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Ferromagnetic and Antiferromagnetic Curie Temperatures*†

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The methods of calculating Curie temperatures used by Opechowski and Weiss are extended to higher spin values. Using the former, Curie temperatures are found for the face-centered, body-centered, and simple cubic and the hexagonal and quadratic layer lattices for spin $\frac{1}{2}$ to 3. Weiss' method is applied to the body-centered and simple cubics for spin $\frac{1}{2}$ to 2 and to the quadratic layer lattice for spin $\frac{1}{2}$ and 1. Numerical results show good agreement between the two methods for three-dimensional ferromagnetic lattices. However, the Opechowski method fails to locate the antiferromagnetic transition and predicts a transition for the two-dimensional lattices while the Weiss method does not. A classical-spin approximation is investigated and is found to give Curie temperatures within a few percent of the quantum-mechanical results for spin 1 or greater.

I. INTRODUCTION

THE Heisenberg model of a ferromagnetic[1] provides a means of calculating Curie temperatures which has the advantage of involving only one parameter, the exchange integral, while retaining some of the physical properties of the system. The present work is concerned with the extension of two previous calculations, both based on the Heisenberg model, to the values of spin greater than $\frac{1}{2}$. These two methods begin with the same Hamiltonian and arrive at predictions of the Curie temperatures by alternate routes; the one proceeding, without further assumption, to find the high-temperature series expansion of the partition function, whereas the other, by means of a physical approximation, treats a simplified problem in semiclosed form. The agreement of the results of the two methods would seem to indicate that they are both reasonably close to the exact solution.

The first method was suggested by Kramers[2] and carried through by Opechowski[3] and is hereafter referred to as the K-O method. We begin with the Heisenberg Hamiltonian for a lattice of N atoms with nearest-neighbor (n.n.) exchange:

$$\mathcal{H}=-2J\sum \mathbf{S}_i\cdot\mathbf{S}_j-g\beta\mathbf{H}_0\cdot\sum \mathbf{S}_k, \tag{1}$$

where $\mathbf{S}_i$ is the spin operator for the ith atom, J the exchange integral, and $\mathbf{H}_0$ the external field. The first sum is over all pairs of n.n. atoms and the second over all atoms. The partition function,

$$Z=\text{trace}\exp(-\mathcal{H}/kT), \tag{2}$$

is evaluated by expanding the exponential and evaluating traces of successively higher powers of $(\mathcal{H}/kT)$. The Curie temperature, which will manifest itself as a singularity in the partition function or one of its derivatives, is inferred from the behavior of the power series expansions, which, for practical reasons, are limited to four or five terms.

The second calculation was performed by Weiss[4] using a technique due to Bethe[5] and modified by Peierls.[6] The Bethe-Peierls-Weiss (B-P-W) method replaces the Heisenberg Hamiltonian for the entire crystal by the corresponding Hamiltonian for a cluster formed by an atom and its n.ns. Using the simplifying assumption that the interactions of the cluster with the rest of the crystal can be replaced by an internal field, $\mathbf{H}_1$, the cluster Hamiltonian is then

$$\mathcal{H}_{cl}=-2J\mathbf{S}_0\cdot\sum \mathbf{S}_i-g\beta\mathbf{H}_1\cdot\sum \mathbf{S}_i-g\beta\mathbf{H}_0\cdot\mathbf{S}_0, \tag{3}$$

where $\mathbf{S}_0$ is the spin of the central atom which has n n.ns. with spins $\mathbf{S}_i$ $(i=1,\cdots n)$. Using $\mathcal{H}_{cl}$ instead of $\mathcal{H}$, the cluster partition function can be obtained as a power series in the fields $\mathbf{H}_0$ and $\mathbf{H}_1$, but in closed form with respect to the exchange energy. The Curie temperature is located by the existence of a spontaneous magnetization, the internal field being eliminated by a consistency condition.

Both of the above methods have been somewhat limited in their application. The K-O method has been carried to the fourth stage in the approximation (i.e., the traces of $\mathcal{H}^n$ were found up to $n=4$) for the close-packed hexagonal and face-centered cubic (f.c.c.) lattices by Opechowski,[3] and for the simple cubic (s.c.) by Zehler,[7] who also includes some numerical corrections to Opechowski's work. The B-P-W method has been applied to the ferromagnetic b.c.c. (body-centered cubic), s.c., h.l. (hexagonal layer), and q.l. (quadratic layer) lattices by Weiss and the antiferromagnetic case has been treated by Li.[8] All this work is for spin $\frac{1}{2}$ except for a calculation by Weiss using the b.c.c. lattice with spin 1, and a calculation by Van Vleck,[9] who

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[9] J. H. Van Vleck, J. Chem. Phys. **6**, 105 (1938).

carried the K-O method to the second approximation for arbitrary spin.

In the present work, the K-O method will be carried to the fourth approximation and the susceptibility obtained as a function of the spin quantum number, S, for the f.c.c., b.c.c., s.c., h.l., and q.l. lattices (Part II). Numerical solutions for the Curie temperatures are found for $S=\frac{1}{2}$ to $S=3$. The B-P-W method will be applied to the b.c.c., s.c., and q.l. (the method cannot be applied, in the present form, to lattices in which n.ns. to a given atom are n.ns. to each other) and numerical solutions found for $S=\frac{1}{2}$ to $S=2$. (Part III.) Finally, a classical-spin approximation is investigated (Part IV) which allows the extension of the B-P-W method to higher spin without the need for machine computation. A discussion of the numerical results is given in Part V.

