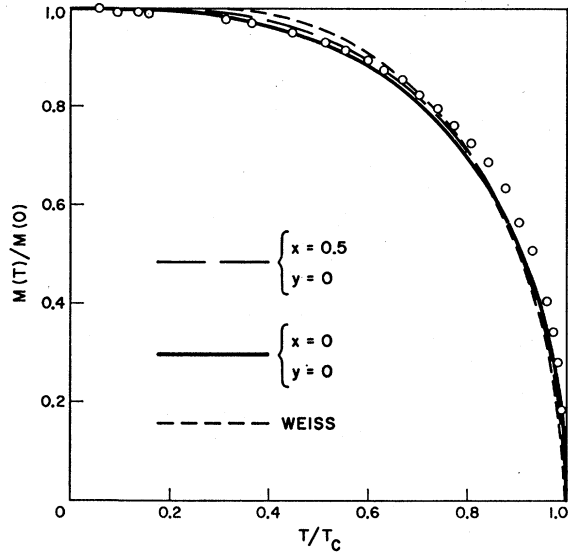


FIG. 2. The temperature dependence of the saturation magnetization. The open circles represent experimental results for nickel. The theoretical curves are as indicated.

same whether inside or outside of a cluster, namely

$$S_0 = \frac{1}{8} \langle M_S \rangle_{cl}. \quad (18)$$

The trivial solution  $S_0 = 0$  always holds for Eq. (18).

For some ranges of  $T$  and  $J$ , a nontrivial solution also obtains indicating the existence of ferromagnetism for  $T \leq T_c$ . In the ferromagnetic state, Eq. (16) reduces to  $F_1 = 0$  and the use of the Weiss field is equivalent to an exact summing of certain terms in the perturbation expansion Eq. (5). The paramagnetic and antiferromagnetic regions for which  $S_0 = 0$  have  $F_1 \propto \langle M_S \rangle_{cl}^2$ . The evaluation of the thermodynamic quantities using Eqs. (14), (16), and (18) is given in the next section.

### III. DISCUSSION

The ferromagnetic state ( $U > 0$ ) is considered first. The dependence of the Curie temperature on the strength of interaction of second and third neighbors is shown in Fig. 1 as a plot of  $kT_c/J$  vs  $x$  with  $y$  as a parameter. The Curie temperature denotes that temperature below which a nontrivial solution exists for Eq. (18). The Curie temperature for only nearest-neighbor interactions ( $x = y = 0$ ) is given by  $T_c = 1.60J/k$ . This value is to be compared with the BPW result<sup>1</sup> of  $1.85 J/k$ , the Kramers-Opechowski result<sup>1</sup> of  $1.9 J/k$ , the Oguchi result<sup>3</sup> of  $2.85 J/k$ , and the molecular field result<sup>6</sup> of  $3.0 J/k$ . For large and negative values of  $x$ , only the trivial solution  $S_0 = 0$  obtains and the system is antiferromagnetic as was pointed out in reference 1. A ferromagnetic third-neighbor interaction which is

30% of the strength of the nearest-neighbor interaction increases the Curie temperature by about  $0.8 J/k$  and an antiferromagnetic third-neighbor interaction has a similar decrease. The Curie temperature is approximately proportional to the strength of second-neighbor interactions.

The spontaneous magnetization is shown in Fig. 2 for two different sets of values of the exchange interactions. The magnetization curve is relatively insensitive to the values of the exchange interaction between second and third neighbors. For comparison, the Weiss theory magnetization curve<sup>6</sup> is included. Experimental points for nickel are also given, although the crystal structure is face-centered cubic. This calculation differs from the Weiss theory both at low and high temperatures.

The temperature dependence of the paramagnetic susceptibility is shown in Fig. 3 for two different values of the exchange constants. For convenience, the dimensionless susceptibility  $\alpha\chi$  is plotted in Fig. 3, in which  $\alpha = 16J/Ng^2\mu_B^2$ . Each of the susceptibility curves is fitted

