A straightforward calculation along the lines of the previous case leads to the following result for the probability of photon emission in a direction **k** into the solid angle $d\Omega$.

$$dP' \simeq [e^2\mu^2/2][1/(2\pi)^2] \times [(\kappa v^2-1)/\kappa][(\kappa)^{\frac{1}{2}}/(1+\kappa)]d\Omega. \quad (100)$$

The conservation of momentum and energy give for the angle α of the direction of the emitted photon with the velocity v

$$\cos\alpha \simeq -[v^0/2mv]k-[1/(\kappa v^2)^{\frac{1}{2}}].$$

Thus for $d\Omega$ we may write

$$d\Omega = \sin\alpha d\alpha d\varphi = (v^0/2vm)dkd\varphi.$$

If we calculate the total momentum transferred to the electron per unit time, we find the expression

$$F=-\int k\cos\alpha dP'$$

or for the ith component,

$$F_i=[e^2\mu^2/4\pi][1/(1+\kappa)] \times [(\kappa v^2-1)/\kappa v^3]v_i\int kdk. \quad (101)$$

This expression is identical with the classical expression obtained in Eq. (77) for the static self-force of an electron at rest in a moving medium.

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The Application of the Bethe-Peierls Method to Ferromagnetism*

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The method introduced by Bethe and Peierls for treating the problem of order-disorder in alloys is applied to the problem of ferromagnetism. The method is first applied to the Ising model of the spin in which case the treatment is much the same as it is for the alloy problem, as has already been pointed out by Peierls. The correct treatment of the spin is used for spin values of $\frac{1}{2}$ and 1 per atom. The critical temperatures of different types of lattices are investigated. The method gives results in agreement with the rigorous results of the Bloch spin-wave theory in that only three-dimensional lattices are found to be ferromagnetic. The values of the critical temperatures of these lattices are found to lie between the values predicted by the two Heisenberg approximations. The discontinuity of the specific heat at the critical temperature is computed for a body-centered lattice and for the two values of the spin. The magnitude of the discontinuity is larger than that predicted by Heisenberg's first approximation. The magnitude for the spin 1 is 3.4 k per atom and compares favorably with the experimental value for iron. The susceptibility is computed as a function of the temperature above the critical point. The variation of the susceptibility with temperature does not obey the Curie-Weiss Law but displays some curvature. This curvature explains qualitatively the difference between the "paramagnetic" and ferromagnetic critical temperatures and also helps remove some of the discrepancy between the number of Bohr magnetons per atom as measured at high and low temperatures.

I. INTRODUCTION

THE calculations described below are based on the physical model of ferromagnetism first introduced by Heisenberg.[1] This model can be described briefly as follows. Each atom in a domain has a spin **S** which is the resultant of the spins of individual electrons (or holes) residing in an incomplete inner shell. The orbital moment is quenched so that the magnetization arises entirely from the spins and is, in the first approximation, isotropic. The exchange interaction integral is significant only when it refers to electrons in neighboring atoms and is the same for all such pairs of atoms of the domain. The exchange integral, J, is positive. The incomplete inner shell referred to is, in iron, nickel, and cobalt, the 3-d shell and, in gadolinium, the 4-f shell. It is also assumed in this model that all

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* Some of the developments reported here are contained in a thesis submitted in 1940 in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Harvard University. These developments are also contained in a review article, J. H. Van Vleck, Rev. Mod. Phys. **17**, 27 (1945).

[1] W. Heisenberg, Zeits. f. Physik **49**, 619 (1928).

atoms are in the same atomic state so that the same spin quantum number applies to all atoms. Measurements at low temperatures on the saturation intensity of magnetization show the number of contributing spins per atom to be nonintegral. The model, therefore, is not complete but does have the virtue of simplicity from a mathematical point of view.

The spin-dependent part of the exchange interaction can be shown to be, in vector form,

$$\mathbf{H} = -2J \sum_{i>j} \mathbf{S}_i \cdot \mathbf{S}_j, \tag{1}$$

where J is the exchange integral, i and j refer to neighboring atoms, and the summation is taken over all N atoms of the domain. The solution of this Hamiltonian for the energy levels is practically impossible, and consequently several approximation schemes have been tried. The most notable of these are the two Heisenberg[2] approximations and the method of spin waves introduced by Bloch.[3] The latter method, which is rigorous at very low temperatures, shows that only three-dimensional lattices can display ferromagnetism. The criteria arrived at by the Heisenberg approximations can be expressed in the coordination number of lattice (the number of nearest neighbors about any one atom). In the first approximation, which neglects entirely the spread of energy levels, every lattice type becomes ferromagnetic at sufficiently low temperatures; in the second approximation, in which the energy levels are distributed according to a Gaussian distribution about the mean value, the criterion is simply that the coordination number must be equal to or greater than eight.

A different type of approximation is afforded by the method introduced by Bethe[4] and Peierls[5] in connection with the theory of order-disorder transformations in binary substitution alloys. The method can be described in terms of the present problem as follows. An arbitrary atom of a domain, the central atom, and its immediate neighbors $2n$ in number ($2n$ = the coordination number) are considered in detail. The exchange energy (1) of this cluster which consists of only a few atoms can be diagonalized in a correct fashion. The interaction of the neighbor atoms with those outside the cluster and of the remaining atoms with each other are replaced by an internal field, H_1, which acts on the atoms of the first shell alone, and not on the central atom. The internal field H_1 is determined by the condition that the average magnetic moment of the central atom in an applied magnetic field H_0 is to be the same as the average magnetic moment of an atom of the first shell in this field since, actually, there is no distinction to be made between the central atom and an atom in the first shell. The two fields are in the same direction since, in this approximation, directional effects are being neglected. The critical temperature is determined as that temperature below which the internal field does not vanish in the absence of an externally applied field.

Conceptually, this is the first of a series of approximations. At each stage an additional shell is included in the part which is treated rigorously, the remaining interactions being replaced by an internal field which acts only on the outermost shell. The second of this set has been carried through in the problem of alloys and yields results only slightly different from the first. Presumably the series converges rapidly which may be assumed to be true in the present problem as well. It should be remarked that this approach imposes the character of the transformation at the critical point, namely, that of a transformation of the second kind, in which the specific heat is discontinuous. On the other hand, the very first approximation includes more properties of the lattice than the coordination number because the structure of the first shell has a direct bearing on the exchange energy of the cluster. Moreover, the results of this method are different from those of the Heisenberg procedure since this method yields different approximations to the higher (than second) moments of the distribution function.