II. KRAMERS-OPECHOWSKI METHOD

Since the procedure is adequately explained by Opechowski,[3] we will give only a brief outline. By the rules of statistical mechanics, the zero-field susceptibility per atom is

$$\chi=\frac{kT}{N}\left(\frac{\partial^2 \ln Z}{\partial H_0{}^2}\right)_{H_0=0}=\frac{g^2\beta^2}{NkT}\left(\frac{\partial^2 \ln Z}{\partial \lambda_0{}^2}\right)_0, \tag{4}$$

with

$$\lambda_0=\frac{g\beta H_0}{kT}.$$

This gives us the expression

$$\chi=\frac{g^2\beta^2 S(S+1)}{3kT}\sum_{n=0}^{\infty}\frac{a_n}{t^n}, \tag{5}$$

where $t=kT/J$, and the a_n are lattice and spin-dependent coefficients which are related to the A_n of Opechowski[3] by

$$a_n=-\frac{3}{S(S+1)}\left(\frac{d^2A_n}{d\lambda_0{}^2}\right)_0. \tag{6}$$

The evaluation of the susceptibility is thus formally reduced to the problem of evaluating the coefficients a_n, which can be shown to be equal to a sum of products of numerical factors which depend on the number of ways certain "graphs" can be drawn on the lattice, and traces which depend only on the spin and can be found directly as functions of S. Details of this calculation will be published later. The results are:

$$a_0=1, \tag{7}$$

$$a_1=(4/3)f\bar{S}^2, \tag{8}$$

$$a_2=(8/9)f(2f-1)\bar{S}^4-\tfrac{2}{3}f\bar{S}^2, \tag{9}$$

$$\begin{aligned}a_3=(8/27)f\bar{S}^2\{&[2(2f-1)^2-2L_2-(6/5)]\bar{S}^4\\&-[3(2f-1)+L_2+(6/5)]\bar{S}^2+(6/5)\},\end{aligned} \tag{10}$$

$$a_4=(f\bar{S}^2/1215)\{A\bar{S}^6-B\bar{S}^4+C\bar{S}^2-270\}, \tag{11}$$

where $f=\frac{1}{2}n=$ one-half the number of n.ns. and $\bar{S}^2$ means $S(S+1)$, and

$$A=\begin{vmatrix}578208\\154848\\55200\\44832\\10272\end{vmatrix},\quad B=\begin{vmatrix}158592\\57792\\29280\\33168\\10848\end{vmatrix},\quad C=\begin{vmatrix}14112\\8352\\6120\\6768\\3888\end{vmatrix};\quad L_2=\begin{vmatrix}4\\0\\0\\2\\0\end{vmatrix}.$$

The "column vectors" of numbers refer to the five lattices considered, the convention being that from top to bottom, the numbers refer to the f.c.c., b.c.c., s.c., h.l., and q.l. lattices, respectively.

Denoting by χ_n the nth approximation to the susceptibility, we see that the zeroth approximation is Weiss' law $\chi_0=g^2\beta^2\bar{S}^2/3kT$, and the first approximation is the Curie-Weiss law with $kT_c=(4/3)JfS(S+1)$, which is the molecular field theory result.[10]

The susceptibility of a ferromagnetic has a singularity at the Curie temperature which will appear as a root of the inverse susceptibility. We attempt to locate this singularity by finding the roots of the successive approximations, $\chi_n{}^{-1}=0$, obtaining the numbers that are found in Table I under the heading, "K-O Method, *QM*, roots." For the second approximation, setting $\chi_2{}^{-1}=0$ gives a quadratic equation of which the high-temperature root is

$$\frac{J}{kT_c}=\frac{1}{4\bar{S}^2+1}\left\{1-\left(1-\frac{4\bar{S}^2+1}{2f\bar{S}^2}\right)^{\frac{1}{2}}\right\}. \tag{12}$$

For $S=\frac{1}{2}$, this reduces to the result found by Heisenberg,[1] and for $S=1$ to that found by Nakano[11] who duplicated the Heisenberg calculation for spin 1.

An alternate procedure for finding the singularity of a function expressed as a power series is to find the radius of convergence of the series. Thus, if $f=\sum_n c_nx^n$, the radius of convergence is $x_c=\lim c_{n-1}/c_n$ for $n\rightarrow\infty$. This method, applied to $\sum_n a_n/t^n$ gives the series of approximations $kT_c/J=a_n/a_{n-1}$ which are listed in Table I under "K-O Method, *QM*, ratios."

It is a weakness of the K-O method that there is not a unique criterion for defining the Curie temperature. An inspection of the results of the two methods employed here shows that successive approximations always seem to be converging to some definite T_c, that the rapidity of convergence is such that the fourth approximation is usually enough to locate the convergence limit within several percent, and that the limits of convergence of the two methods are the same or nearly the same in all cases. There is therefore, *a posteriori*, justification of the series expansion method and of the criteria used to define the Curie temperatures for ferromagnetics.

For antiferromagnetics, the only change is in the

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

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TABLE I. Calculated values of (kT_c/J).

