of the newer experimental data. Actually our plot of the formula does take account of the newer values for the masses of the neutron and proton.

The present study is being systematically extended to higher masses. The results obtained, when supplemented by masses for the unstable isotopes in the region, will provide a large block of coherent data. Such information will make it possible to determine more precisely the numerical values for the various terms in formulas proposed for nuclear binding energies and should shed light on shell structure theories. In Fig. 3 it is interesting to note the close correspondence in undulations of the two curves and to observe the apparent discontinuities occurring at masses 40 and 48.

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# Application of the Bethe-Weiss Method to the Theory of Antiferromagnetism

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The P. R. Weiss method developed in the theory of ferromagnetism is applied to antiferromagnetism by introducing sublattices. Atomic lattices (spin $\frac{1}{2}$ per atom) with negative Heisenberg exchange coupling $J$ between the nearest neighbors are investigated. It has been found that two-dimensional lattices cannot sustain antiferromagnetic order. The Curie temperatures of the simple cubic and b.c.c. structure are, respectively, $2.004|J|/k$ and $3.18|J|/k$. That the f.c.c. lattice cannot be ordered by the interactions among the nearest neighbors is deduced from the disorder of a quadratic layer and the ineffectiveness of the interactions between layers in a f.c.c. lattice in producing order. This helps to understand why the ordering pattern of spins in Mn ions in MnO should be such as observed by Shull. Curves are obtained for reciprocal susceptibility and for short-range order *vs* temperature above the Curie point $T_c$. The experimental formula $\chi=\text{const}/(T+\theta)$ is compared with our theory. We obtain for the simple cubic and b.c.c. lattice $\theta=1.5T_c$ and $1.25T_c$ respectively if we extrapolate our theoretical curve from extremely high temperatures, and $\theta$ is slightly higher than these values if we extrapolate from the temperature range at which experimental readings are taken. This compares more favorably with the experimental data than the prediction $\theta=T_c$ of the molecular field theory. The general validity of our theory and its failure in the range of low temperatures are discussed.

## I. INTRODUCTION

A MAGNETIC medium with negative exchange coupling between the neighboring atoms cannot be ferromagnetic, but under certain circumstances the spins of the neighboring atoms are ordered antiparallel at low temperatures. This ordering effect is called antiferromagnetism. Its existence was first suggested by the discovery of an anomalous specific heat in MnO near the ordering transition temperature, at which a maximum susceptibility has also been observed.[1] The latter phenomenon made possible the proper understanding of this transition. We can imagine that, as the temperature is lowered, the inner field which causes the staggering of spins becomes stronger and makes it harder for the applied field to align the spins in one direction. Quite a few substances are found to show antiferromagnetic transitions; among them are most of the ionic salts of transition metals. Theoretical interpretations of this phenomenon have been given by Néel,[2] Bitter,[3] and Van Vleck[4] using the molecular field method in which the ordering "force" is assumed to be uniquely determined by the existing degree of order over all the lattice. Increasing attention has turned to antiferromagnetism since the development of the neutron diffraction technique, which makes possible a direct investigation of the ordering pattern.[5] Using this technique, Shull *et al.*[6] have found in MnO a rather unexpected structure: The spins of $Mn^{++}$ are ordered in such a manner that spins are lined up antiparallel in each of the four simple cubic sublattices of which the face-centered cubic lattice of Mn ions is composed. This indicates that the exchange interaction between the next-nearest neighboring Mn ions is more effective in ordering spins than that between the immediate neighboring Mn ions. A satisfying explanation of the strong exchange force between next-nearest neighbors has been offered by Anderson,[7] in which he takes into considera-

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[1] See the review article, J. H. Van Vleck, Revs. Modern Phys. **17**, 27 (1945).

[2] L. Néel, Ann. phys. **17**, 64 (1932); **5**, 256 (1936).

[3] F. Bitter, Phys. Rev. **54**, 79 (1938).

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

[5] C. G. Shull and J. S. Smart, Phys. Rev. **76**, 1256 (1949).

[6] Shull, Strauser, and Wollan, Phys. Rev. **83**, 333 (1951).

[7] P. W. Anderson, Phys. Rev. **79**, 350 (1950).

tion the perturbation of the excited state of the O ion between two next-nearest Mn ions.

The ordering effect of antiferromagnetism is one of the so-called cooperative phenomena in which the interaction between the unit systems is vitally important. A cooperative assembly usually means a difficult problem for statistical mechanics. It is almost unnecessary to mention that an exact solution of the cooperative assembly with the Heisenberg exchange interaction is not in sight at this time, since the diagonalization of the hamiltonian of the crystal is overwhelmingly involved. In the case of a negative exchange integral even the lowest energy levels have not been worked out except for the linear chain.[8] The purpose of this work is to undertake an approximate statistical theory of antiferromagnetism, more refined than the molecular field theory. As usual, only the most important Heisenberg exchange interaction, which is not always the interaction between nearest neighbors, will be considered. We assume that the orbital moment is quenched, so that the magnetic interaction arises entirely from the spins and is isotropic. Naturally we look to the methods developed for the theory of ferromagnetism. The elegant method of Bloch's spin-waves[9] is not available in antiferromagnetism, because the lowest energy levels cannot be obtained with his scheme when they are the states of very small magnetic quantum number. The Opechowski method,[10] in which the partition function is evaluated as an expansion series of $1/T$, has been used to locate approximately the ferromagnetic Curie temperatures by making an extrapolation from the first few terms of the series expression of the reciprocal (magnetic) susceptibility, which becomes zero at the Curie point. However, for the case of antiferromagnetism the series becomes violently oscillatory, reaching $\pm\infty$ at absolute zero; hence, an extrapolation for the Curie point, at which the susceptibility reaches its maximum, cannot be effected with the terms given by Opechowski and by Zehler.[11] A few more terms can be obtained only with immense labor. The P. R. Weiss method,[12] which is the reformulation of Bethe's well-known method[13] (for the theory of superstructure in alloys), is the most convenient one to use. Consequently, we shall apply the P. R. Weiss method to the problem of antiferromagnetic transitions by introducing sublattices. A discussion of the failure of this method in the range of very low temperatures[14] will be given in a later part of this article.