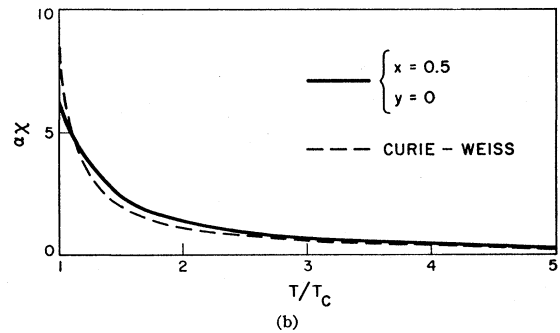
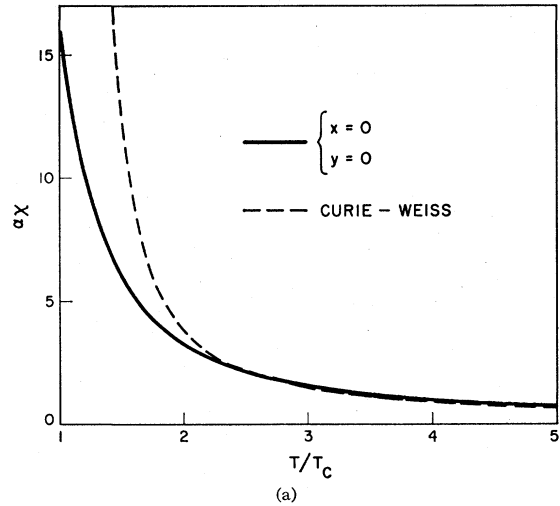


FIG. 3. The temperature dependence of the dimensionless paramagnetic susceptibility above the Curie temperature  $T_c$ . The constant  $\alpha$  is defined in the text. Curve (a) is for nearest-neighbor interactions only and curve (b) is for a ratio of second- to first-neighbor interaction of 0.5. The Curie-Weiss curves have been plotted using the parameters listed in Table I.

<sup>5</sup> H. A. Brown and J. M. Luttinger, Phys. Rev. **100**, 685 (1955).

<sup>6</sup> C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956), 2nd ed.; J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932), p. 334.

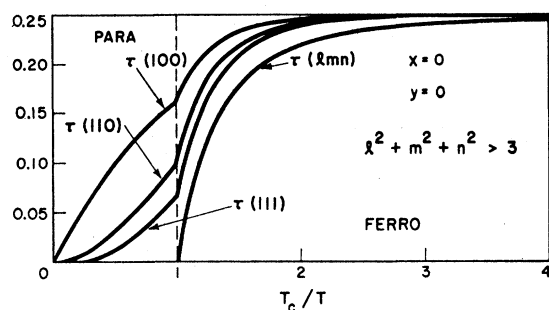


FIG. 4. Spin correlation functions vs  $T_c/T$ .  $\tau(100)$  corresponds to the thermal average of the scalar product between nearest-neighbor spins. The para- and ferromagnetic regions are separated by a dashed vertical line at  $T/T_c=1$ .

to the Curie-Weiss law of the form

$$\alpha\chi = C/(T+\theta) \quad (19)$$

at values of the temperature  $T=4J/k$  and  $20J/k$ . The values of the constants  $C$  and  $\theta$  which are obtained are shown in Table I and the resulting Curie-Weiss plots are included in Fig. 3. The simple Weiss theory<sup>6</sup> corresponds to  $kC/J=4.0$  and  $\theta=-T_c$ . The arbitrary choice of the temperatures at which to make the two curves coincide is not appropriate for all regions of  $x$  and  $y$ ; this accounts for the limited number of entries in Table I. Experimentally, it is found that as the temperature approaches  $T_c$  the paramagnetic susceptibility becomes infinite, a feature which is not contained in this calculation. It is seen that for  $T \gtrsim T_c$ , the expansion for the free energy is only converging slowly.

The temperature dependence of the spin correlation function is shown in Fig. 4. The curves show short-range order for  $T > T_c$  and long-range order for  $T < T_c$ . The spin correlation function  $\tau(lmn)$  for  $l^2+m^2+n^2 > 3$  is proportional to the square of the magnetization. Increasing the range of the exchange interaction, i.e., by increasing  $x$  and  $y$ , results in a state with less short-range order at the Curie temperature.

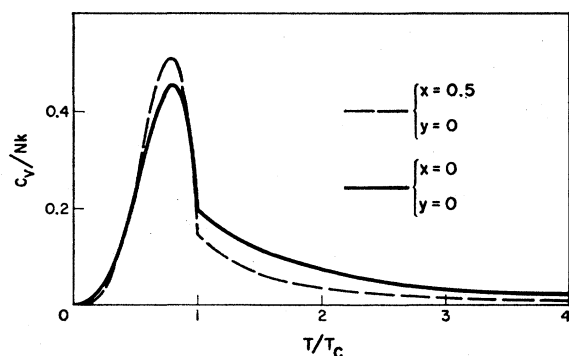


FIG. 5. The temperature dependence of the magnetic heat capacity for two different values of the exchange constants. ( $x=y=0.0$  corresponds to nearest-neighbor interaction.)