II. THE ISING MODEL**

The simplest application of the method lies in the use of the Ising[6] model of the spin. In this

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[2] See J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, Teddington, 1932), Chap. XII.

[3] F. Bloch, Zeits. f. Physik **61**, 206 (1930).

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

[5] R. Peierls, Proc. Roy. Soc. **154**, 207 (1936).

** After this had been submitted, a paper by U. Firgau (Ann. d. Physik **40**, 295 (1941)) came to my attention. This contains the results of Section II and uses a method identical with that of Bethe and Peierls.

[6] E. Ising, Zeits. f. Physik **31**, 253 (1925).

model the spin per atom is $\frac{1}{2}$ and the off-diagonal elements of the matrix representatives of the spin operators in (1) are equated to zero. This means that each spin is oriented either parallel to or anti-parallel to an applied field. Peierls[7] has already remarked that with this model of the spin, the mathematical problem of ferromagnetism is the exact parallel to that of order-disorder in alloys. For this reason the mathematical development of this section parallels closely the treatment of Bethe.[5]

In the presence of the applied field H_0 in the z direction, the Hamiltonian is

$$H=-2JS_{0z}S_{1z}-g\beta S_{0z}H_0-g\beta S_{1z}H_1. \tag{2}$$

Here g is the spin g-factor $(=2)$, β is the Bohr magneton $e\hbar/2mc$. S_{0z}, S_{1z} are the z-components of the spins of the central atom and of the first shell. S_{0z} has the values $\pm\frac{1}{2}$ while S_{1z} assumes the values $-(n)$, $-(n-1)\cdots+(n)$. The number of states associated with a given value of S_{1z} is just the number of ways in which $(S_{1z}+n)$ spins pointing parallel to H_0 can be arranged on the $(2n)$ sites, or

$$w(S_{1z})=(2n)!/(S_{1z}+n)!(n-S_{1z})!. \tag{3}$$

For convenience in writing we replaced $g\beta H_0$ and $g\beta H_1$ by H_0 and H_1; kT by T, and set

$$x_0=\exp\frac{H_0}{2T},\quad x_1=\exp\frac{H_1}{2T},\quad y=\exp\frac{J}{2T}. \tag{4}$$

The partition function is

$$P=\sum w(S_{1z})\left\{\frac{1}{x_0}\left(\frac{y}{x_1}\right)^{2S_{1z}}+x_0(x_1y)^{-2S_{1z}}\right\}, \tag{5}$$

with the summation taken between the limits $S_{1z}=-n$ and $S_{1z}=+n$. The summation can be performed and is

$$P=\frac{1}{x_0}\left\{\frac{x_1}{y}+\frac{y}{x_1}\right\}^{2n}+x_0\left\{yx_1+\frac{1}{yx_1}\right\}^{2n}. \tag{6}$$

The average magnetic moments of the central atom $\bar{m}_0$ and of an atom in the first shell $\bar{m}_1$, in the direction of H_0 are, according to the rules of statistical mechanics,

$$\bar{m}_0=\beta x_0\frac{\partial}{\partial x_0}\ln P \quad\text{and}\quad \bar{m}_1=\beta\frac{1}{2n}x_1\frac{\partial}{\partial x_1}\ln P, \tag{7}$$

accordingly,

$$P\frac{\bar{m}_0}{\beta}=x_0\left\{yx_1+\frac{1}{yx_1}\right\}^{2n}-\frac{1}{x_0}\left\{\frac{y}{x_1}+\frac{x_1}{y}\right\}^{2n}, \tag{8a}$$

$$P\frac{\bar{m}_1}{\beta}=x_0\left\{yx_1+\frac{1}{yx_1}\right\}^{2n-1}\left\{yx_1-\frac{1}{yx_1}\right\}$$
$$+\frac{1}{x_0}\left\{\frac{y}{x_1}+\frac{x_1}{y}\right\}^{2n-1}\left\{\frac{x_1}{y}-\frac{y}{x_1}\right\}. \tag{8b}$$

H_1 is determined by setting

$$\bar{m}_1=\bar{m}_0. \tag{9}$$

In the region below the critical point it is sufficient to consider these quantities in the limit of vanishing external field, $x_0=1$. This yields

$$\left(yx_1+\frac{1}{yx_1}\right)^{2n-1}=x_1^2\left(\frac{y}{x_1}+\frac{x_1}{y}\right)^{2n-1}, \tag{10}$$

which after some manipulation can be separated to give

$$\exp\frac{J}{T}=\left[\sinh\frac{n}{2n-1}\frac{H_1}{T}\right]\bigg/\left[\sinh\frac{n-1}{2n-1}\frac{H_1}{T}\right]. \tag{11}$$

This is precisely the result which Bethe[5] obtains in the case of binary alloys. As there, the critical point is evidence by the fact that as the temperature increases from very low values, where $H_1\approx(2n-1)J$, the right-hand side of (10) approaches a minimum value of $(n)/(n-1)$. At this point H_1 vanishes (i.e., the intensity of magnetization vanishes) in the absence of H_0. The temperature where this occurs is

$$J/T_c=\ln 2n/(2n-2)=\ln n/(n-1). \tag{12}$$

In the temperature region immediately below the critical point the internal field is given by

$$\left(\frac{H_1}{2T}\right)^2\approx\frac{3}{2n}(2n-1)(n-1)\left(\exp\frac{J}{T}-\exp\frac{J}{T_c}\right). \tag{13}$$

To the same degree of approximation, the relative intensity of magnetization

$$\zeta=\bar{m}_0/\beta, \tag{14}$$

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[7] R. Peierls, Proc. Camb. Phil. Soc. 32, 477 (1936).

is given by

$$\zeta \approx \frac{2n}{2n-1}\left(\frac{H_1}{2T}\right)$$

or,

$$\zeta \approx \frac{2n}{2n-1}\left\{\frac{3}{2n}(2n-1)(n-1) \times\left(\exp\frac{J}{T}-\exp\frac{J}{T_c}\right)\right\}^{\frac{1}{2}}, \quad (15)$$

so that the saturation intensity of magnetization increases below the critical point as the square root of the temperature departure from the critical temperature. The complete expression for ζ is

$$\zeta = \tanh(n/2n-1)(H_1/T), \quad (16)$$

as can be seen from the first of (8) and from (9). Thus ζ has the same behavior below the critical point as does the long distance order, S, in reference 5.