## II. STATISTICAL METHOD AND CURIE TEMPERATURES

As in the theory of order in binary alloys, it is convenient for the present problem to describe the long-range order in terms of sublattices. This makes the problem of antiferromagnetic transitions formally more complicated than its counterpart, the ferromagnetic case. A proper assignment of sublattices must be such that we find the lowest energy state when all the spins on each of the sublattices are perfectly aligned but antiparallelism prevails between certain different sublattices. The lattices to be considered in this section are the simple and body-centered cubic structures, the quadratic net, the honey-comb net, and the linear chain. For these we need only two equivalent sublattices; all the nearest neighbors of any site ($\alpha$- or $\beta$-site) are on the other sublattice ($\beta$- or $\alpha$-site). At the lowest energy state a spin is antiparallel with respect to all its nearest neighbors. In the Bethe-Weiss method the interactions in a cluster containing an arbitrary atom (the central atom) and all its immediate neighbors (the $n$ "first shell" atoms) are treated in detail. The exchange energy of this group is diagonalized. The interaction between a first-shell atom and those outside the group is replaced by an internal field. After the assignment of sublattices we find two different kinds of clusters; one with the central atom on an $\alpha$-site, and the other with the central atom on a $\beta$-site. Therefore, we must consider two different internal fields $\mathbf{H}_\alpha$ and $\mathbf{H}_\beta$ acting respectively on the first-shell spin on an $\alpha$-site or a $\beta$-site. The central spin is, of course, acted upon by the applied field only, since all its neighboring interactions are accounted for. The average magnetic moment of the central atom and that of the first-shell atom can be derived from the partition function of the cluster. The self-consistency of this formulation requires that the magnetic moment of a central atom on a certain sublattice equals that of the first-shell atom on the same sublattice. These relations determine $\mathbf{H}_\alpha$ and $\mathbf{H}_\beta$. $\mathbf{H}_\alpha$ and $\mathbf{H}_\beta$ will be treated as either parallel or antiparallel to the applied field $\mathbf{H}_0$. The neglect of directional effects is not a real shortcoming except in the highly ordered states at low temperatures, but in the latter range our approximation is inadequate under any circumstance (see Sec. IV). Theoretically, the higher approximations can be obtained by taking larger clusters, i.e., including the second-shell neighboring atom, the third-shell, and so on, but the complexity of the computation increases very rapidly.

The hamiltonian of the cluster of atoms is given by

$$\mathcal{H} = -2J\sum_{i=1}^{n}\mathbf{s}_0\cdot\mathbf{s}_i - s_{0z}H_0 - \sum_{i=1}^{n} s_{iz}H_f \tag{2.1}$$

where $s_z$ is the $z$-component of $\mathbf{s}$ and the direction of the applied field is taken as the $z$-axis. $H_f = H_\alpha$ or $H_\beta$ according as the central atom of the cluster is on a $\beta$-site or an $\alpha$-site. (In this article, the symbol $H$ stands for a magnetic field in gauss multiplied by $\mu$ where $\mu$ is the product of the Bohr magneton and the Lande $g$-factor.) The energy states may be labeled by the quantum numbers $S_1$, $S$, and $m$; $S$ is the total spin quantum

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[8] L. Hulthén, Arkiv. f. Mat. Astron. Fys. **26A**, No. 11 (1938).

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[10] W. Opechowski, Physica **4**, 181 (1937); **6**, 1112 (1938).

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[12] P. R. Weiss, Phys. Rev. **74**, 1493 (1948).

[13] H. A. Bethe, Proc. Roy. Soc. (London) **150A**, 552 (1935).

[14] P. W. Anderson, Phys. Rev. **80**, 922 (1950).

number of the cluster, $S_1$ that of the $n$ outer atoms, and $m$ the magnetic quantum number of the cluster. In what follows we shall consider only the case in which each atom as spin $\frac{1}{2}$. (The generalization to cases of higher spin is straightforward.) The partition function of the cluster of atoms has been given by P. R. Weiss:

$$P(H_0, H_f, T)=\sum_S\sum_{S_1}\omega(S_1)\sum_m \times\exp[-W(S, S_1, m)/kT], \tag{2.2}$$

where

$$\omega(S_1)=\frac{n!}{(\frac{1}{2}n+S_1)!(\frac{1}{2}n-S_1)!}-\frac{n!}{(\frac{1}{2}n+S_1+1)!(\frac{1}{2}n-S_1-1)!} \tag{2.3}$$

for $S_1<\frac{1}{2}n$, and $\omega(S_1=\frac{1}{2}n)=1$. The energy levels obtained by diagonalizing (2.1) are

$$W(S_1\pm\tfrac{1}{2}, S_1, m)=E_{(\pm)}-mH_0+e_{1(\pm)}(H_f-H_0)+e_{2(\pm)}(H_f-H_0)^2+\ldots \tag{2.4}$$

with

$$\begin{aligned}
&E_{(+)}=-JS_1,\quad E_{(-)}=J(S_1+1),\\
&e_{1(\pm)}=-m\left(1\mp\frac{1}{2S_1+1}\right),\\
&e_{2(\pm)}=\mp\frac{1}{4J(2S_1+1)}\left(1-\frac{4m^2}{(2S_1+1)^2}\right),\\
&e_{3(\pm)}=\mp\frac{m}{2J^2(2S_1+1)^3}\left(1-\frac{4m^2}{(2S_1+1)^2}\right),\\
&e_{4(\pm)}=\pm\frac{m}{16J^3(2S_1+1)^3}\times\left(1-\frac{24m^2}{(2S_1+1)^2}+\frac{80m^4}{(2S_1+1)^4}\right).
\end{aligned} \tag{2.5}$$

The subscripts (+) and (−) stand respectively for $S=S_1+\frac{1}{2}$ and $S=S_1-\frac{1}{2}$ and the upper and lower signs in (2.5) correspond to (+) and (−) respectively. For the cluster with a central $\beta$-site, we write

$$P_\alpha=P(H_0, H_\alpha, T), \tag{2.6a}$$

and for a central $\alpha$-site

$$P_\beta=P(H_0, H_\beta, T). \tag{2.6b}$$

Considering the central site, we get the average magnetic moments per atom,

$$\bar{m}_\alpha{}^c=\mu kT\partial \ln P_\beta/\partial H_0,\quad \bar{m}_\beta{}^c=\mu kT\partial \ln P_\alpha/\partial H_0 \tag{2.7}$$

for the atoms on the two sublattices. On the other hand, from the consideration of the outer atoms of the cluster, we have

$$\begin{aligned}
\bar{m}_\alpha{}^s&=n^{-1}\mu kT\partial \ln P_\alpha/\partial H_\alpha,\\
\bar{m}_\beta{}^s&=n^{-1}\mu kT\partial \ln P_\beta/\partial H_\beta.
\end{aligned} \tag{2.8}$$

Since no distinction should be made between the central spin and one of the first shell, we must have $\bar{m}_\alpha{}^c=\bar{m}_\alpha{}^s$ and $\bar{m}_\beta{}^c=\bar{m}_\beta{}^s$. This consistency requirement gives a set of equations which relates $H_\alpha$ and $H_\beta$ to the applied field $H_0$ and temperature $T$. They are,

$$nP_\alpha\partial P_\beta/\partial H_0-P_\beta\partial P_\alpha/\partial H_\alpha=0, \tag{2.9a}$$

$$nP_\beta\partial P_\alpha/\partial H_0-P_\alpha\partial P_\beta/\partial H_\beta=0. \tag{2.9b}$$