In Fig. 5, the temperature dependence of the magnetic heat capacity at constant volume is shown for two values of the parameters  $x$  and  $y$ . Increasing the Curie temperature by the addition of a second-neighbor ferromagnetic exchange decreases the value of  $C_V$  above  $T_c$  and increases  $C_V$  below  $T_c$ . This effect is related to the decrease in the short-range order discussed with reference to the spin correlation function. A discontinuity in the slope of the heat capacity is found at  $T_c$ .

The antiferromagnetic state ( $U < 0$ ) allows only the trivial solution ( $S_0=0$ ) to Eq. (18), so that no simple criterion is available for defining a transition temperature. The transition temperature to the antiferromagnetic state  $T_N$  has been related by various workers<sup>7</sup> to characteristic features of the temperature dependence of the susceptibility and related thermodynamic quantities.

The temperature dependence of the susceptibility is shown in Fig. 6 for two different values of the exchange constants. In the paramagnetic region, the curves have been fitted to the Curie-Weiss form of Eq. (19) using

TABLE I. Parameters of the ferromagnetic Curie-Weiss law Eq. (19) obtained by fitting the calculated results to the Curie-Weiss form at  $kT/2J=2$  and 10. In this table third-neighbor interactions are neglected, i.e.,  $y=0$ .

$x$	$k\theta/J$	$kC/J$	$\theta/T_c$
0.0	-2.1	4.2	-1.3
0.1	-2.3	4.2	-1.2
0.2	-2.6	4.3	-1.1
0.3	-2.7	4.4	-1.0
0.4	-2.9	4.5	-0.9
0.5	-3.0	4.6	-0.8
0.6	-3.1	4.7	-0.8

Table II which was obtained by the procedure described previously. The simple Weiss theory<sup>6</sup> gives  $kC/J=4.0$  and  $\theta=T_N$ . If a ferromagnetic next-nearest-neighbor interaction is added to an antiferromagnetic nearest-neighbor interaction, the maxima in the susceptibility curves become larger and more sharply peaked and occur at larger  $kT/J$ . If both first- and second-neighbor interactions are antiferromagnetic and of comparable magnitude, two peaks in the susceptibility become apparent. The position of these maxima  $kT_M/J$  is plotted as a function of second-neighbor interactions in Fig. 7. A qualitative discussion of the nature of the antiferromagnetic state is given after the results on the spin correlation functions are presented.

The temperature dependence of the spin correlation function is shown in Fig. 8 for two values of the parameters  $x$  and  $y$ . At high temperatures short-range order is found. As the temperature decreases, the amount of short-range order increases, but no long-range order is exhibited by this calculation to terms in  $F_1$  in the free

<sup>7</sup> See, for example, A. Danielian and K. W. H. Stevens [Proc. Phys. Soc. (London) **77**, 116 (1961)] have argued that  $T_N$  corresponds to the point of inflection of the  $\chi$  vs  $T$  curve.

energy. There are at least two possible reasons for finding no long-range order in this calculation of the antiferromagnetic state. Either higher order terms in the expansion of the free energy may be required, or the model represented by Eq. (1) may not show long-range order even if solved exactly. There is evidence from the exact solution to the one-dimensional problem<sup>8</sup> that the existence of long-range order depends upon the