The consideration of the energy per atom is somewhat different in the present case since there is no convenient parameter which takes the place of that which describes the *local* order in alloys. This is to be expected since the numbers of the two different types of atoms is fixed in the alloy while here the numbers of the atoms parallel and anti-parallel to the fields change as the temperature decreases from the critical point. In view of this, it is rather surprising that, as will be shown, the discontinuities in the specific heat at the critical temperatures are the same in the two cases for the same lattice types. The total energy of a domain consisting of N atoms can be obtained as follows. Suppose there are N_1 spins which point parallel to and $N_2 = N - N_1$ spins which point anti-parallel to a given direction. If n_1 is the average number of atoms neighboring a parallel type which are also parallel, and if n_2 is the average number of atoms neighboring an anti-parallel type which are also anti-parallel, then the total number of different neighboring pairs which are aligned parallel to each other is

$$\tfrac{1}{2}(N_1 n_1 + N_2 n_2).$$

The total number of different pairs is $\frac{1}{2}Nz$ and, therefore, the number of different pairs which are aligned oppositely to each other is

$$\tfrac{1}{2}[Nz - (N_1 n_1 + N_2 n_2)].$$

The energy for a pair which are similarly aligned is $-\frac{1}{2}J$; for a pair which are oppositely aligned $+\frac{1}{2}J$. The total energy is then

$$E = -\tfrac{1}{2}J(N_1 n_1 + N_2 n_2) + (1/4)NzJ. \quad (17)$$

N_1 and N_2 are determined by the intensity of magnetization

$$N_1 = \tfrac{1}{2}N(1+\zeta), \quad N_2 = \tfrac{1}{2}N(1-\zeta). \quad (18)$$

n_1 is given by

$$n_1 = \frac{\sum \binom{2n}{k} \exp\frac{1}{T}(J+H_1)(k-n)}{\sum \binom{2n}{k} \exp\frac{1}{T}(J+H_1)(k-n)}. \quad (19)$$

The limits in the summations are $k=0$ and $(2n)$. A similar expression obtains for n_2 although here the sign of H_1 is reversed. The results are

$$n_{1,2} = n\left(1+\tanh\frac{J \pm H_1}{2T}\right). \quad (20)$$

The total energy is, except for a term independent of ζ and H_1,

$$E = -\frac{n}{4}NJ\left\{(1+\zeta)\tanh\frac{J+H_1}{2T} + (1-\zeta)\tanh\frac{J-H_1}{2T}\right\}. \quad (21)$$

The energy per atom is $E/N = \epsilon$. Above the critical point the energy is

$$\epsilon_0 = -(n/2)J\tanh(J/2T). \quad (22)$$

On expanding the tanh functions in $(H/2T)$ and in using (11) and (14) the energy immediately below the critical point is

$$\epsilon - \epsilon_0 = \frac{2n^2(n-1)}{(2n-1)^2}J\left(\frac{H}{2T}\right)^2. \quad (23)$$

The discontinuity in the specific heat is

$$\Delta C/k = \left(\frac{\partial}{\partial T}(\epsilon - \epsilon_0)\right)_{T=T_c} = \frac{3n^2(n-1)}{(2n-1)}\left(\ln\frac{n}{n-1}\right)^2. \quad (24)$$

III. ENERGY LEVELS OF THE CLUSTER

An advantage of the present method is that the Hamiltonian of the cluster can be dealt with in a correct fashion without invoking an approximate model of the spin as was done in the previous section. The Hamiltonian is

$$\mathbf{H}_0=-2J\sum_{i>j}\mathbf{S}_i\cdot\mathbf{S}_j-S_{0z}H_0-S_{1z}H_1,\quad(25)$$

where we have replaced $g\beta H_0$ by H_0 and $g\beta H_1$ by H_1. The summation is taken over the $(2n+1)$ atoms of the cluster and can be written as

$$\mathbf{S}_0\cdot\sum_{j=1}^{2n}\mathbf{S}_j+\sum_{i>j}\mathbf{S}_i\cdot\mathbf{S}_j=\mathbf{S}_0\cdot\mathbf{S}_1+\sum_{i>j}\mathbf{S}_i\cdot\mathbf{S}_j.\quad(26)$$

$\mathbf{S}_1$ is the spin of the combined first shell; the second summation takes account of interactions within the first shell. This interaction is absent in the linear chain, the quadratic layer lattice, the simple cubic, and body-centered lattices. In the hexagonal layer lattice, each atom of the first shell has two of its six nearest neighbors in that shell; in the face-centered lattice, each atom of the first shell interacts with four other atoms of the first shell. The simplest cases are those for which such interactions are absent and these are considered first.

The vector model yields the energy values

$$\begin{array}{ll}E-_{\text{exch}}=+J(S_1+1), & S=S_1-\frac{1}{2},\\ E+_{\text{exch}}=-JS_1, & S=S_1+\frac{1}{2}.\end{array}\quad(27\text{a})$$

When the spin per atom is $\frac{1}{2}$ and

$$\begin{array}{ll}E-_{\text{exch}}=+2J(S_1+1), & S=S_1-1,\\ E^0{}_{\text{exch}}=-2J, & S=S_1,\\ E+_{\text{exch}}=-2JS_1, & S=S_1+1,\end{array}\quad(27\text{b})$$

when the spin per atom is 1. A system of representation is used in which the exchange energy is diagonal. m is the magnetic quantum number of the total spin $S=S_0+S_1$. When the spin per atom is $\frac{1}{2}$ the levels are:

$$W=-JS_1\mp\tfrac{1}{2}(2S_1H_1+H_0),\quad(28\text{a})$$

for $m=\pm(S_1+\frac{1}{2})$ and when $|m|\leq(S_1-\frac{1}{2})$ the matrix is

$$\begin{pmatrix}A_a & B\\ B & A_p\end{pmatrix},\quad(28\text{b})$$

with

$$A_a=J(S_1+1)-mH_1-\frac{m}{2S_1+1}(H_1-H_0),$$

$$A_p=-JS_1-mH_1+\frac{m}{2S_1+1}(H_1-H_0),\quad(28\text{c})$$

$$B=\frac{1}{2}\left[1-\frac{4m^2}{(2S_1+1)^2}\right]^{\frac{1}{2}}(H_1-H_0).$$

The Hamiltonian is more complicated when the spin per atom is 1. First, it is of third rather than second order and second, there is a degeneracy in the exchange energy when $S_1=1$ for the levels $S=S_1+1$ and $S=S_1$. Because of these difficulties, a discussion of this Hamiltonian is reserved for an appendix.