By exchanging the roles of $H_\alpha$ and $H_\beta$ in (a) we get (b) and vice versa. For any given $H_0$ and $T$ there is a set of solutions of (2.9) with $H_\alpha=H_\beta$ corresponding to the paramagnetic case. However, this is not always the only solution of (2.9). For a substance with negative exchange integral ($J<0$) and at sufficiently low temperatures a set of solutions with $H_\alpha$ different from $H_\beta$ may appear to be the solution for the equilibrium state. With $H_0=0$, $P_\alpha$ (or $P_\beta$) is an even function of $H_\alpha$ (or $H_\beta$), and both $\partial P_\alpha/\partial H_0$ (or $\partial P_\beta/\partial H_0$) and $\partial P_\alpha/\partial H_\alpha$ (or $\partial P_\beta/\partial H_\beta$) are odd functions of $H_\alpha$ (or $H_\beta$). Consequently, $H_\beta=-H_\alpha$ offers a set of solutions for (2.9) by making them identical, giving $\bar{m}_\alpha=-\bar{m}_\beta$. Near the Curie temperature $T_c$ the antiferromagnetic solution can be determined from

$$A+CH_\alpha{}^2=0, \tag{2.10}$$

which is obtained by putting $H_\beta=-H_\alpha\neq 0$ in (2.9) and neglecting all the terms in the ascenting power series of $H_\alpha$ except the first two. Detailed evaluation gives

$$A=\sum_{S_1}\omega(S_1)\sum_{(\pm)}\left\{a_{0(\pm)}+\frac{a_{1(\pm)}}{kT}\right\}\exp\left[-\frac{E_{(\pm)}}{kT}\right] \tag{2.11}$$

$$C=\sum_{S_1}\omega(S_1)\sum_{(\pm)}\left\{c_{0(\pm)}+\frac{c_{1(\pm)}}{kT}+\frac{c_{2(\pm)}}{k^2T^2}+\frac{c_{3(\pm)}}{k^3T^3}\right\}\times\exp\left[-\frac{E_{(\pm)}}{kT}\right], \tag{2.12}$$

where

$$\begin{aligned}
a_0&=\textstyle\sum_m(-2e_2),\\
(n-1)a_1&=\textstyle\sum_m\{(n-1)e_1{}^2+nme_1\},
\end{aligned} \tag{2.13}$$

$$\begin{aligned}
c_0&=\textstyle\sum_m(-4e_4),\\
(n-1)c_1&=\textstyle\sum_m\{2(n-1)(e_2{}^2+2e_1e_3)+nme_3\},\\
(n-1)c_2&=\textstyle\sum_m\{-2(n-1)e_1{}^2e_2-nme_1e_2\},\\
6(n-1)c_3&=\textstyle\sum_m\{(n-1)e_1{}^4+nme_1{}^3\}.
\end{aligned} \tag{2.14}$$

Incidentally, we might mention that if we change the symbol $n$ into $-n$ in the coefficients $A$ and $C$ of (2.10) we get Weiss' Eq. (36), the counterpart of (2.10) in the ferromagnetic case. The simple connection is an out-

TABLE I. The curie transition of different lattices. Each atom has spin $\frac{1}{2}$. The numerical values are those of $kT_c/|J|$.

| Lattice | Number of nearest neighbors | Antiferro-magnetism | Present method ferromagnetism[a] | Ising model[b] | Molecular field method[b] |
|---|---|---|---|---|---|
| Linear chain | 2 | *no* transition | *no* transition | *no* transition | 1 |
| Honey-comb net | 3 | *no* transition | *no* transition | 0.910 | 1.5 |
| Quadratic layer | 4 | *no* transition | *no* transition | 1.44 | 2 |
| Hexagonal layer | 6 | *no* transition[c] | *no* transition | $2.47 (J>0)$<br>*no* transition $(J<0)$ | transition |
| Simple cubic | 6 | 2.004 | 1.85 | 2.47 | 3 |
| Body-centered cubic | 8 | 3.18 | 2.90 | 3.48 | 4 |
| Face-centered cubic | 12 | *no* transition[c] | transition | transition | transition |

[a] After P. R. Weiss.
[b] For both the antiferromagnetic and the ferromagnetic cases.
[c] See Sec. V.

come of the fact that if we put $H_\alpha = H_\beta \neq 0$ in (2.9) our theory reduces to that of ferromagnetism.

A transition of second order takes place at a certain temperature, such that $A$ changes sign and above this temperature (2.10) yields an imaginary value of $H_\alpha$. By numerical computations using the condition $A=0$, which involves different coefficients for different lattices, we find that without the external field[15] the values of $kT_c/|J|$ for the simple cubic and b.c.c. lattices are respectively 2.004 and 3.18 and that none of the two-dimensional nets investigated show antiferromagnetism. Previously, the latter conclusion had been suggested by its counterpart in the theories of ferromagnetism.

For convenience of comparison, the results of the P. R. Weiss theory for both antiferromagnetic and ferromagnetic cases and those obtained by Van Vleck using the molecular field method are listed in Table I. Also included in Table I are the results of the present method with the Ising model. In this model spin vectors are replaced by scalars $s=\pm\frac{1}{2}$ so that

$$\mathcal{H} = -2Js_0\sum_i s_i - s_0H_0 - H_f\sum_i s_i, \tag{2.15}$$

and

$$P(H_0, H_f, T) = x_0^{-1}\{x_f y^{-1} + x_f^{-1} y\}^n + x_0\{x_f y + x_f^{-1} y^{-1}\}^n, \tag{2.16}$$

with

$$x_0 = \exp[H_0/2kT], \quad x_f = \exp[H_f/2kT],$$
$$y = \exp[J/2kT].$$

## III. PHYSICAL PROPERTIES

### (a) Magnetic Susceptibility

When the crystal is antiferromagnetically ordered, its magnetic susceptibility depends on the direction of the applied field with respect to the existing internal field. Our theory is not qualified to evaluate the susceptibility below the curie temperature, since from the beginning the directional effect is neglected. For the disordered state the consideration of sublattices is unnecessary, and so the formula for $\chi$ given in Weiss' article is valid for both the ferromagnetic and antiferromagnetic cases. In the present notation it reads

$$\chi = \frac{\mu^2/kT}{(n+1)P_0}\sum_{S_1}\omega(S_1)\sum_{(\pm)}\sum_m\left(m^2 - \frac{H_f - H_0}{H_0} m e_{1(\pm)}\right) \times \exp[-E_{(\pm)}/kT] \tag{3.1}$$

where

$$(H_f - H_0)/H_0 = \{\textstyle\sum_{S_1}\omega(S_1)\sum_{(\pm)}\sum_m \times [nm^2 + (n+1)me_{1(\pm)}]\exp[-E_{(\pm)}/kT]\} \div \{\textstyle\sum_{S_1}\omega(S_1)\sum_{(\pm)}\sum_m[nme_{1(\pm)} + (n+1) \times (e_{1(\pm)}{}^2 - 2kTe_{2(\pm)})]\exp[-E_{(\pm)}/kT]\} \tag{3.2}$$

$$P_0 = P(H_0 = 0, \quad H_f = 0, T). \tag{3.3}$$

$\chi$ may be written as power series in $J/kT$, such that

$$\chi = \frac{\mu^2}{4kT}\left\{1 + \sum_{r=1}^{\infty}\frac{B_r}{(kT/J)^r}\right\}. \tag{3.4}$$

Both P. R. Weiss and Opechowski have found $B_1 = \frac{1}{2}n$ and $B_2 = \frac{1}{2}n\ (\frac{1}{2}n - 1)$ for all the lattice structures under consideration. The coefficients of the higher terms are not functions only of $n$. By detailed calculations we get for the simple cubic lattice

$$\chi = \frac{\mu^2}{4kT}\left\{1 + \frac{3}{kT/J} + \frac{6}{(kT/J)^2} + \frac{2579}{224(kT/J)^3} + \frac{10725}{448(kT/J)^4} + \cdots\right\}, \tag{3.5}$$

with the coefficients of the third and higher powers slightly different from those in the series,

$$\chi = \frac{\mu^2}{4kT}\left\{1 + \frac{3}{kT/J} + \frac{6}{(kT/J)^2} + \frac{11}{(kT/J)^3} + \frac{165}{8(kT/J)^4} + \cdots\right\}, \tag{3.6}$$