Spin			Kramers-Opechowski method																			
			f.c.c.				b.c.c.				s.c.				h.l.				q.l.			
			$n=1$	$n=2$	$n=3$	$n=4$	$n=1$	$n=2$	$n=3$	$n=4$	$n=1$	$n=2$	$n=3$	$n=4$	$n=1$	$n=2$	$n=3$	$n=4$	$n=1$	$n=2$	$n=3$	$n=4$
1/2	*QM*	Roots	6.00	4.73	4.26	4.24	4.00	2.00	2.95	2.39	3.00	(1.73)	2.00	1.93	3.00	(1.73)	(1.86)	1.75	2.00	(1.41)	1.25	1.09
		Ratios	6.00	5.00	4.60	4.43	4.00	3.00	2.89	2.76	3.00	2.00	1.83	1.88	3.00	2.00	1.42	1.10	2.00	1.00	0.67	0.81
	Class	Roots	6.00	5.45	5.23	5.11	4.00	3.41	3.45	3.25	3.00	2.37	2.43	2.28	3.00	2.37	1.76	(1.81)	2.00	1.00	1.38	(1.22)
		Ratios	6.00	5.50	5.29	5.17	4.00	3.50	3.46	3.33	3.00	2.50	2.44	2.36	3.00	2.50	2.24	2.08	2.00	1.50	1.40	1.27
1	*QM*	Roots	16.00	13.89	13.10	12.74	10.67	8.31	8.66	7.82	8.00	5.16	5.93	5.36	8.00	5.16	(4.79)	(4.53)	5.33	(3.13)	3.21	(3.01)
		Ratios	16.00	14.17	13.43	13.04	10.67	8.83	8.65	8.27	8.00	6.17	5.91	5.70	8.00	6.17	5.19	4.62	5.33	3.50	3.05	2.68
	Class	Roots	16.00	14.53	13.94	13.63	10.67	9.10	9.21	8.67	8.00	6.31	6.49	6.08	8.00	6.31	4.70	(4.82)	5.33	2.67	3.68	(3.26)
		Ratios	16.00	14.67	14.11	13.80	10.67	9.53	9.22	8.89	8.00	6.67	6.51	6.28	8.00	6.67	5.97	5.56	5.33	4.00	3.73	3.40
3/2	*QM*	Roots	30.00	26.62	25.32	24.67	20.00	16.33	16.71	15.42	15.00	10.86	11.60	10.63	15.00	10.86	(8.80)	(8.94)	10.00	(5.48)	6.32	(5.94)
		Ratios	30.00	27.00	25.78	25.11	20.00	17.00	16.72	16.03	15.00	12.00	11.61	11.18	15.00	12.00	10.42	9.49	10.00	7.00	6.32	5.63
	Class	Roots	30.00	27.25	26.14	25.56	20.00	17.07	17.27	16.25	15.00	11.83	12.17	11.40	15.00	11.83	8.82	(9.04)	10.00	5.00	6.90	(6.10)
		Ratios	30.00	27.50	26.45	25.87	20.00	17.50	17.29	16.67	15.00	12.50	12.20	11.78	15.00	12.50	11.20	10.42	10.00	7.50	7.00	6.37
2	*QM*	Roots	48.00	42.98	41.02	40.00	32.00	26.59	27.08	25.17	24.00	18.00	18.89	17.46	24.00	18.00	(13.93)	(14.28)	16.00	(8.48)	10.43	(9.63)
		Ratios	48.00	43.50	41.65	40.64	32.00	27.50	27.09	26.03	24.00	19.50	18.93	18.24	24.00	19.50	17.15	15.76	16.00	11.50	10.53	9.44
	Class	Roots	48.00	43.60	41.83	40.89	32.00	27.31	27.64	26.00	24.00	18.93	19.48	18.23	24.00	18.93	14.11	(14.46)	16.00	8.00	11.05	(9.77)
		Ratios	48.00	44.00	42.33	41.40	32.00	28.00	27.66	26.66	24.00	20.00	19.52	18.85	24.00	20.00	17.92	16.68	16.00	12.00	11.20	10.19
5/2	*QM*	Roots	70.00	62.95	60.19	58.74	46.67	39.11	39.75	37.10	35.00	26.70	27.82	25.81	35.00	26.70	(20.19)	(20.76)	23.33	(12.16)	15.48	(14.13)
		Ratios	70.00	63.67	61.05	59.61	46.67	40.33	39.77	38.25	35.00	28.67	27.87	26.88	35.00	28.67	25.36	23.39	23.33	17.00	15.66	14.11
	Class	Roots	70.00	63.58	61.00	59.63	46.67	39.83	40.30	37.91	35.00	27.60	28.40	26.59	35.00	27.60	20.58	(21.09)	23.33	11.67	16.11	(14.24)
		Ratios	70.00	64.17	61.73	60.37	46.67	40.83	40.33	38.88	35.00	29.17	28.47	27.49	35.00	29.17	26.13	24.32	23.33	17.50	16.33	14.86
3	*QM*	Roots	96.00	86.56	82.85	80.89	64.00	53.91	54.70	51.19	48.00	36.97	38.37	35.74	48.00	36.97	(27.58)	(28.77)	32.00	(16.49)	21.45	(19.43)
		Ratios	96.00	87.50	83.98	82.03	64.00	55.50	54.75	52.69	48.00	39.50	38.45	37.09	48.00	39.50	35.07	32.43	32.00	23.50	21.73	19.62
	Class	Roots	96.00	87.19	83.66	81.77	64.00	54.63	55.27	52.00	48.00	37.86	38.95	36.47	48.00	37.86	28.22	(28.92)	32.00	16.00	22.09	(19.54)
		Ratios	96.00	88.00	84.65	82.79	64.00	56.00	55.31	53.32	48.00	40.00	39.04	37.70	48.00	40.00	35.84	33.36	32.00	24.00	22.40	20.38