The secular equation for the levels belonging to the matrix (25) is of second degree and consequently the expressions for the energy levels contain a complicated square root of a sum of terms involving J, H_1, and H_0. Numerical computations of the intensity of magnetization are difficult to perform when these expressions are used. The internal field is small in the immediate vicinity of the critical temperature and a series expansion in terms of H/J is possible in this temperature region. This expansion permits the computation of the critical temperature, of the variation of the susceptibility with temperature, and of the discontinuity in the specific heat. It is necessary to include terms in the fourth powers of H/J although the computation of the critical temperature and of the susceptibility require only terms through the second degree in H/J. The levels are, for a spin of $\frac{1}{2}$,

$$\begin{aligned}W_k(S_1m)=A_k&+b_kH_1+c_k(H_1-H_0)\\&+d_k(H_1-H_0)^2+e_k(H_1-H_0)^3\\&+f_k(H_1-H_0)^4.\quad(29)\end{aligned}$$

$k=1$, 2 corresponds to the anti-parallel and parallel alignments of the spins of the central atom and of the first shell. A corresponding expression to be given in the appendix applies as well for the case of a spin of 1. The coefficients

TABLE I. Ratio of exchange integral to critical temperature (J/kT_c) for different lattice types as computed by different approximations.

Lattice	Number of nearest neighbors	Spin per atom	Heisenberg App.		Present method
			I	II	
Linear chain	2	½	1.000	None	None
Quadratic layer	4	½	0.500	None	None
Simple cubic	6	½	0.333	None	0.540
Hexagonal layer	6	½	0.333	None	None
Body-centered	8	½	0.250	0.500	0.3445
Modified body-centered	8	½	0.250	0.500	0.4620
Body-centered	8	1	0.0937		0.1502

here are

$$\begin{aligned}
&A_1=J(S_1+1);\quad A_2=-JS_1;\quad b_1=b_2=-m,\\
&c_{1,2}=\mp\frac{m}{(2S_1+1)},\\
&d_{1,2}=\pm\frac{1}{4J(2S_1+1)}\left(1-\frac{4m^2}{(2S_1+1)^2}\right),\\
&e_{1,2}=\pm\frac{m}{2J^2(2S_1+1)^3}\left(1-\frac{4m^2}{(2S_1+1)^2}\right),\\
&f_{1,2}=\mp\frac{1}{16J^3(2S_1+1)^3}\\
&\qquad\times\left(1-\frac{24m^2}{(2S_1+1)^2}+\frac{80m^4}{(2S_1+1)^4}\right).
\end{aligned}\tag{30}$$

IV. THE CRITICAL TEMPERATURE

The partition function of the cluster is

$$P=\sum w(2n,S_1)\left\{\sum \exp-\frac{1}{T}W_1(S_1m)\right.\\
\left.+\sum \exp-\frac{1}{T}W_2(S_1m)\right\}.\tag{31}$$

The first summation is over S_1 from 0 to n; the first of the inner summations is over m from $m=-(S_1-\frac{1}{2})$ to $m=+(S_1-\frac{1}{2})$; the second of the inner summations is over m from $m=-(S_1+\frac{1}{2})$ to $m=+(S_1+\frac{1}{2})$. The multiplicities $w(2n, S_1)$ of the different S_1 levels are obtained from the branching rule expressed in the formula

$$w(2n,S_1)=\frac{(2n)!}{(n-S_1)!(n+S_1)!}\\
-\frac{(2n)!}{(n-S_1-1)!(n+S_1+1)!},\tag{32}$$

for a spin $\frac{1}{2}$ and

$$w(2n,S_1)=L(S_1)-L(S_1+1),$$

with

$$L(S_1)=\text{coefficient of } X^{S_1} \text{ in } (X+1+X^{-1})^{2n},\tag{33}$$

for a spin 1. The parts of the exponentials containing the field strengths can be expanded in power series, again preserving terms through the fourth powers. The average magnetic moments of the central atom and of an atom in the first shell are found by

$$m_0=-g\beta T\frac{\partial}{\partial H_0}\ln P.\quad m_1=-\frac{1}{2n}g\beta T\frac{\partial}{\partial H_1}\ln P.\tag{34}$$

The field H_0 can be taken to be zero in the resulting expressions in the computation of the critical temperature; both moments then have terms in H_1 and $H_1{}^3$. The consistency requirement (9) yields the equation which determines H_1

$$A+CH_1{}^2=0,\tag{35}$$

one factor of H_1 having been canceled from each term. This indicates that $H_1=0$ is one (an unstable one) solution. The quantities A and C are:

$$A=\sum_{k=1}^{2}\sum_{S_1}w(2n,S_1)\left\{A_k{}^0+\frac{A_k{}^1}{T}\right\}\\
\times\exp-\frac{A_k}{T},\tag{36}$$

$$\begin{aligned}
C&=\sum_{k}\sum_{S_1}w(2n,S_1)\left\{C_k{}^0+\frac{1}{T}C_k{}^1\right.\\
&\qquad\left.+\frac{1}{T^2}C_k{}^2+\frac{1}{T^3}C_k{}^3\right\}\exp-\frac{A_k}{T},\\
A_k{}^0&=\sum_m(-2d_k),\\
(1+2n)A_k{}^1&=\sum_m\{(b_k+c_k)^2+2nc_k(b_k+c_k)\},\\
C_k{}^0&=\sum_m(-4f_k),\\
(1+2n)C_k{}^1&=\sum_m\{2(1+2n)d_k{}^2+(4+6n)e_kb_k\\
&\qquad+4(1+2n)e_kc_k\},\\
-(1+2n)C_k{}^2&=\sum_m\{2d_k(b_k+c_k)^2\\
&\qquad+2nd_k(b_k+c_k)(b_k+2c_k)\},\\
6(1+2n)C_k{}^3&=\sum_m\{(b_k+c_k)^4+2nc_k(b_k+c_k)^3\}.
\end{aligned}\tag{37}$$