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[15] In general, the Curie temperature is a function of $H_0$ and can be determined by using (2.9). The calculation for the case of non-vanishing applied field is much too involved. However, that $T_c$ should decrease as $H_0$ is increased is shown qualitatively in a previous note (Y. Y. Li, Phys. Rev. **80**, 457 (1950)) by drawing an analogy with the well-developed theory of Ising model.

obtained by Opechowski and by Zehler (see Sec. IV). For extremely high temperatures, we may take only the first two terms in the series and rewrite in the form of the modified Curie's law

$$\chi=\mu^2/4k(T\pm T'), \tag{3.7}$$

with

$$T'=n|J|/2k, \tag{3.8}$$

where the upper sign is for antiferromagnetism. The molecular field theory gives this formula as its prediction of susceptibility for any temperature above the Curie point. This is equivalent to the neglect of all the terms except the first two in (3.4).

It is customary for experimentalists to fit their data taken at temperatures above the Curie point with the formula $\chi=\text{const}/(T\pm\theta)$. If we compare this formula with (3.7) we simply get $\theta=T'$. However, this is an extrapolation from the range of extremely high temperatures and is not in conformity with the ordinary experimental practice, in which the data are taken from temperatures immediately above $T_c$ to those of several times $T_c$ in the absolute scale. Therefore, in order to obtain a theoretical value of $\theta$, the so-called "paramagnetic critical temperature," we should effect a linear extrapolation from the theoretical curve $1/\chi$ against $T$ in the range $T=2T_c$ to $3T_c$. The tangent of this section of the curve is then extended to meet the abscissa at $-\theta$ in the case of antiferromagnetism. Table II shows the ratios of $\theta/T_c$ and $T'/T_c$ for both antiferromagnetism and ferromagnetism. The values obtained with the molecular field theory are also included. We see that in the antiferromagnetic case $\theta>T'$ noticeably, but in the ferromagnetic case $\theta<T'$ and is only slightly higher than $T_c$. In general, an experimentalist would notice that, as the temperature goes higher, the value of $\theta$ in his empirical expression must be shifted in order to obtain the best fit for his data when they are taken over a wide range of temperatures; in the ferromagnetic case $\theta$ increases with increasing temperature, but in the antiferromagnetic case $\theta$ decreases. This difference is an outcome of the fact that the tangent of extrapolation meets the $T$-axis at a point immediately above $T_c$ in the ferromagnetic case, but the intersection is on the negative $T$-axis in the antiferromagnetic case. Experimentally, it is found that for various antiferromagnetic salts $\theta/T_c$ ranges from 1.4 to 5.0, though for the iron group $\theta$ is only higher than $T_c$ by only a few percent. These results agree nicely with our theory. The well-known prediction $\theta=T_c$ is a consequence of the simple theory of the molecular field method. Therefore, it is not essential to include the next-nearest interactions in order to explain the appreciable deviation of $\theta$ from $T_c$,[16,17] though it may be required for getting better quantitative agreement with experimental data.

TABLE II. The paramagnetic critical temperatures for two cubic lattices.

| | | The present method | | Moleculat field method[b] |
|---|---|---|---|---|
| | | Antiferro-magnetism | Ferro-magnetism[a] | |
| simple cubic | $\theta/T_c$ | 1.7 | 1.1 | 1 |
| | $T'/T_c$ | 1.50 | 1.62 | 1 |
| b.c.c. | $\theta/T_c$ | 1.5 | 1.05 | 1 |
| | $T'/T_c$ | 1.26 | 1.38 | 1 |

[a] After P. R. Weiss.
[b] For both antiferromagnetism and ferromagnetism.

The quantity $\chi$ is calculated numerically from (3.1) for the simple cubic lattice and is presented in Fig. 1 with $\chi(T_c)/\chi$ against $T/T_c$. At the Curie point we have $\chi(T_c)=3.63\ 10^{-2}\mu^2/|J|$. Our curve is concave upward, instead of being a straight line as required by the modified curie's law. The experimental data of Bizette *et al.*[18] on MnO are also presented for comparison. The Mn ions in the f.c.c. lattice are ordered on four superimposed simple cubic lattices, and therefore it seems legitimate to compare their data with our calculation for a simple cubic lattice, if we identify our $J$ with the exchange coupling between two next-nearest Mn ions. The Mn ion has a spin 5/2 instead of $\frac{1}{2}$. In making the comparison we assume that the spin quantum number per atom does not have much influence on the behavior of $\chi/\chi(T_c)$, though it has a great effect on the value of $\chi$ itself. Figure 1 evidently shows that our calculated curve is much nearer to the experimental one than is that of the molecular field theory, although the present theory must still be regarded as only a fair approximation in the temperature range directly above the Curie point.

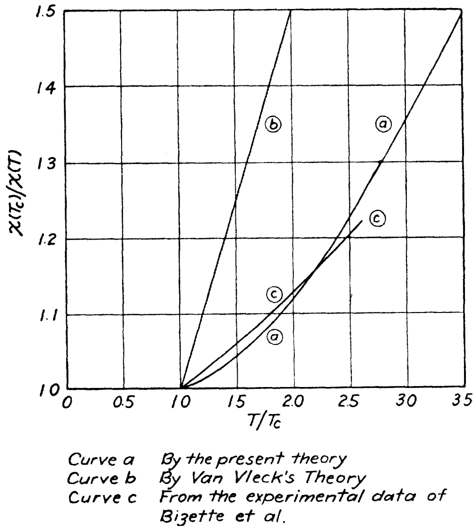

FIG. 1. Reciprocal susceptibility *vs* temperature.

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[16] L. Néel, Ann phys. 3, 137 (1948).
[17] P. W. Anderson, Phys. Rev. **79**, 705 (1950).
[18] Bizette, Squire, and Tsai, Compt. rend. **207**, 449 (1938).

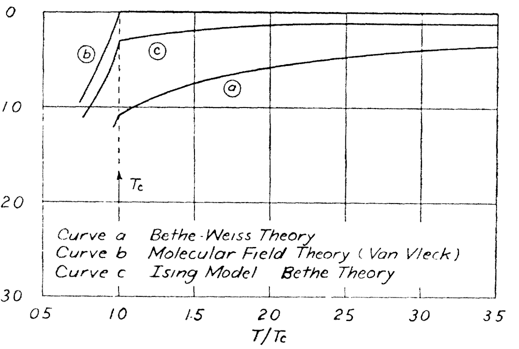

FIG. 2. Energy *vs* temperature for a simple cubic lattice.