Spin			Bethe-Peierls-Weiss method		
			b.c.c.	s.c.	q.l.
1/2	*QM*	Ferro	2.91	1.85	no root
		Antiferro	3.16	2.01	
	Class	"Exact"	3.46	2.44	1.40
		"Asymptotic"	3.41	2.37	1.00
1	*QM*	Ferro	8.72	5.91	no root
		Antiferro	9.03	6.19	
	Class	"Exact"	9.22	6.50	3.72
		"Asymptotic"	9.10	6.31	2.67
3/2	*QM*	Ferro	16.72	11.59	
		Antiferro	17.04	11.91	
	Class	"Exact"	17.28	12.19	6.97
		"Asymptotic"	17.07	11.83	5.00
2	*QM*	Ferro	27.09	18.91	
		Antiferro	27.41	19.23	
	Class	"Exact"	27.65	19.50	11.16
		"Asymptotic"	27.31	18.93	8.00
5/2	Class	"Exact"	40.32	28.45	16.28
		"Asymptotic"	39.83	27.60	11.67
3	Class	"Exact"	55.30	39.00	22.30
		"Asymptotic"	54.63	37.86	16.00

sign of J. It follows that

$$\chi=\frac{g^2\beta^2 S(S+1)}{3kT}\sum_{n=0}^{\infty}(-1)^n\frac{a_n}{t^n}. \tag{13}$$

Experimental observations show that χ is finite at all temperatures but has a cusp-like maximum at the Curie temperature. Several attempts to locate this maximum using the series expansions led to inconsistent results, the convergence limits being different for each criterion used.[12] It is believed that the antiferromagnetic susceptibility may be composed of two analytic functions, the Curie temperature being merely the intersection of these two which is impossible to locate since the series expansion in $1/T$ would give information about the high-temperature function only.

III. BETHE-PEIERLS-WEISS METHOD

The cluster approach of Bethe is applicable to both ferromagnetics and antiferromagnetics. Using the cluster Hamiltonian (which is of the form of the Zeeman effect interaction with strong L-S coupling included), Weiss[4] and Li[8] find the eigenvalues exactly and evaluate the partition function as a power series in the applied and internal fields. For spin 1 and greater the diagonalization operation becomes very cumbersome and we have resorted to a technique for obtaining the trace directly as a power series in the fields.[13] This method, which is equivalent to the use of second-order perturbation theory for the eigenvalues of $\mathcal{H}_{cl}$, gives the following result for the partition function to second order in the fields (see Appendix A):

$$\begin{aligned}Z_{cl}=\textstyle\sum_{S_1}\sum_{S} w(S_1)e^{p\sigma_0}(2S+1/S(S+1))\\ \times\{S(S+1)+(1/24)(\lambda_0\sigma_0+\lambda_1\sigma_1)^2\\ +(1/24)(\lambda_0-\lambda_1)^2\sigma_0\sigma_1/pS(S+1)\}\\ +\textstyle\sum_{S}\delta_S{}^0 w(S_0)\{1-4(\lambda_0-\lambda_1)^2 S_0(S_0+1)/24p\}. \end{aligned}\tag{14}$$

The sum over S is from $|S_1-S_0|$ to S_1+S_0, the sum over S_1 from 0 to nS_0, excluding the term $S_1=S_0$, $S=0$, which is accounted for by the last sum in (14). The symbols are defined as follows:

$n=2f=$ number of n.ns. to a given atom,
$\mathbf{S}_0=$ spin of the central atom in the cluster,
$\mathbf{S}_1=\sum_i \mathbf{S}_i=$ resultant spin of the n.n. atoms,
$\lambda_0=g\beta\mathbf{H}_0/kT$,
$\lambda_1=g\beta\mathbf{H}_1/kT$,
$p=J/kT$,
$\sigma_1=S(S+1)+S_1(S_1+1)-S_0(S_0+1)$,
$\sigma_0=S(S+1)-S_1(S_1+1)+S_0(S_0+1)$,
$\delta_s{}^0=$ the Kronecker delta,

and $w(S_1)$ is the number of ways of forming a spin of magnitude S_1 from the n components S_i and is computed from the relation $w(S_1)=v(S_1)-v(S_1+1)$ where $v(M)$ is the coefficient of X^M in the expansion of

$$(X^{S_0}+X^{S_0-1}+X^{S_0-2}\cdots+X^{-S_0})^n.$$

The magnetic moments of the central atom and one of the n.n. atoms are, respectively,

$$m_0=g\beta(\partial\ln Z_{cl}/\partial\lambda_0), \tag{15}$$

and

$$m_1=(g\beta/n)(\partial\ln Z_{cl}/\partial\lambda_1). \tag{16}$$

The internal field, $\mathbf{H}_1$, is eliminated in principle by the requirement that, for a ferromagnetic

$$C^F:\qquad m_0=m_1, \tag{17}$$

and for an antiferromagnetic in zero external field,

$$C_0{}^{AF}:\qquad m_0=-m_1\quad(H_0=0). \tag{18}$$

These conditions are required at all temperatures. Just below the Curie temperature, when H_1 is still small ($\lambda_1\ll 1$), the partition function (14) allows us to obtain the magnetic moments to linear terms in λ_1. The "consistency" conditions (17) and (18) for zero external field then require that the temperature-dependent coefficient of λ_1 shall vanish. This leads to a complicated transcendental equation, the roots of which are found by machine. The equation found is

$$\begin{aligned}&C_0{}^{F,AF}(T_c):\\ &\textstyle\sum_{S_1}\sum_{S} w(S_1)\exp(p_c\sigma_0)(2S+1/S(S+1))\\ &\qquad\times\{\sigma_0(n\sigma_1\mp\sigma_0)-(n\pm1)\sigma_0/p_cS(S+1)\}\\ &\qquad\qquad+\textstyle\sum_{S}\delta_S{}^0 4(n\pm1)S_0(S_0+1)/p_c=0,\end{aligned}\tag{19}$$

the upper sign referring to the ferromagnetic and the lower to the antiferromagnetic case and the summation intervals are as above. The roots, $p_c=J/kT_c$, were obtained for $n=8$ (b.c.c.) and $n=6$ (s.c.), for $S_0=\frac{1}{2}$ to 2, and for $n=4$ (q.l.), for $S_0=\frac{1}{2}$ and 1 no roots were found. (The $S_0=\frac{1}{2}$ values agree with those previously found by Weiss and Li but a discrepancy exists between our result and that of Weiss for b.c.c. with spin 1; the values of p_c found being 0.11465 and 0.1502, respectively.)