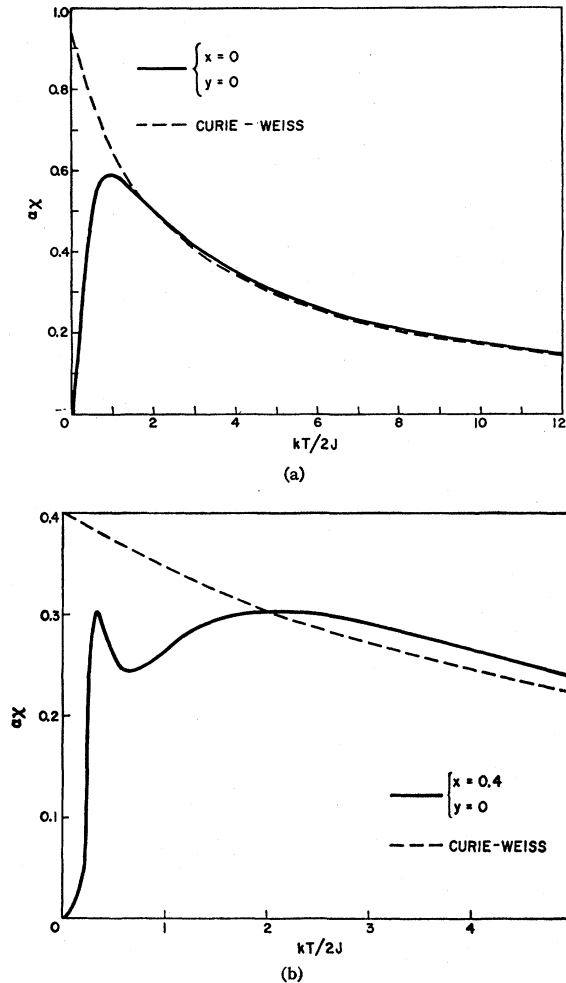


FIG. 6. The temperature dependence of the dimensionless susceptibility in the "antiferromagnetic" state. Curve (a) is for nearest-neighbor interactions. Curve (b) is for a value of the parameters in which two maxima occur in the susceptibility. The Curie-Weiss curves have been plotted using the parameters listed in Table II.

inclusion of crystalline anisotropy in the formulation of the problem. If anisotropy is also necessary for long-range order in the three-dimensional case, then the model which is treated here is perhaps converging to the correct mathematical result even though not all

<sup>8</sup> E. Lieb, T. Shultz, and D. Mattis, Ann. Phys. (New York) 16, 407 (1961); W. Marshall, Proc. Roy. Soc. (London) A232, 48 (1955).

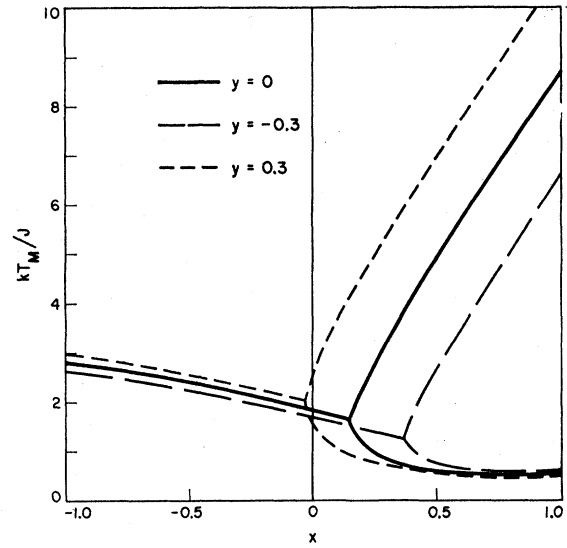


FIG. 7. Plot showing the position of the maxima in the susceptibility curves  $kT_M/J$  as a function of the second-nearest-neighbor exchange interaction  $xJ$  with the third-neighbor interaction  $yJ$  as a parameter.

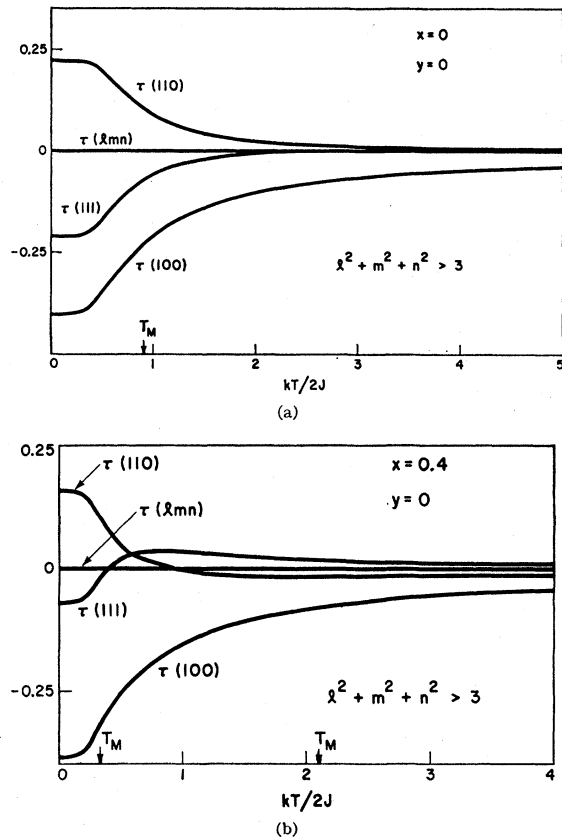


FIG. 8. The temperature dependence of the spin correlation functions for (a) nearest-neighbor interactions only and (b) a value of the parameters for which the susceptibility curves show two maxima. The positions of the susceptibility maxima  $T_M$  are indicated (see Fig. 6).