## (b) Energy and Short-Range Order

It is trivial to verify that Weiss' formula for $\epsilon$, the energy per atom, when $H_0=0$, is unchanged by the introduction of sublattices. We have

$$\begin{aligned}\epsilon&=-J\langle \mathbf{s}_0\cdot\textstyle\sum_i \mathbf{s}_i\rangle_{\mathrm{Av}}\\ &=\{\textstyle\sum_{S_1}\omega(S_1)\sum_{(\pm)}\sum_m E_{(\pm)}\\ &\qquad\times\exp-W(S_1\pm\tfrac{1}{2},S_1,m,H_f)/kT\}/2P.\end{aligned}\tag{3.9}$$

With $T\geqslant T_c$ the above formula reduces to

$$\epsilon=-\frac{|J|}{P_0}\sum_{S_1}\omega(S_1)S_1(S_1+1)\times\left\{\exp-\frac{E_{(-)}}{kT}-\exp-\frac{E_{(+)}}{kT}\right\}.\tag{3.10}$$

Figure 2 shows $\epsilon$ *versus* the temperature for a simple cubic lattice.

As the energy decreases with the temperature, more antiparallel pairs are formed at the expense of the parallel pairs. The very similar situation of finding more unlike neighboring atoms than like ones is well-known in the theory of order in alloys and is called the *short-range order* or *order of neighbors*. With the use of neutron diffraction patterns, Shull *et al.*[6] have found evidences of the short-range order in MnO up to room temperature, which is *ca.* $2.5T_c$ in the absolute scale. The degree of the short-range order $\sigma$ may be defined as the percentage abundance of antiparallel pairs minus that of parallel pairs, i.e.,

$$\sigma=-\frac{4}{n}\langle s_{0z}\sum_i s_{iz}\rangle_{\mathrm{Av}}.\tag{3.11}$$

At temperatures above $T_c$ and in the absence of applied field we have $\langle s_{0z}\sum_i s_{iz}\rangle_{\mathrm{Av}}=\frac{1}{3}\langle \mathbf{s}_0\cdot\sum_i \mathbf{s}_i\rangle_{\mathrm{Av}}$. Therefore

$$\epsilon=-\tfrac{3}{4}n|J|\sigma.\tag{3.12}$$

The corresponding relation for the Ising coupling reads

$$\epsilon=-\tfrac{1}{4}n|J|\sigma.\tag{3.13}$$

From (3.12) the $\sigma$ *vs* $T$ curves (Fig. 3) are calculated for the two cubic lattices with $J<0$. Table III is compiled for comparison between different theories and models. We see that the values of $\sigma(T_c)$ obtained by using the Ising model are quite close to our results, but it is not so for $\epsilon(T_c)$. The equation for $\sigma$ the short-range order of parallel spins in the ferromagnetic case is different from (3.12) only by a negative sign.

In (3.9) $H_f$ vanishes at $T_c$ but not its derivative with respect to temperature, so our theory gives a jump of the specific heat at $T_c$. Using Weiss' formula we obtain for a simple cubic lattice the discontinuity of specific heat at $T_c$

$$\Delta c=1.0k.\tag{3.14}$$

Millar[19] measured the specific heat of MnO. From his data we have

$$\Delta c=50k.\tag{3.15}$$

A close agreement between (3.14) and (3.15) is not expected, since the MnO have a spin 5/2 in contradiction to our assumption of $\frac{1}{2}$, and we have neglected the interactions other than the most important ones. Besides, the result of an exact solution,[20] or of even a better approximation, might yield a quite different value for $\Delta c$. However, we notice that Millar's value of $\Delta c$ is exceptionally large as compared with the specific heat jump found in other second-order transitions such as order-disorder transitions in alloys (say, $\beta$-brass). We should like to point out certain complications which are profoundly associated with the antiferromagnetic transition. First of all, the appearance in the lattice of a periodic change of spin directions gives a new characteristic behavior to the electrostatic interaction and influences the wave functions of the crystal. We can make it clear by considering the Hartree-Fock equation, following the interpretation given by Slater.[21] At the ordered states $\rho_+$ and $\rho_-$, the densities of electrons with $+$ and $-$ spins respectively, are two different periodic functions with a period twice the crystal spacing. Ac-

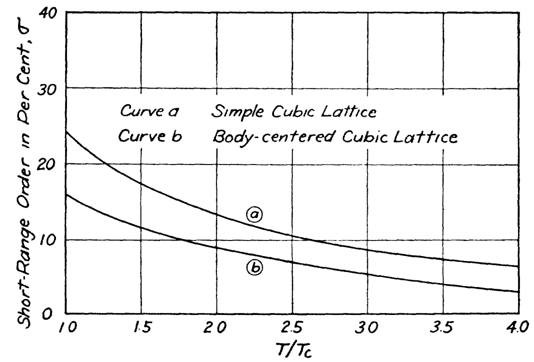

FIG. 3. Short-range order above Curie temperature.

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[19] R. W. Millar, J. Am. Chem. Soc. **50**, 1875 (1928).

[20] L. Onsager, Phys. Rev. **65**, 117 (1944); this exact solution of the two-dimensional Ising problem gives an infinite specific heat at $T_c$ instead of a finite discontinuity of specific heat as shown by the approximate solutions.

[21] J. C. Slater, Phys. Rev. **81**, 385 (1951).

cordingly, we have two different periodic potentials for each electron; one is the ionic potential and the other is the electronic interaction corrected by the so-called Fermi or exchange hole. The latter potential depends on the long-range order and is different for electrons with opposite spins mostly by a phase shift of a half period.[22] In the Heisenberg approximation, the wave functions and the integral $J$ must change appreciably as the order of antiparallelism increases. For simplicity of manipulation, $J$ is assumed in our theory to be a constant, which is certainly not true even when the thermal change of lattice spacing is considered. (The variation of $J$ with the degree of antiparallel order is more profound than with the thermal expansion.) At the Curie point the rate of change of $J$ with temperature reaches its maximum because here we have the highest rate of the increase of order as temperature is lowered. Our theory has neglected this effect, as well as its contribution to the jump of specific heat. Furthermore, the recent observations of a slight change of crystal symmetry and space parameters in the vicinity of $T_c$ of most antiferromagnetic salts[23] add one more complication to the transition and its specific heat. As pointed out by Greenwald and Smart, the change of crystal symmetry is connected with the change of $J$.

TABLE III. Short-range order and energy at $T_c$.

| | | The present method | | | Molecular field method[a] |
|---|---|---|---|---|---|
| | | Antiferromagnetic | Ferromagnetic | Ising model[a] | |
| simple cubic | $\sigma(T_c)$ | 0.242 | 0.175 | 0.200 | 0 |
| | $\epsilon(\infty)-\epsilon(T_c)$ | $1.09\|J\|$ | $0.788J$ | $0.300\|J\|$ | 0 |
| b.c.c. | $\sigma(T_c)$ | 0.159 | 0.130 | 0.143 | 0 |
| | $\epsilon(\infty)-\epsilon(T_c)$ | $0.954\|J\|$ | $0.779J$ | $0.286\|J\|$ | 0 |

[a] For both the antiferromagnetic and ferromagnetic cases.