The numerical values of kT_c/J are included in Table I under "B-P-W Method, QM, Ferro" and ". . . Antiferro." A striking feature of the results for the b.c.c. and s.c. lattices is that they agree so well with those of the third K-O approximation, especially for large spin. (The two methods are not identical since some of the terms which contribute to the third approximation involve next-nearest neighbor interactions which are not included in the cluster approach.)

It should be mentioned that although the present approach to the B-P-W method yields an equation for the Curie temperatures which is applicable to all spin values and several lattices, it cannot be used to obtain more information about the transition. This is because

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[12] The methods used to define the ferromagnetic Curie temperatures give the same results here except for the sign of T_c. The negative Curie temperatures are merely the asymptotes of the $\chi-T$ curve and are not, without additional assumptions, related to the positive transition temperature.

[13] R. Karplus and J. Schwinger, Phys. Rev. 73, 1020 (1948), Appendix 1.

such things as the specific heat and the spontaneous magnetization require the explicit elimination of the internal field. This means obtaining the partition function to λ_1^4 instead of λ_1^2 which, by the present method, is out of the question.

IV. CLASSICAL-SPIN APPROXIMATION

The classical-spin approximation consists of replacing the quantum-mechanical spin operators by classical vectors fixed in length, but free to orient in any direction. [In the equations following, the magnitude of the spin is written as S, but in numerical use, we replace S^2 by $S(S+1)$.] The classical partition function is an integral over phase space defined by the solid angle available to each spin vector. Thus,

$$Z=\int \exp(-\mathcal{H}/kT)d\Gamma,$$

where, in the K-O method, (20)

$$d\Gamma=\prod_{i=1}^{N} d\Omega_i,$$

and $d\Omega_i$ is the element of solid angle in the direction $\mathbf{S}_i$. Although the classical approximation gives nothing that cannot be found by the quantum-mechanical K-O calculation, it does serve as a useful check on some of the quantum-mechanical results and the validity of the approximation itself can be tested. The result for the susceptibility can be found from that quoted for the quantum-mechanical method by dropping all but the highest power of S in each a_n. The values of kT_c/J are listed in Table I under the "K-O Method, Class., Roots" and ". . . Ratios."

The classical approximation is more useful when applied to the B-P-W method. Using the cluster Hamiltonian we have

$$Z_{cl}=\int \exp(-\mathcal{H}_{cl}/kT)d\Gamma_{cl}=\int d\Omega_0 \exp(\boldsymbol{\lambda}_0\cdot\mathbf{S}_0)P^n, \quad (21)$$

where

$$P=\int d\Omega_i \exp(2p\mathbf{S}_0\cdot\mathbf{S}_i+\boldsymbol{\lambda}_1\cdot\mathbf{S}_i). \quad (22)$$

To evaluate P, consider $\mathbf{S}_0$ to be the polar axis and integrate over the directions of $\mathbf{S}_i$. If ϑ and ψ are the angles made by $\mathbf{S}_i$ with $\mathbf{S}_0$ and $\mathbf{H}_1$, respectively, we obtain

$$P=\int d\Omega_i \exp(2pS^2 \cos\vartheta+\lambda_1 S \cos\psi). \quad (23)$$

Assuming $\mathbf{H}_0$ and $\mathbf{H}_1$ to be parallel and letting η be the angle between $\mathbf{S}_0$ and $\mathbf{H}_0$, we have

$$\cos\psi=\cos\eta \cos\vartheta+\sin\eta \sin\vartheta \cos(\phi_1-\phi_0),$$

where ϕ_1 and ϕ_0 are the azimuthal angles of $\mathbf{S}_1$ and $\mathbf{H}_0$ in the plane perpendicular to $\mathbf{S}_0$.

For the purposes of locating the Curie temperature, it is sufficient to evaluate Z_{cl} to terms in λ_1^2 so that we need only

$$P=\int d\Omega_i \exp(2pS^2 \cos\vartheta)\{1+\lambda_1 S \cos\psi +\tfrac{1}{2}(\lambda_1 S)^2 \cos^2\psi\}. \quad (24)$$

The integrations are elementary and give

$$P=4\pi\{\alpha+\lambda_1 S\alpha' \cos\eta+\tfrac{1}{2}(\lambda_1 S)^2[\alpha'' \cos^2\eta +\tfrac{1}{2}(\alpha-\alpha'') \sin^2\eta]\} \quad (25)$$

from which we have to first order in λ_0 and second order in λ_1,

$$Z_{cl}=\text{const}\,\alpha^n\{1+\tfrac{1}{3}\lambda_0\lambda_1 nS^2\mathcal{L}+\tfrac{1}{6}\lambda_1^2 nS^2[1+(n-1)\mathcal{L}^2]\}$$

where $\alpha=\sinh 2pS^2/2pS^2$ and

$$\mathcal{L}=\alpha'/\alpha=\coth 2pS^2-1/2pS^2$$
$$=\text{Langevin function.}$$