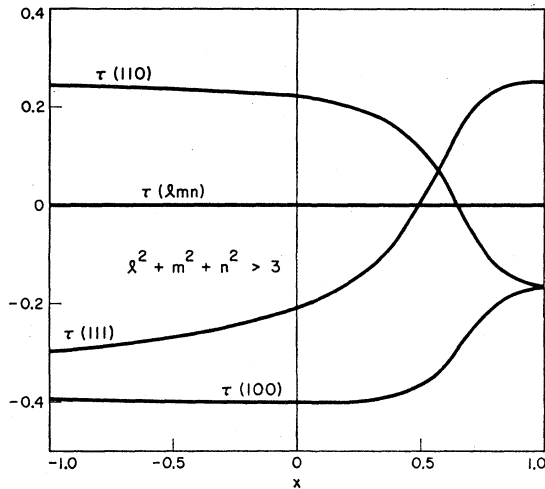


FIG. 9. Spin correlation functions at  $T=0^\circ\text{K}$  as a function of the strength of the second-neighbor interaction  $xJ$  with third-neighbor interaction taken equal to zero.

physical results are contained, i.e., no second-order phase transition is found.

The spin correlation functions at low temperature give insight into the nature of the antiferromagnetic state. For only nearest-neighbor interactions [Fig. 8(a)], there is a strong indication that a Néel-type configuration with  $\tau(lmn) \cong \frac{1}{4} \sin[\pi(l+m+n)]$  would represent the  $T=0^\circ\text{K}$  limit. If second neighbors are included, as in Fig. 8(b) in which  $x=0.4$ , a Néel-type configuration still describes the  $T=0^\circ\text{K}$  behavior. At higher temperatures there is evidence for a spiral state, i.e., a state in which nearest neighbors have antiparallel spins, second-nearest neighbors have spins essentially

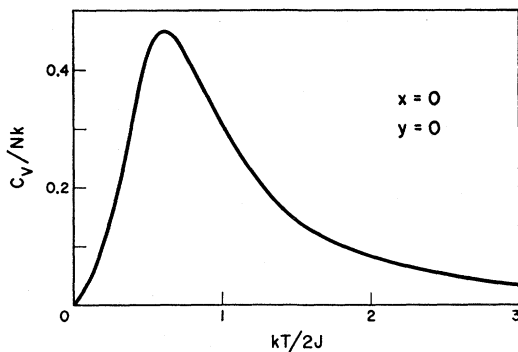


FIG. 10. The temperature dependence of the magnetic heat capacity for nearest-neighbor antiferromagnetic exchange interaction.

orthogonal to each other, and third neighbors are parallel. This behavior in the correlation function occurs in the vicinity of the broad high temperature susceptibility maximum [see Fig. 6(b)]. The sharp low-temperature susceptibility maximum corresponds to the transition to the Néel-type configuration.

The dependence of the spin correlation functions at  $T=0^\circ\text{K}$  on the strength of the second-neighbor interactions is shown in Fig. 9. For  $x \lesssim 0.5$ , the Néel-type state with spins parallel and antiparallel to the (100) direction is favored. For  $x \approx 1.0$ , a configuration with spins along the (111) directions is indicated. Over much of the range of  $x$ , the spin correlation functions are less than  $-1/4$ , i.e., the spins are "more than antiparallel." This is associated with the fact that the magnitude of the spin is  $\sqrt{3}/2$  and the minimum value of the spin correlation function is thus  $-3/4$ .

TABLE II. Parameters of the antiferromagnetic Curie-Weiss law Eq. (19) obtained by fitting the calculated results to the Curie-Weiss form at  $kT/2J=2$  and 10. In this table third-neighbor interactions are neglected, i.e.,  $y=0$ .

$x$	$k\theta/J$	$kC/J$	$\theta/T_M$
-0.5	1.0	4.2	0.4
-0.4	1.4	4.1	0.6
-0.3	2.0	4.1	0.9
-0.2	2.6	4.1	1.2
-0.1	3.4	4.2	1.7
0.0	4.4	4.2	2.4
0.1	5.6	4.3	3.3
0.2	7.2	4.4	3.2
0.3	9.1	4.6	2.8
0.4	$\sim 12.0$	5.0	2.9
0.5	$\sim 16.0$	5.4	3.2

The heat capacity is plotted in Fig. 10. No discontinuity is found in the slope of the heat capacity curve, since no second-order phase transition is calculated to first order in the free energy.

This work is considered a first step in the extension of the BPW method to include distant-neighbor interactions. Further refinements which are indicated include the calculation of the next order in perturbation theory and the inclusion of crystalline anisotropy.

#### ACKNOWLEDGMENTS

The author has profited from discussions with Dr. T. A. Kaplan, Dr. H. J. Zeiger, Professor G. W. Pratt, Jr., and Dr. J. S. Smart. In addition, Dr. M. S. Dresselhaus has contributed a number of helpful suggestions as well as programming the calculation for the IBM 7090.