## IV. LIMITATION OF THE METHOD

Before we proceed to treat more complicated lattices, we must discuss the validity of our method and its limitations. Bethe's theory of atomic order in alloys, as shown by Fowler and Guggenheim,[24] has its sound origin in the customary statistical mechanics as an approximate evaluation of the grand partition function of the whole crystal. In the problem of atomic interactions in alloys or of the Ising coupling, the states of the cluster can be simply stated as $n_A$ atoms of one kind and $n-n_A$ of another kind around the central one, and the interaction of these atoms with the rest of the crystal can be brought in by introducing the factors $\xi_A{}^{n_A}$ and $\xi_B{}^{n-n_A}$ (only one of $\xi_A$ and $\xi_B$ is independent). It is evident that the use of the inner fields $H_f$ in Sec. II for the Ising problem is nothing more than writing $\xi$ as $\exp H_f/2kT$ (see Eq. (2.16)). In dealing with the problem of the Heisenberg exchange couplings, we cannot rejoice in the simplicity of scalar quantities; for different eigenstates, different parameters are needed to adjust the ordering effect of the rest of the crystal to the cluster. These parameters are somehow related to each other, but their inter-relations are by no means known. This situation forces us to make a reasonable assumption that the interaction between the cluster and the rest of the crystal is $-S_{1z}(H_f-H_0)$, which sounds so natural from the viewpoint of the molecular field. It becomes clear that besides inheriting Bethe's approximation in statistics, the P. R. Weiss method contains an assumption which does not have a sound basis in the quantum-mechanical treatment. Therefore, we can hardly expect P. R. Weiss' theory to yield results for the true exchange coupling case as good as those given by Bethe's theory for the Ising problem. It is in the lowest temperature range that the theory meets its failure, as can be easily seen from the behavior at extremely low temperatures of several equations in the preceding section. Anderson[14] has made this point clear by a comparison with Bloch's theory. In the latter theory, the dominant states at lowest temperatures are certain spin-waves with rather long wavelength, but the cluster considered in Weiss' theory can accommodate only the shortest spin-waves. Anderson shows that in the extremely low temperature range the second-order perturbation of the ordering field $H_f$ offsets the ferromagnetism even for ferromagnetic lattices. With numerical calculations, he finds the existence of an anti-Curie point at a temperature about 1/7 of that of the Curie point computed by Weiss for the simple cubic lattice; only in the range between these two temperatures should the crystal be ferromagnetic, if Weiss' theory were correct. These remarks remain true for the present application of the P. R. Weiss method to antiferromagnetism. From the equation $A=0$, the anti-Curie points are found at $0.981|J|/k$ and $0.714|J|/k$ for the simple and body-centered cubic (antiferromagnetic) lattice respectively. We also notice from $A$, as a function of $T$, that half-way between the Curie and anti-Curie points the theory already shows its failure. For higher temperatures, however, the thermal excitation then outweighs the improper influence of $H_f$.

On the other hand, the justification of our theory in the range of higher temperatures can be inferred by a comparison with the Opechowski theory. In the latter, the free energy function is written in the form of an

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[22] When we use the "band" approximation, the effect of the superstructure of antiparallel spins within the atomic lattice would split one energy band into two, which may overlap. This situation, however, could not occur in the case of ferromagnetic order in which spins are lined up simply in a certain direction without periodic variation. See the recent article by J. C. Slater, Phys. Rev. **82**, 538 (1951).

[23] S. Greenwald and J. S. Smart, Nature **166**, 523 (1950); J. S. Smart and S. Greenwald, Phys. Rev. **82**, 113 (1951).

[24] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, London, 1939), Chapter 13.

infinite power series of $J/kT$,

$$F/N=-(kT/J)\ln(2\cosh H_0/kT)+\sum_{r=1}^{\infty} A_r/(kT/J)^{r-1} \quad (4.1)$$

where $A_r$ is the coefficient of $N$ in the expression

$$[(-1)^{r+1}/r!]\,\mathrm{spur}[\epsilon_0{}^r \exp(-\epsilon_H/kT)]/\mathrm{spur}\times[\exp(-\epsilon_H/kT)] \quad (4.2)$$

$$\epsilon_0=-2J\sum_{j,k}(\mathbf{s}_j\cdot\mathbf{s}_k) \quad (4.3)$$

$$\epsilon_H=-H_0\sum_j(\mathbf{s}_j)_z \quad (4.4)$$

with $j$ summed over all the $N$ atoms in the assembly and $k$ over all the nearest neighbors of the $j$-th atom. Only the first four coefficients $A_1, \cdots, A_4$ have been worked out. The longest chain of connected spins $(\mathbf{s}_{j1}\cdot\mathbf{s}_{j2})\ (\mathbf{s}_{j2}\cdot\mathbf{s}_{j3})\cdots(\mathbf{s}_{j_r}\cdot\mathbf{s}_{j_{r+1}})$ involved in the calculation of $A_r$ contains $r+1$ spins (see Table I and II of the article by Opechowski). Our center-and-the-first-shell cluster can take in only the two-spin and three-spin chains. Consequently, when we expand the closed expression of our theory into the power series of $J/kT$, we obtain for $A_1$ and $A_2$ in the free energy function and for $B_1$ and $B_2$ in $\chi$ the same values as by the Opechowski theory. Furthermore, our first approximation, in which the smallest Bethe cluster includes all but one of the configurations involved in the calculation of $A_3$ in the Opechowski series, gives a very accurate value for $B_3$ in the series of $\chi$ (3.5). As the power of $J/kT$ in the series goes higher, the fact that our clusters no longer contain the configurations of spin groups involved in the correct evaluation of the coefficient of $(J/kT)^r$ becomes worse, and so the accuracy of the coefficient given by our theory decreases. ($B_4$ in (3.5) is 15 percent higher than the correct value.) In general, if a central atom and its first $r$ shells are taken as the Bethe cluster, we should expect to get the correct value for $B_1$, $B_2$, $\cdots$, $B_{r+1}$ in $\chi$ and a very accurate $B_{r+2}$. For the diamond lattice the first approximation of the Bethe-Weiss theory produces the same result as for the quadratic layer. However, the second approximation (with a center-and-the-first-two-shells cluster) would correctly give different results for these two lattices. In parallel, the Opechowski theory gives the same values of $A_1$ and $A_2$ but different $A_r$ $(r\geqslant 3)$ for these two lattices. The advantage of our method lies in its ability to obtain approximately closed expressions for the thermodynamic functions instead of the finite number of terms of an infinite series obtained by the Opechowski theory, leaving the coefficients of all the higher powers of $J/kT$ unknown. Both theories cannot produce dependable results for very low temperatures, since then the very high powers of $1/T$ become important. It is beyond any doubt that, in the temperature range around the Curie points of the cubic lattices, the Bethe-Weiss method gives at least semi-quantitatively correct results (see reference 14).