The sums are to be taken with $|m| \leq (S_1 - \frac{1}{2})$ for $k=1$ and $|m| \leq (S_1 + \frac{1}{2})$ for $k=2$. Only terms in even powers of m are involved because sums over odd powers vanish. The summations can be performed by using

$$\sum_{m=-T}^{+T} 1 = 2T+1;$$

$$\sum_{m=-T}^{+T} m^2 = \tfrac{1}{3}T(T+1)(2T+1);$$

and

$$\sum_{m=-T}^{+T} m^4 = \frac{1}{15}T(T+1)(3T^2+3T-1). \tag{38}$$

The complexity of the expressions (36) and (37) arises from the off-diagonal elements of the matrix representatives of the spins. It is not possible to perform the summations over S_1 in closed form and computation shows it is not possible to neglect those terms which arise from the off-diagonal elements. In fact, it is primarily these terms which give results concerning the critical temperature which are different from the Ising model, and from the Heisenberg approximations.

The critical point is found by numerical computation as the temperature for which A of (35) and (36) changes its sign. Each lattice requires a separate computation number. The critical temperatures provided by Heisenberg's first and second approximations for a spin of $\frac{1}{2}$

$$(J/T_c)_I = 1/n, \quad (J/T_c)_{II} = \frac{1}{2}\left[1-\left(1-\frac{4}{n}\right)^{\frac{1}{2}}\right], \tag{39}$$

provide useful starting points. The results of the computation for several lattice structures are shown in Table I.

The hexagonal layer lattice and the modified body-centered lattice contain interactions between atoms in the first shell. The exchange energy for the configuration presented by the first shell of the hexagonal layer lattice has been solved by Serber.[8] The levels in units of J along with their multiplicities are:

$S_1=0$	$S_1=1$	$S_1=2$	$S_1=3$	
-4.606 (1)	-4.561 (2)	-5.000 (2)	-6.000 (1)	(40)
-2.000 (2)	-4.000 (1)	-3.000 (2)		
$+2.606$ (1)	-3.236 (1)	-2.000 (1)		
	-1.000 (2)			
	-0.4385 (2)			
	$+1.236$ (1)			

To these must be added the interaction of the central atom with the first shell $+(S_1+1)$ and $-S_1$ for the anti-parallel and parallel alignments respectively. The corresponding values of A_p and A_{ap} can be inserted into (36). The "modified" body-centered lattice is an imaginary one in which the eight atoms of the first shell are divided into two groups of four; in each group all atoms are nearest neighbors to each other but not to any of the atoms of the other group. This is an artificial lattice imagined in order to try to determine the effect of the interactions inside the first shell on the critical temperature. The exchange energy is

$$\mathbf{H}_{\text{exch}} = -2J\mathbf{S}_0\cdot\mathbf{S}_1 - 2J\sum_{i>j=1}^{4}\mathbf{S}_i\cdot\mathbf{S}_j - 2J\sum_{i>j=5}^{8}\mathbf{S}_1\cdot\mathbf{S}_j, \tag{41}$$

$$W_{\text{exch}} = -2JS_0\cdot S_1 - J\{S_1'(S_1'+1)-3\} - J\{S_1''(S_1''+1)-3\}.$$

Here S_1', S_1'' are the total spin numbers of the two groups of four atoms. The terms independent of spin can be dropped; the energies are:

$$\begin{aligned} A_p &= -J\{S_1+S_1'(S_1'+1)+S_1''(S_1''+1)\}, \\ A_{ap} &= +J\{(S_1+1)-S_1'(S_1'+1) - S_1''(S_1''+1)\}. \end{aligned} \tag{42}$$

The summation over the S_1 levels must be taken as

$$\sum_{S_1}^{4}\sum_{S_1'}^{S_1-S_1''}\sum_{S_1''}^{2} w(4,S_1')w(4,S_1'')\exp -\frac{1}{T}A_k, \tag{43}$$

with $S_1 = S_1'-S_1''\cdots S_1'+S_1''$. The w factors are computed with (32) using $2n=4$, as indicated.

The results as shown in Table I are notable in that of the lattice types investigated only those which are three-dimensional display a critical temperature. This is in agreement with the rigorous results of the Bloch theory and, perhaps, attests the effectiveness of the present method. Also, the critical temperatures found lie between the two Heisenberg approximations, the second of which is known to overemphasize the dispersion of the energy levels. The method also takes into account in the first approximation the inter-

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

action inside the first shell. In this respect, it takes into account some terms which enter first in the moment method only in the third power of the energy. The critical temperature is found to be lower in the modified than in the actual body-centered lattice. The interaction inside the first shell serves merely to increase the *local* order and does not serve to increase the long-distance order.

V. THE DISCONTINUITY IN THE SPECIFIC HEAT

The discontinuity in the specific heat at the critical temperature is one of the properties of ferromagnetics through which the theory can be compared with experiment. Actually, this is complicated by the fact that it is not certain, on the basis of measurements of the specific heat, that the transformation is one of the second kind. Usually, the specific heat falls sharply on the high temperature side of the critical point but not in the fashion required for this type of transformation. This essential feature is easily obscured by non-uniformity of temperature in the samples. At any rate, the usual practice is to extrapolate back to the critical point from the high temperature side and to measure the discontinuity from this point to the maximum value of the specific heat reached on increasing the temperature from below the critical point.