The zero-field magnetizations of a central and a n.n. atom are

$$m_0=\tfrac{1}{3}g\beta S^2\lambda_1 n\mathcal{L}, \quad (26)$$

$$m_1=\tfrac{1}{3}g\beta S^2\lambda_1[1+(n-1)\mathcal{L}^2]. \quad (27)$$

The consistency conditions require

$$C_0^F \qquad (n-1)\mathcal{L}^2-n\mathcal{L}+1=0, \quad (28)$$

$$C_0^{AF} \qquad (n-1)\mathcal{L}^2+n\mathcal{L}+1=0, \quad (29)$$

which are the same if we note that $\mathcal{L}(X)$ is an odd function. The roots of the quadratics are

$$\mathcal{L}(2|p_c|S^2)=1, \quad (30)$$

and

$$\mathcal{L}(2|p_c|S^2)=1/(n-1), \quad (31)$$

the first of which implies $p_c=\infty$ or $T_c=0$ and corresponds to the "anti-Curie point" found by Anderson[14] in the quantum-mechanical case. The other root gives the following values:

n	4 (q.l.)	6 (s.c.)	8 (b.c.c.)
$2\|J\|S^2/kT_c$	1.08	0.615	0.434.

The values of kT_c/J, which are listed in Table I, under "B-P-W method, Class, Exact," are seen to be, except for the q.l. lattice, reasonably close to the quantum-mechanical results for spin ≥ 1. The existence of a root for $n=4$ is interesting since the quantum-mechanical calculation does not predict a transition (for $S=\frac{1}{2}$ and 1) and the Ising model[4] (B-P-W method) does.

Before leaving the classical model we will mention one more approximation which enables us to find the cluster partition function more easily and more completely than above. As before, let $\mathbf{S}_1=\sum \mathbf{S}_i$. The element

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

of volume in phase space can then be written as

$$d\Gamma_{cl}=d\Omega_0 W(S_1)S_1^2dS_1d\Omega_1,$$

where $W(S_1)$ is the probability of forming a total spin S_1 which, for classical vectors, is the result of a random walk and can be calculated without great difficulty for small n, leading to the same partition function already found. For large n, however, the "asymptotic" limit of the random walk formula is[15] $W(S_1)=(q/\sqrt{\pi})^3\times\exp(-q^2S_1^2)$, where $q=(3/2nS^2)^{\frac{1}{2}}$. It is now possible to evaluate Z_{cl} as a closed function of J/kT and H_1/kT. The result is

$$Z_{cl}=4\pi\exp(u^2+h^2)(\alpha+\lambda_0S\alpha')$$

where

$$\alpha=\alpha(2uh)=\sinh 2uh/2uh,\quad u=pS/q,\quad h=\lambda_1/2q.$$

The Curie temperatures are given by the roots of $\mathfrak{L}(2uh)\mp h/(A-u)=0$, $(A=qnS=(3n/2)^{\frac{1}{2}})$ for small h, namely, $J/kT_c=(3/4S^2)\{1-(1-4/n)^{\frac{1}{2}}\}$, which is of the same form as Heisenberg's result—as it should be, since the random walk formula is Gaussian. This result is exactly the same as found by the second approximation in the classical K-O method or in the limit $S\rightarrow\infty$ of the quantum-mechanical K-O method [Eq. (12)]. Numerical values of kT_c/J are given in Table I under "B-P-W Method, Class, Asymptotic." The classical B-P-W method can be used to calculate other properties of the transition. Further results will be published later.

V. CONCLUSIONS

The mass of numerical data obtained allows certain conclusions to be drawn regarding the two methods employed. In brief, these conclusions are as follows:

The K-O method, when applied to ferromagnetic lattices, leads to sequences of approximations which are rapidly convergent, especially for large f and S. The limit of convergence can usually be located within a few percent and is apparently unique. Moreover, the convergence limits for the b.c.c. and s.c. lattices agree satisfactorily with the results of the B-P-W method. Since the B-P-W and K-O methods begin with the same Hamiltonian and arrive at solutions by different, and somewhat complementary types of approximation, the validity of both approximations for three-dimensional ferromagnetic lattices is evident from the agreement of the results.

For the q.l. lattice, dissimilar results are found. The B-P-W method predicts no transition for this lattice (or for the h.l. lattice[4,8]) except in the limit of classical spin. (This is in agreement with the Bloch theory according to which only three-dimensional lattices are ferromagnetic.) However, the K-O method leads to sequences of approximations that behave normally for both the h.l. and q.l. lattices, implying that a transition temperature exists.

For antiferromagnetics, the sequences of approximations obtained by the K-O method do not have a unique convergence limit and the limits found do not agree with the results of the B-P-W method. It is suggested that the antiferromagnetic susceptibility does not have a singularity at the Curie temperature and that the Opechowski method is therefore inapplicable.