## V. HEXAGONAL LAYER AND FACE-CENTERED CUBIC LATTICE

In this section we shall treat the hexagonal layer and f.c.c. structures, in which we find nearest interactions among the first-shell spins. The work will be presented rather briefly, since it involves no complications beyond that just mentioned. The hexagonal layer (triangular net) has a coordination number 6, as does the simple cubic lattice, but each of the 6 nearest neighboring spins has two nearest neighbors to itself. Even if we adopt the Ising model this lattice sustains no antiferromagnetic ordering, as has been shown by Wannier[25] who obtained an exact solution. In our approximate method, the proper assignment of sublattices has alternate rows of $\alpha$- and $\beta$-sites (Fig. 4). When all the spins in each sublattice are aligned and those in different sublattices are antiparallel to these, we have a maximum number of antiparallel paired spins and the lowest energy. As shown by Wannier, the lowest energy state of a triangular net of Ising spins can be arranged not only in the above manner, but also in many quite different ways. Our assignment of sublattices, perhaps, has an effect of over emphasizing the possibility of ordering. The cluster which we consider in detail has a central $\alpha$- (or $\beta$-) site, and four $\beta$- (or $\alpha$-) sites and two $\alpha$- (or $\beta$-) sites in the first shell. With the Ising model, the present method obtains the same conclusion as the exact solution of Wannier. The details of its derivation are not given, since they are very similar to the following consideration for the case of the Heisenberg exchange coupling. We have the hamiltonian

$$\mathcal{H}=-2J(\mathbf{s}_0\cdot\textstyle\sum_i\mathbf{s}_i+\mathbf{s}_1\cdot\mathbf{s}_2+\mathbf{s}_2\cdot\mathbf{s}_3+\cdots+\mathbf{s}_6\cdot\mathbf{s}_1)-H_{12}\tau_2-H_{11}\tau_1-H_0s_{0z}, \quad (5.1)$$

where

$$\tau_1=s_{2z}+s_{5z}, \quad (5.2a)$$

and

$$\tau_2=s_{1z}+s_{3z}+s_{4z}+s_{6z}. \quad (5.2b)$$

$H_{11}$ stands for $H_{\alpha\alpha}$ or $H_{\beta\beta}$ and $H_{12}$ for $H_{\alpha\beta}$ or $H_{\beta\alpha}$; $H_{\alpha\beta}$ is the internal field acting on the spin of a $\beta$-site in the shell of an $\alpha$-centered cluster, and similarly we have $H_{\beta\alpha}$, $H_{\alpha\alpha}$, and $H_{\beta\beta}$. The eigenfunctions of $(\mathbf{s}_1\cdot\mathbf{s}_2+\cdots+\mathbf{s}_6\cdot\mathbf{s}_1)$ and the expectation values of $\tau_1$ and $\tau_2$ are given in the Appendix. The diagonalization of the perturbing part $-2J\mathbf{s}_0\cdot\sum_i\mathbf{s}_i-H_{12}\tau_2-H_{11}\tau_1-H_0s_{0z}$ is similar to that carried out in a previous section. The energy levels of $\mathcal{H}$ are now

$$W(S_1\pm\tfrac{1}{2}, S_1, j, m)=E_j(S_1)+E_{(\pm)}-mH_0+e_{1(\pm)}X_j(S_1)+e_{2(\pm)}X_j{}^2(S_1)+\cdots, \quad (5.3)$$

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[25] G. H. Wannier, Phys. Rev. **79**, 357 (1950); see also G. F. Newell, Phys. Rev. **79**, 876 (1950); R. M. F. Houtappel, Physica **16**, 425 (1950).

with

$$X_j(S_1)=d_j(S_1)(H_{11}-H_0)+(1-d_j(S_1))(H_{12}-H_0), \quad (5.4)$$

where $E_{(\pm)}$ and $e_{(\pm)}$'s are as defined above. $E_j(S_1)$ and $d=\tau_1/\tau_1+\tau_2$ are given in Table V of the Appendix. The index $j$ refers to the different eigenstates listed in Table V. With these data the partition functions for an $\alpha$-centered and a $\beta$-centered cluster,

$$P_\alpha=P(H_0, H_{\alpha\beta}, H_{\alpha\alpha}, T) \text{ and } P_\beta=P(H_0, H_{\beta\alpha}, H_{\beta\beta}, T),$$

can be written. The condition of self-consistency requires

$$m_\alpha{}^c=m_\alpha{}^{(\alpha)}=m_\alpha{}^{(\beta)}, \quad (5.5a)$$

$$m_\beta{}^c=m_\beta{}^{(\beta)}=m_\beta{}^{(\alpha)}, \quad (5.5b)$$

where $m_\beta{}^{(\alpha)}$ is the average magnetic moment of the first-shell spins on $\beta$-sites in an $\alpha$-centered cluster. These quantities can be derived easily from the respective partition functions. It can be shown that, when $H_0=0$, the possible antiferromagnetic solution with $H_{\alpha\alpha}=-H_{\beta\beta}(=H_1)$ and $H_{\alpha\beta}=-H_{\beta\alpha}(=H_2)$ sends (5.5a) into (5.5b) and vice versa. The internal field intensities are to be determined by equations

$$F(H_1, H_2, T)=0, \quad G(H_1, H_2, T)=0 \quad (5.6)$$

obtained from (5.5). $H_1$ and $H_2$ can apparently take small but nonvanishing values near a temperature $T_1$ which is determined by the equation

$$\partial(F, G)/\partial(H_1, H_2)=0; \quad (5.7)$$

at this temperature $H_1=H_2=0$ is a double solution. We find by actual calculations that the only solution of (5.7) is $T_1=0$, and above zero temperature there is no nonvanishing solution for $H_1$ and $H_2$. So we conclude that the hexagonal layer does not sustain an antiferromagnetic order. As an immediate consequence of this, we may point out that the spin superlattice of the cations in the salt of $FeCl_2$ group should conform with the "superexchange" interaction between the next-nearest neighboring cations which are separated by anions, since the nearest neighbors of cations form hexagonal layers. A neutron diffraction experiment could easily reveal this.

Finally, we come to the problem of a f.c.c. lattice with negative exchange coupling. With the Ising model we can show that antiparallel order exists at low temperatures and the transition is one of the first order with a latent heat.[26] We have no reason to believe this conclusion would hold for the quantum-mechanical exchange. To follow our treatment, we need first to solve the problem of exchange energy of 12 electrons in the first-shell atoms of the cluster. There are accordingly 924 $S_1$-states ($S_1=6, 5, 4, \cdots, 0$). The work would be immensely laborious. So we decided to resort to an argument which makes use of the result we have obtained for the simpler lattices. The f.c.c. lattice may be viewed as consisting of quadratic layers. Since a quadratic layer with the Heisenberg coupling does not sustain antiferromagnetism, the ordering in a f.c.c. lattice can only be effected by the interactions among the spins on neighboring layers. For any atom there are four nearest neighbors in the next layer. When they are ordered, two spins are opposite to the others. Therefore, we cannot count on their total effect on their common neighbor in the next layer (i.e., on the interaction between layers) to produce order. We may safely conclude that an antiferromagnetic transition does not occur in a f.c.c. lattice. (On the other hand, the same argument shows that, either with the Ising model or in the molecular field theory, the f.c.c. lattice should sustain antiferromagnetism, because then each quadratic layer does so.) This offers an explanation for the fact that the f.c.c. lattice of manganous ions in MnO is not ordered in a superlattice corresponding to the nearest interactions, but is found to show ordered structure agreeing with the superexchange interaction between next-nearest neighbors. The above argument, which was hinted at by Anderson in his articles,[7,17] is very useful if not rigorous. It applies to the hexagonal layer as well. The latter may be considered as made of linear chains; each spin has two neighbors in the next chain. When they are ordered, one of the two neighbors is opposite the other. (See Fig. 4: sites 1, 0, and 4 are on one chain and so forth.) Therefore, the ordering cannot be effected by the coupling between chains. Since a linear chain cannot be ordered regardless of the interaction (Ising type or quantum-mechanical), the hexagonal layer must not sustain antiferromagnetism.