The average energy of a domain of N atoms is, since there are N central atoms

$$E=\tfrac{1}{2}N(-2J)\langle S_0\cdot S_1\rangle_{\text{Av}}=\tfrac{1}{2}NJ\{\langle S(S+1)\rangle_{\text{Av}} -\langle S_1(S_1+1)\rangle_{\text{Av}}-S_0(S_0+1)\}. \quad (44)$$

The angular brackets denote ensemble averages and the factor of ½ is inserted since otherwise the interaction energy of each pair would be counted twice. These expressions are valid for lattice types in which the atoms of the shell do not interact with each other; the modifications necessary to take such interactions into account are obvious. The numerical computation of the discontinuity in the specific heat have been carried through for the body-centered lattice for the two spin values ½ and 1. The expression (44) agrees with the development in Section II when the specialization required by the Ising model of the spin is made: $S(S+1)$ and $S_1(S_1+1)$ are replaced by S^2 and S_1^2 respectively. The ensemble averages are, for the case of a spin value of ½,

$$P(\langle S(S+1)\rangle_{\text{Av}}-\langle S_1(S_1+1)\rangle_{\text{Av}})=\sum_{S_1} w(2n, S_1) \times\{(S_1-\tfrac{1}{2})(S_1+\tfrac{1}{2})-S_1^2-S_1\}\sum_m \times\exp\frac{1}{T}W_1(m, S_1)+\sum_{S_1} w(2n, S_1) \times\{(S_1+\tfrac{1}{2})(S_1+\tfrac{3}{2})-S_1^2-S_1\}\sum_m \times\exp-\frac{1}{T}W_2(m, S_1). \quad (45)$$

TABLE II. Values of the discontinuity in the specific heat at the critical temperature per atom in units of k. The computed values are all based on a spin of 1 per atom and are for a body-centered lattice.

Heisenberg approx. I	Present method	Experiment
2.00	3.40	3.6

In the neighborhood of the critical point, the field dependent parts of the exponentials can be expanded in series in H_1. To terms in H_1^2 (45) is, except for a constant term which can be dropped,

$$P(\langle S(S+1)\rangle_{\text{Av}}-\langle S_1(S_1+1)\rangle_{\text{Av}}) =-\frac{1}{J}\{2P_0\epsilon_0+H^2P_3\}, \quad (46)$$

with:

$$2P_0\epsilon_0=\sum_k\sum_{S_1} w(2n, S_1)\sum_m A_k\exp-\frac{A_k}{T},$$

$$P_0=\sum_k\sum_{S_1} w(2n, S_1)\sum_m \exp-\frac{A_k}{T},$$

$$P_3=\sum_k\sum_{S_1} w(2n, S_1)\sum_m \times\left(\frac{J^2(b_k+c_k)^2}{2T^2}-\frac{J^2d_k}{T}\right)A_k\exp-\frac{A_k}{T}.$$

To this degree of approximation, the partition function P is

$$P=P_0+\frac{H^2}{J^2}P_2,$$

with

$$P_2=\sum_k \sum_{S_1} w(2n,\,S_1)\sum_m \times\left(\frac{J^2(b_k+c_k)^2}{2T^2}-\frac{J^2d_k}{T}\right)\exp-\frac{A_k}{T}. \quad (47)$$

The energy per atom is

$$\epsilon=\epsilon_0+\frac{1}{2}\frac{H^2}{J}\left(\frac{P_3}{P_0}-2\epsilon_0\frac{P_2}{P_0}\right), \quad (48)$$

numerical computation yields, for a spin of $\frac{1}{2}$,

$$\epsilon=\epsilon_0-(0.0498)\frac{H^2}{J}. \quad (49)$$

With the use of (35) one obtains, in this case,

$$\frac{H^2}{J}=221\left(\frac{J}{T}-\frac{J}{T_c}\right). \quad (50)$$

The discontinuity in the specific heat per atom is,

$$\Delta C/k=2.05. \quad (51)$$

The Ising model discussed in Section II yields the numerical value

$$\Delta C/k=1.71. \quad (52)$$

The computation for a spin 1 follows the same procedure. Here, however, the levels for $S=S_1$ make no contributions to the quantities ϵ_0 and P_3 in (46), so that in the summation over k, the term with $k=2$ must be omitted. One finds that

$$\left(\frac{H}{2J}\right)^2=404\left(\frac{J}{T}-\frac{J}{T_c}\right), \quad (53)$$

corresponding to (50) and

$$\epsilon=\epsilon_0-\left(\frac{H}{2J}\right)^2\cdot J(0.3740), \quad (54)$$

corresponding to (49). The discontinuity in specific heat per atom is

$$\Delta C/k=3.40.$$

The experimental data on the discontinuity in the specific heat is meager and not very consistent for iron. Stoner[9] quotes the values 3.4, 2.3, and 3.6 obtained by Weiss, Piccard, and Carrard, by Umino, and by Klinkhardt, respectively, and gives greatest weight to the value 3.6. The computed value of 3.4 compares very favorably with this. The Heisenberg first approximation leads to a value of 2.0 for $\Delta C/k$. The results are listed in Table II.

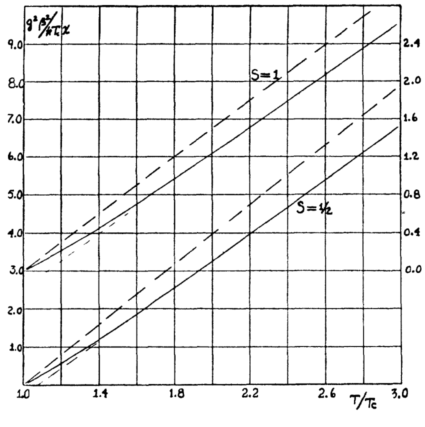

FIG. 1.

VI. THE SUSCEPTIBILITY

The internal field is zero in the temperature region above the critical temperature so long as the external field is absent. In the presence of an external field, however, the internal field is no longer zero because of the exchange interaction. It is because of this internal field that the Curie-Weiss Law is not obeyed immediately above the Curie Point. In fact, it is easily seen that the susceptibility is increased there by the exchange interactions and consequently the reciprocal of the susceptibility is decreased. Moreover, the ratio of the internal to the external field decreases with increasing temperature so that the reciprocal susceptibility *vs.* temperature curve is convex toward the temperature axis. The difference between the "paramagnetic" and "ferromagnetic" critical temperatures and the difference between the low and high temperature magneton numbers find a natural explanation in the present method.