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APPENDIX A

The derivation of the cluster partition function [Eq. (14)] will now be considered. Following Karplus and Schwinger,[13] we introduce the function

$$F(X)=e^{X(A+B)},$$

where, if

$$A=2p\mathbf{S}_0\cdot\mathbf{S}_1$$

and

$$B=\boldsymbol{\lambda}_0\cdot\mathbf{S}_0+\boldsymbol{\lambda}_1\cdot\mathbf{S}_1,$$

$$Z_{cl}=\mathrm{trace}F(1).$$

The defining equation for F leads to the differential equation $(d/dX)F(X)=(A+B)F(X)$ and the boundary condition $F(0)=1$. A function $G(X)$ defined by

$$F(X)=e^{XA}G(X),$$

then satisfies the differential equation

$$(d/dX)G(X)=e^{-XA}Be^{XA}G(X),$$

with the boundary condition, $G(0)=1$. This is equivalent to the integral equation,

$$G(X)=1+\int_0^X e^{-X'A}Be^{X'A}G(X')dX',$$

which is our starting point. Choosing as a zeroth approximation, $G(X')=1$, a double iteration leads to

$$G(X)=1+\int_0^X e^{-X'A}Be^{X'A}dX'$$
$$+\int_0^X e^{-X'A}Be^{X'A}\int_0^{X'} e^{-X''A}Be^{X''A}dX''dX',$$

and

$$F(1)=e^A+\int_0^1 e^{(1-X')A}Be^{X'A}dX'$$
$$+\int_0^1 e^{(1-X')A}Be^{X'A}\int_0^{X'} e^{-X''A}Be^{X''A}dX''dX'.$$

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[15] S. Chandrasekhar, Revs. Modern Phys. 15, 1 (1943).

Using the S_0S_1SM representation (in more usual notation, the $LSJM$ scheme) with $\mathbf{S}=\mathbf{S}_0+\mathbf{S}_1$, we have

$$\text{trace}F(1)=\sum_{S_1} w(S_1)\sum_S \sum_M F(1),$$

which, for convenience, we write as

$$\text{trace}F(1)=\sum_{S_1} w(S_1)\ \text{trace}F(1).$$

We have then

$$\text{trace}F(1)=f_0+f_1+f_2,$$

where

$$f_0=\text{trace}e^A=\sum_S \sum_M (SM|e^A|SM)$$
$$=\sum_S (2S+1)e^\alpha,$$

where α= eigenvalues of

$$A=p[S(S+1)-S_0(S_0+1)-S_1(S_1+1)]$$

and

$$f_1=\text{trace}\int_0^1 e^{(1-X')A}Be^{X'A}dX'$$
$$=\int_0^1 dX' \sum_S \sum_M (SM|e^{(1-X')A}Be^{X'A}|SM)$$

=0 since B is an odd function of M,

and

$$f_2=\text{trace}\int_0^1\int_0^{X'} dX'dX''e^{(1-X')A}Be^{(X'-X'')A}Be^{X''A}$$
$$=\text{trace}\int_0^1\int_0^{X'} dX'dX''Be^{(1+X''-X')A}Be^{(X'-X'')A}.$$

Transforming variables by means of

$$X^1-X^{11}=u,\quad X^1+X^{11}=v,$$

and performing the integration over v, we arrive at

$$f_2=\int_0^1 du(1-u)\ \text{trace}(Be^{(1-u)A}Be^{uA}).$$

Replacing $1-u$ by u leads to the integral

$$f_2=\int_0^1 udu\ \text{trace}(Be^{(1-u)A}Be^{uA}).$$

Taking one-half of the sum of these two expressions gives us

$$f_2=\tfrac{1}{2}\int_0^1 du\ \text{trace}(Be^{(1-u)A}Be^{uA}).$$

In this representation, A is diagonal and B is the z-component of a vector which, by writing $\mathbf{T}=\mathbf{S}_0-\mathbf{S}_1$, takes the form

$$\mathbf{B}=\tfrac{1}{2}(\lambda_0+\lambda_1)\mathbf{S}+\tfrac{1}{2}(\lambda_0-\lambda_1)\mathbf{T}.$$

Then, since $\text{trace}P_zQ_z=\frac{1}{3}\ \text{trace}\mathbf{P}\cdot\mathbf{Q}$, we can write f_2 in the form:

$$f_2=(1/24)[(\lambda_0+\lambda_1)^2g_0+(\lambda_0^2-\lambda_1^2)g_1+(\lambda_0-\lambda_1)^2g_2],$$

where

$$g_0=\int_0^1 du\ \text{trace}(\mathbf{S}e^{(1-u)A}\cdot\mathbf{S}e^{uA}),$$

$$g_1=\int_0^1 du\ \text{trace}(\mathbf{S}e^{(1-u)A}\cdot\mathbf{T}+\mathbf{T}e^{(1-u)A}\cdot\mathbf{S}e^{uA}),$$

and

$$g_2=\int_0^1 du\ \text{trace}(\mathbf{T}e^{(1-u)A}\cdot\mathbf{T}e^{uA}).$$

Since S and A commute, we have

$$g_0=\int_0^1 du\ \text{trace}\mathbf{S}^2e^{uA}$$
$$=\sum_S S(S+1)(2S+1)e^\alpha.$$

For g_1, the identity, $\mathbf{S}\cdot\mathbf{T}=\mathbf{S}_0^2-\mathbf{S}_1^2$, leads to

$$g_1=\int_0^1 du\ \text{trace}2\mathbf{S}\cdot\mathbf{T}e^A$$
$$=2\sum_S (2S+1)[S_0(S_0+1)-S_1(S_1+1)]e^\alpha.$$

To obtain g_2, we make use of several sum rules for angular momentum matrices.[16] Since A is diagonal,

$$\text{trace}\,\mathbf{T}e^{(1-u)A}\cdot\mathbf{T}e^{uA}$$
$$=\sum_{SM}\sum_{S'M'}(SM|\mathbf{T}|S'M')e^{(1-u)\alpha'}\cdot(S'M'|\mathbf{T}|SM)e^{u\alpha}.$$