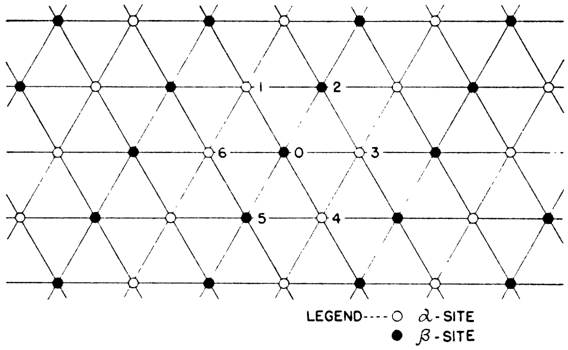

FIG. 4. Hexagonal layer decomposed into two sublattices. (At the center a Bethe cluster is indicated by labeling the sites as shown.)

## ACKNOWLEDGMENTS

The author is deeply indebted to Dr. P. W. Anderson who has kindly made several very helpful suggestions and critiques. He also wishes gratefully to acknowledge the generous encouragement given by Professors F. Seitz and J. H. Van Vleck and the interesting discussions with Dr. F. Fumi.

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[26] Y. Y. Li, Phys. Rev. **80**, 457 (1950).

TABLE IV. Bond eigenfunctions of a benzene ring.

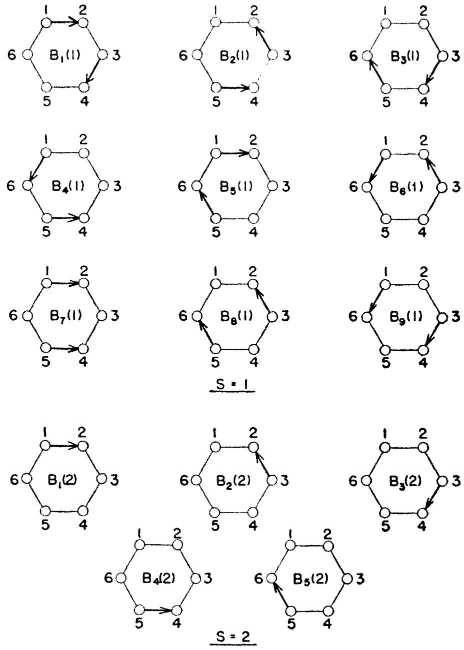

TABLE V. The eigenfunctions of a benzene ring.

| $S_1$ | $\psi_j(S_1)$ | $E_j(S_1)/J$ | $d_j(S_1)$ |
|---|---|---|---|
| 3 | $\psi(3)=B(3)$ | $-3.00$ | 1/3 |
| 2 | $\psi_1(2)=B_1(2)+B_3(2)+B_5(2)$ | 1.00 | 1/3 |
| | $\psi_2(2)=B_1(2)-B_2(2)-B_4(2)+B_5(2)$ | 0.00 | 1/2 |
| | $\psi_3(2)=B_1(2)+B_2(2)-B_4(2)-B_5(2)$ | 0.00 | 1/2 |
| | $\psi_4(2)=B_1(2)-B_2(2)+B_4(2)-B_5(2)$ | $-2.00$ | 1/2 |
| | $\psi_5(2)=B_1(2)-3B_2(2)+4B_3(2)-3B_4(2)+B_5(2)$ | $-2.00$ | 1/6 |
| 1 | $\psi_1(1)=f_1(1)-1.235f_2(1)$ | 4.236 | 1/3 |
| | $\psi_2(1)=f_1(1)+3.236f_2(1)$ | 0.236 | 1/3 |
| | $\psi_3(1)=B_1(1)-B_3(1)-B_4(1)+B_6(1)$ | 2.00 | 1/2 |
| | $\psi_4(1)=B_1(1)+2B_2(1)+B_3(1)-B_4(1)-2B_5(1)-B_6(1)$ | 2.00 | 1/6 |
| | $\psi_5(1)=f_5(1)-1.561f_7(1)$ | 2.561 | 0.4500 |
| | $\psi_6(1)=f_6(1)+1.561f_8(1)$ | 2.561 | 0.2167 |
| | $\psi_7(1)=f_5(1)+2.562f_7(1)$ | 1.561 | 0.4934 |
| | $\psi_8(1)=f_6(1)-2.562f_8(1)$ | 1.561 | 0.1733 |
| | $\psi_9(1)=B_1(1)-B_2(1)+B_3(1)-B_4(1)+B_5(1)-B_6(1)$ | $-1.00$ | 1/3 |

with $f_1(1)=B_1(1)+B_2(1)+B_3(1)+B_4(1)+B_5(1)+B_6(1)$
$f_2(1)=2\{B_7(1)+B_8(1)+B_9(1)\}$
$f_5(1)=B_7(1)-B_8(1)$
$f_6(1)=B_7(1)+B_8(1)-2B_9(1)$
$f_7(1)=B_1(1)-B_3(1)+B_4(1)-B_6(1)$
$f_8(1)=B_1(1)-2B_2(1)+B_3(1)+B_4(1)-2B_5(1)+B_6(1)$.

## APPENDIX: THE ENERGY LEVELS AND EXPECTATION VALUES OF THE FIRST-SHELL OF A BETHE CLUSTER OF A HEXAGONAL LAYER

The 6 atoms in the first shell of our cluster form a benzene ring, the exchange energy of which has been obtained by Serber[27] using algebraic methods. Unfortunately, we need not only the energy levels but also the expectation values of $\tau_1$ and $\tau_2$. Therefore, we must obtain the eigenfunctions of the energy states. The method of achieving this aim has been well developed by Eyring *et al.*[28] The calculations are cut short by using some knowledge of the theory of groups. The six-atom configuration as 20 $S_1$-states: One with $S_1=3$, five with $S_1=2$, nine with $S_1=1$, and five with $S_1=0$, and so the same numbers of bond eigenfunctions corresponding to these are used. They are listed in the following table. Each $S_1$-state is $(2S_1+1)$ fold degenerate. When the $z$-component of $S_1$ is $+1$, the function $B_1(2)$ listed in Table IV is actually $B_1(S_1=2)=(a_1u_1^+b_2u_2^- - a_2u_2^+b_1u_1^-)c_3u_3^+d_4u_4^+e_5u_5^+f_6u_6^-$ + all possible terms of different permutations among the functions of the atoms 3, 4, 5, and 6, where $a$, $b$, $c$, $d$, $e$, and $f$ are the orbital functions. The bond (indicated by an arrow in Table IV) between two electrons requires their taking only antiparallel spins in each term of $B(S_1)$. Following the method of Eyring *et al.*, we have found the eigenfunctions of the exchange energy $-2J(\mathbf{s}_1\cdot\mathbf{s}_2+\cdots+\mathbf{s}_6\cdot\mathbf{s}_1)$ and the expectations of $\tau_1$ and $\tau_2$ as given in Table V. Those for $S_1=0$ states are not shown there, since they are not involved in our calculations. The energy level agrees, of course, with Serber's value except for a shift of the zero level. The eigenfunctions of a degenerate level are chosen, such that they are also eigenfunctions of both $\tau_1$ and $\tau_2$.

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[27] R. Serber, J. Chem. Phys. 2, 697 (1934).

[28] Eyring, Frost, and Turkevich, J. Chem. Phys. 2, 777 (1934); Eyring, Walter, and Kimball, *Quantum Chemistry* (John Wiley and Sons, Inc., New York, 1944).