It is legitimate to neglect saturation effects in this region and therefore the expressions for $\bar{m}_0$ and $\bar{m}_1$ as obtained from (34) need only retain first power terms in H_0 and H_1. Now, however, H_0 is not permitted to be zero. H_1 is replaced by $H_1=H_0+H$ in the expressions for $\bar{m}_0$ and $\bar{m}_1$. The

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[9] E. C. Stoner *Magnetism and Matter* (Methuen and Company, Ltd., London, 1934), p. 373.

internal field H is determined by the consistency requirement to be

$$AH_0+BH=0, \tag{55}$$

where A is defined by (36) and B is

$$(2n+1)TB=\sum_{k=1}^{2}\sum_{S_1}w(2n,S_1)\sum_{m}\times\{b_k^2+(2n+1)b_kc_k\}\exp-\frac{A_k}{T}. \tag{56}$$

It is more convenient in computation to deal with the moment of the entire cluster, $\bar{m}=\bar{m}_1(2n)+\bar{m}_0$ than with the moment $\bar{m}_0$ as obtained from (34) $\bar{m}_0$ is then obtained by

$$\bar{m}_0=(1/2n+1)\bar{m}. \tag{57}$$

The susceptibility is simply $g\beta\bar{m}_0/H_0$ since saturation effects are being neglected. It is

$$\frac{1}{2n+1}\frac{X_0}{g^2\beta^2}TP_0=\sum_{k}\sum_{S_1}w(2n,S_1)\sum_{m}b_k^2\times\exp-\frac{A_k}{T}+\frac{H}{H_0}\sum_{k}\sum_{S_1}w(2n,S_1)\times\sum_{m}b_k(b_k+c_k)\exp-\frac{A_k}{T}. \tag{58}$$

A corresponding expression is obtained when the spin per atom is 1. The computations have been carried through for the body-centered lattice for both spin values and the results are shown in Fig. 1, where $g^2\beta^2/X_0T_c$ is plotted as a function of T/T_c. The curvature is actually surprisingly small and consequently the curve could easily be taken as a straight line but with an intercept on the temperature axis different from the Curie temperature. This is called, generally, the "paramagnetic" critical temperature. In the case of a spin of $\frac{1}{2}$, the relation between the two critical temperatures is roughly $T_p\approx 1.05T_f$, the paramagnetic critical temperature is about 5 percent higher than the ferromagnetic one. For a spin 1, the curve gives $T_p\approx 1.03T_f$. If we ascribe a spin per atom of 1 for iron, this leads to a paramagnetic critical temperature which is about 30° higher than the ferromagnetic one, a value which is somewhat larger than that obtained experimentally. From the slopes of the curves, one can obtain p_B, the number of Bohr magnetons per atom. The values of p_B would be 1.73 and 2.83 for the spins $\frac{1}{2}$ and 1 respectively. The experimental value for iron[10] is higher than either of these and seems to lie between 3.5 and 4.0. The discrepancy has caused some concern since it implies that the number of contributing spins is different in the high and low temperature regions. Some of the discrepancy is removed by the present treatment, for the values of p_B obtained from the curves are 1.87 and 3.06 for spins $\frac{1}{2}$ and 1 respectively.

VII. CONCLUSION

The method, so far as it has been applied, is seen to lead to very satisfactory results. Of the various lattice types considered, only those which are three-dimensional have been found to display ferromagnetism. This is in agreement with rigorous results of the spin-wave treatment. Moreover, in the three-dimensional lattices the critical temperature is found to lie between the two Heisenberg approximations in which the first takes no account of this dispersion of the energy about the mean value and the second overemphasizes this dispersion. The method applied to the body-centered lattice with spin 1 per atom leads to a value for the discontinuity in the specific heat of 3.40 k per atom which is in fair agreement with the experimentally determined value of 3.6 k and in far better agreement than is the value obtained by Heisenberg's first approximation. It must be remarked, however, that the method leads to a transition of the second kind at the critical temperature although this has not been established satisfactorily by experiment. Finally, the method gives some explanation of the difference between the "paramagnetic" and ferromagnetic critical temperatures as being due to the persistence of local order of the spins above the Curie Point, even though the long-distance order is zero. The difference between the high-temperature and the low-temperature magneton numbers is partly explained in the same way.

The author is indebted to Professor J. H. Van Vleck for suggesting the problem and for some discussions concerning it.

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[10] See reference (9), page 379.

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APPENDIX

The system of representation of the Hamiltonian for a spin 1 used here is one which diagonalizes the exchange energy. When the magnetic quantum number $|m|\leq(S_1-1)$ the Hamiltonian is

$$\begin{pmatrix} A_1 & B & 0 \\ B & A_2 & C \\ 0 & C & A_3 \end{pmatrix}, \tag{59}$$

with

$$A_1=2J(S_1+1)-mH_1-\frac{m}{S_1}(H_1-H_0),$$

$$A_2=-2J-mH_1+\frac{m}{S_1(S_1+1)}(H_1-H_0),$$

$$A_3=-2JS_1-mH_1+\frac{m}{(S_1+1)}(H_1-H_0),$$

$$B=\frac{S_1+1}{S_1}\left\{\frac{S_1^2-m^2}{(S_1+1)(2S_1+1)}\right\}^{\frac{1}{2}}(H_1-H_0),$$

$$C=\frac{S_1}{S_1+1}\left\{\frac{(S_1+1)^2-m^2}{S_1(2S_1+1)}\right\}^{\frac{1}{2}}(H_1-H_0).$$

Here, as in the text, the factors $g\beta$ in the magnetic energy have been absorbed in H_0 and H_1. When $m=\pm S_1$ the matrix is of second order

$$\begin{pmatrix} A_2' & C' \\ C' & A_3' \end{pmatrix}, \tag{60}$$

with

$$A_2'=2J\mp S_1H_1\pm\frac{1}{(S_1+1)}(H_1-H_0),$$

$$A_3'=2JS_1\mp S_1H_1\pm\frac{S_1}{(S_1+1)}(H_1-H_0),$$

$$C'=\frac{1}{S_1+1}(S_1)^{\frac{1}{2}}(H_1-H_0),$$

when $m=\pm(S_1+1)$, the matrix has the one term

$$\begin{aligned} A_3''&=2JS_1\mp(S_1+1)H_1\mp(H_1-H_0) \\ &=2JS_1\mp S_1H_1\mp H_0. \end{aligned} \tag{61}$$

(59), (60), and (61) hold for all values of S_1 except $S_1=0$ and 1. When $S_1=0$, the exchange energy is zero and the total energy is only magnetic.