Using equation 13^31^1, 10^32b^1, and 10^32a of reference 21, this becomes

$$\text{trace}\,\mathbf{T}e^{(1-u)A}\cdot\mathbf{T}e^{uA}$$
$$=\sum_S\{(P(S)Q(S-1)/S)e^{p[S(S-1)-b]+2upS}$$
$$+((2S+1)a^2/S(S+1))e^{p[S(S+1)-b]}$$
$$+(P(S+1)Q(S)/(S+1))e^{p[(S+1)(S+2)-b]+2up(S+1)},$$

where

$$b=S_0(S_0+1)+S_1(S_1+1),\quad a=S_0(S_0+1)-S_1(S_1+1),$$

and

$$P(S)=(S-S_0+S_1)(S+S_0+S_1+1),$$
$$Q(S)=(S+S_0-S_1)(-S+S_0+S_1+1).$$

After performing this integration and combining terms we have

$$g_2=\sum_S e^\alpha\{(2S+1)a^2/S(S+1)+P(S)Q(S-1)/pS^2$$
$$-P(S+1)Q(S)/p(S+1)^2\}.$$

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[16] E. U. Condon and G. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, London, 1935), Chap. III.

Finally, adding g_0, g_1, and g_2 gives, after some rearrangement,

$$f_2=(1/24)\sum_S e^{\alpha}\{(2S+1)/S(S+1)[\lambda_0(S(S+1)+a)+\lambda_1(S(S+1)-a)]^2+(\lambda_0-\lambda_1)^2[P(S)Q(S-1)/pS^2-P(S+1)Q(S)/p(S+1)^2]\}.$$

By taking out the term $S=0(S_0=S_1)$ from the sum (if it occurs), and using the identities

$$\begin{aligned}P(S)Q(S-1)/S^2-P(S+1)Q(S)/(S+1)^2&=(2S+1)\sigma_0\sigma_1/S(S+1)\quad \text{for}\quad S\neq 0\\&=4S_0(S_0+1),\qquad\qquad \text{for}\quad S=0\end{aligned}$$

and

$$\alpha=S(S+1)-b=\sigma_0-2S_0(S_0+1),$$

where σ_0 and σ_1, are as defined in Eq. (14), we can write the cluster partition function as given there if we multiply through by the constant $e^{2pS_0(S_0+1)}$.

This result can also be derived by standard perturbation theory methods, considering B as the perturbation. The eigenvalues of $\mathcal{H}_{cl}$ are then

$$E_{cl}=\alpha+(\alpha|B|\alpha)+\sum_{\alpha'}{}'\frac{|(\alpha|B|\alpha')|^2}{\alpha-\alpha'}$$

to second order in B,

$$\begin{aligned}Z_{cl}&=\sum_{S_1}w(S_1)\sum_\alpha e^{-E_{cl}/kT}\\&=\sum_{S_1}w(S_1)\sum_\alpha e^{\alpha}\left\{1+(\alpha|B|\alpha)+\tfrac{1}{2}(\alpha|B|\alpha)^2+\sum_{\alpha'}{}'\frac{|(\alpha|B|\alpha')|^2}{\alpha-\alpha'}\right\},\end{aligned}$$

with $\sum_\alpha=\sum_S\sum_M$. Again employing the properties of angular momentum matrices we arrive, after a similar amount of manipulation, at the result found above.

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Nuclear Magnetic Resonance in Semiconductors. I. Exchange Broadening in InSb and GaSb

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Nuclear magnetic resonances have been observed for the more abundant nuclear species in the semiconductors InSb and GaSb. Broad lines have been observed and explained by a nuclear spin exchange mechanism where the interaction between the nuclei is of the form $E_{ij}=A_{ij}\mathbf{I}_i\cdot\mathbf{I}_j$. The exchange coupling involves the hyperfine interaction between nuclear spins and electron spins. Therefore it is very sensitive to the electron energy states in both valence and conduction bands. It is particularly sensitive to the energy surfaces far from the Fermi level and provides information about the band structure of these normally inaccessible regions.

1. INTRODUCTION

NUCLEAR magnetic resonance has proved to be a valuable means for studying metals and insulators.[1] Resonance width, shape, multiplet structure, intensity, frequency and relaxation times all depend upon the environment or lattice in which the nucleus is situated. Study of the resonances therefore yields information about the nuclear environment. Investigation of nuclear magnetic resonances in semiconductors is being undertaken with the double purpose of studying the materials themselves and of using the delicate control that can be exercised over various properties of semiconductors to contribute to the theory of nuclear magnetic resonance. Intensive research in the past several years has produced materials of extremely high purity with consequent advances in the understanding of their properties. Impurities can be introduced in known concentration and the resultant changes in electronic structure have been investigated by other means in previous studies. In this way one can control and vary the concentration of conduction electrons and paramagnetic impurities, a situation which makes nuclear resonance investigations exceedingly attractive. The electronic structures, intermediate in many respects between those of metals and insulators, should allow a variety of interactions between the nuclei and their lattice.

The nuclear magnetic resonances of dielectric substances have been extensively investigated and the lines observed are usually broadened by internuclear dipole-dipole interactions. Van Vleck[2] has shown that dipole-dipole broadening is a fundamental property of a crystal lattice and the effects are observed in metals as well as insulators. From Van Vleck's theory one can obtain lattice parameters in favorable instances. Pound[3] and Bloembergen[4] have shown quadrupole interactions

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[1] H. S. Gutowsky, Ann. Rev. Phys. Chem. **5**, 333 (1953).

[2] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

[3] R. V. Pound, Phys. Rev. **79**, 685 (1950).

[4] N. Bloembergen, *Nuclear Magnetic Relaxation* (Martinus Nijhoff, The Hague, 1948).