$$W=-mH_0,\quad m=0,\ \pm 1. \tag{62}$$

When $S_1=1$, there is a degeneracy in the exchange energy for the levels $S=S_1$ and $S=S_1+1$ and this case must be considered separately. S has the values 0, 1, 2 so that the Hamiltonian is of third order for $m=0$, of second order for $m=\pm 1$ and of first order for $m=\pm 2$. The energy levels can now be obtained through the fourth power terms in the field strengths and are

$$S_1=0,\qquad W=mH_0,$$

$$S_1=1,\quad m=0,\qquad W=4J+\frac{1}{9J}(H_1-H_0)^2 -\frac{1}{972J^3}(H_1-H_0)^4, \tag{63}$$

$$W=-2J\mp\frac{+1}{\sqrt{3}}(H_1-H_0) -\frac{1}{18J}(H_1-H_0)^2 \mp\frac{\sqrt{3}}{648J^2}(H_1-H_0)^3 +\frac{1}{1944J^3}(H_1-H_0)^4, \tag{64}$$

$$\begin{aligned} &S_1=1,\quad m=\pm 1,\quad W=-2J\mp H_0, \\ &\qquad\qquad\qquad\quad\ \ W=-2J\mp H_1, \end{aligned} \tag{65}$$

$$S_1=1,\quad m=\pm 2,\quad W=-2J\mp(H_1+H_0).$$

When $S_1>1$ the energy values are

$$W_k(S_1,m)=A_k+b_kH_1+c_k(H_1-H_0) +d_k(H_1-H_0)^2+e_k(H_1-H_0)^4 +f_k(H_1-H_0)^4, \tag{66}$$

where

$$A_1=2J(S_1+1),\quad A_2=-2J,\quad A_3=-2JS_1, \tag{67}$$

$$b_1=b_2=b_3=-m;\quad c_1=\frac{-m}{S_1},$$

$$c_2=\frac{+m}{S_1(S_1+1)},\quad c_3=+\frac{m}{S_1+1},$$

$$d_1=\frac{(S_1+1)}{2J(S_1+2)(2S_1+1)}\left(1-\frac{m^2}{S_1^2}\right),$$

$$\begin{aligned}d_2=\frac{1}{2J(2S_1+1)}\Bigg\{&\frac{S_1}{S_1-1}\left(1-\frac{m^2}{(S_1+1)^2}\right)\\&-\frac{S_1+1}{S_1+2}\left(1-\frac{m^2}{S_1^2}\right)\Bigg\},\end{aligned}$$

$$d_3=-\frac{S_1}{2J(S_1-1)(2S_1+1)}\left\{1-\frac{m^2}{(S_1+1)^2}\right\},$$

$$e_1=+\frac{m}{4J^2S_1(S_1+2)(2S_1+1)}\left(1-\frac{m^2}{S_1^2}\right),$$

$$\begin{aligned}e_2=-\frac{m}{4J^2(2S_1+1)}\Bigg\{&\frac{1}{S_1(S_1+2)}\left(1-\frac{m^2}{S_1^2}\right)\\&-\frac{1}{(S_1-1)(S_1+1)}\left(1-\frac{m^2}{(S_1+1)^2}\right)\Bigg\},\end{aligned}$$

$$\begin{aligned}e_3=&-\frac{m}{4J^2(S_1-1)(S_1+1)(2S_1+1)}\\&\times\left(1-\frac{m^2}{(S_1+1)^2}\right),\end{aligned}$$

$$\begin{aligned}f_1=&\frac{1}{8J^3(2S_1+1)(S_1+2)}\left(1-\frac{m^2}{S_1^2}\right)\\&\times\Bigg\{\frac{m^2}{(S_1+1)S_1^2}-\frac{(S_1+1)^2}{(S_1+2)^2(2S_1+1)}\left(1-\frac{m^2}{S_1^2}\right)\\&+\frac{S_1(S_1+1)}{(S_1+2)(2S_1+1)^2}\left(1-\frac{m^2}{(S_1+1)^2}\right)\Bigg\},\end{aligned}$$

$$\begin{aligned}f_2=&\frac{1}{8J^3(S_1-1)(2S_1+1)}\left(1-\frac{m^2}{(S_1+1)^2}\right)\\&\times\Bigg\{\frac{m^2}{S_1(S_1+1)^2}-\frac{S_1^2}{(S_1-1)^2(2S_1+1)}\\&\times\left(1-\frac{m^2}{(S_1+1)^2}\right)\Bigg\}+\frac{1}{8J^3(S_1+2)(2S_1+1)}\\&\times\left(1-\frac{m^2}{S_1^2}\right)\Bigg\{\frac{(S_1+1)^2}{(S_1+2)^2(2S_1+1)}\left(1-\frac{m^2}{S_1^2}\right)\\&-\frac{m^2}{(S_1+2)^2(S_1+1)}\Bigg\}\\&+\frac{3S_1(S_1+1)}{8J^3(S_1-1)^2(S_1+2)^2(2S_1+1)^2}\\&\times\left(1-\frac{m^2}{S_1^2}\right)\left(1-\frac{m^2}{(S_1+1)^2}\right),\end{aligned}$$

$$\begin{aligned}f_3=&\frac{-1}{8J^3(S_1-1)(2S_1+1)}\left(1-\frac{m^2}{(S_1+1)^2}\right)\\&\times\Bigg\{+\frac{m^2}{S_1(S_1+1)^2}-\frac{1}{(S_1-1)^2(2S_1+1)}\\&\times\left(1-\frac{m^2}{(S_1+1)^2}\right)+\frac{S_1(S_1+1)}{(S_1-1)(2S_1+1)^2}\\&\times\left(1-\frac{m^2}{S_1^2}\right)\Bigg\}.\end{aligned}$$

The summations over m where indicated are

$$\begin{aligned}&m=-(S_1-1)\cdots+(S_1-1) &&\text{for } S=S_1-1,\\&m=-S_1\quad\cdots+S_1 &&\text{for } S=S_1,\\&m=(S_1+1)\quad\cdots+(S_1+1) &&\text{for } S=S_1+1,\end{aligned}$$

and can be performed by use of (38). The entire procedure followed for a spin $\frac{1}{2}$ can be repeated for a spin 1 using the energy values given here. The multiplicities of the different S_1 levels are given by (33).