Ferromagnetic Curie Temperatures of the Heisenberg Model with Next-Nearest-Neighbor Interactions

D. W. WOOD*
Department of Physics, University of Alberta, Edmonton, Alberta, Canada
AND
N. W. DALTON
Theoretical Physics Division, Atomic Energy Research Establishment, Harwell, Didcot, Berkshire, England

(Received 20 February 1967)

The Curie temperatures of the Heisenberg ferromagnet with nearest-neighbor interactions $-2J_1\mathbf{S}_i\cdot\mathbf{S}_j$ and next-nearest-neighbor interactions $-2J_2\mathbf{S}_k\cdot\mathbf{S}_l$ are calculated for the bcc, sc, and fcc lattices on the basis of exact high-temperatures series expansions of the zero-field susceptibility χ_0. The dependence of $T_c(\alpha, S)$ $(\alpha=J_2/J_1)$ on α is examined, and it is found that $T_c(\alpha)/T_c(0)$ is well represented by $T_c(\alpha)/T_c(0)=1+m_1(S)\alpha$ for values of α between 0 and 1. The Curie points are also examined for $\alpha<0$, where J_2 is antiferromagnetic in sign.

I. INTRODUCTION

THE experimental data presently available on the critical-point behavior of insulating ferromagnets[1–7] have recently provided opportunities for examining in detail the predictions of statistical theories of the ideal Heisenberg ferromagnet. (For a recent review on the subject see Domb and Miedema.)[8] In making such comparisons between theory and experiment, it has become clear that both nearest-neighbor and next-nearest-neighbor exchange interactions $(-2J_1\mathbf{S}_i\cdot\mathbf{S}_j$ and $-2J_2\mathbf{S}_k\cdot\mathbf{S}_l$, respectively) must often be included in the theory if an accurate interpretation of experimental work is to be obtained. Attempts have been made by several authors[9–13] to estimate the exchange constants J_1/k and J_2/k on the basis of the critical and thermodynamic properties of these compounds. Values of the two exchange constants which ensure close agreement between theory and experiment for a wide variety of thermal and magnetic properties can be found by comparing the following theoretical and experimental quantities:

(a) the critical point $kT_c(\alpha)/J_1(\alpha=J_2/J_1)$, the critical energy $[E_\infty-E_c(\alpha)]/kT_c(\alpha)$, the critical entropy $[S_\infty-S_c(\alpha)]/k$, the high-temperature specific heat constant C_vT^2, the Curie-Weiss constant $\theta(\alpha)$, and

(b) the low-temperature $(T\ll T_c)$ specific heat $C_v(\alpha, T)$ and Magnetisation $M(\alpha, T)$ curves.

The most reliable theoretical estimates of properties (a) are determined by extrapolating high-temperature $(T>T_c)$ series expansions for the thermodynamic functions[14]; low-temperature spin-wave expansions form an adequate basis for (b) in the region $T<0.5T_c$.[9,10,13] We have previously calculated the critical properties (a) for the case $S=\frac{1}{2}$,[14] and performed the comparison (a) and (b), for the two ferromagnetic salts $Cu(NH_4)_2\cdot Cl_4\cdot 2H_2O$, and $CuK_2\cdot Cl_4\cdot 2H_2O$.[13] Unlike the latter compounds the appropriate spin values in the majority of cases are $S>\frac{1}{2}$ and it is therefore desirable to have reliable theoretical estimates of the critical points $kT_c(\alpha, S)/J_1$. In this paper we report the calculation of the Curie points of cubic lattices for various spin values and relative interaction strengths.

II. CURIE TEMPERATURES

The calculations of Dalton and Wood[14] for the case $S=\frac{1}{2}$ have recently been extended by Dalton[15] to include an arbitrary spin value for both the Heisenberg and Ising models. The zero-field susceptibility expansion is in the form

$$\frac{kT}{m^2}\chi_0=\frac{x}{3S^2}\{1+\sum_{r+s=1}^{\infty}b_{rs}(x)K_1^rK_2^s\},\qquad(1)$$

where $K_r=J_r/2S^2kT$ and $x=S(S+1)$, and has been expanded up to the fifth power in reciprocal temperature.[16] We have examined both the Padé approximants to $(d/dK_1)(\ln\chi_0)$ and the ratios of successive terms in the expansion to obtain estimates of the Curie temperatures for the bcc, fcc, and sc lattices.

* On leave of absence from the Mathematics Department, University of Nottingham, Nottingham, England.

[1] I. Tsubokawara, J. Phys. Soc. Japan **15**, 1664 (1960).
[2] B. T. Matthias, R. M. Bozorth, and J. H. Van Vleck, Phys. Rev. Letters **7**, 160 (1961).
[3] T. R. McGuire, B. E. Argyle, M. W. Shafer, and J. S. Smart, Appl. Phys. Letters **1**, 17 (1962); J. Appl. Phys. **34**, 1345 (1963).
[4] W. P. Wolf, M. Leask, B. Magnum, and A. F. G. Wyatt, J. Phys. Soc. Japan, (Suppl.) **17**, 487 (1962).
[5] V. L. Moruzzi and D. T. Teaney, Solid State Commun. **1**, 127 (1963).
[6] A. R. Miedema, R. F. Wielinga, and W. J. Huiskamp, Phys. Letters **17**, 87 (1965).
[7] A. R. Miedema, H. Van Kempen, and W. J. Huiskamp, Physica **29**, 1256 (1963).
[8] C. Domb and A. R. Miedema, Progr. Low Temp. Phys. **4**, 296 (1964).
[9] S. H. Charap and E. L. Boyd, Phys. Rev. **133**, A811 (1964).
[10] G. G. Low, Proc. Phys. Soc. (London) **82**, 992 (1963).
[11] P. J. Wojtowicz and R. I. Joseph, Phys. Rev. **135**, A1314 (1964).
[12] H. B. Callen and E. Callen, Phys. Rev. **136**, A1675 (1964).
[13] D. W. Wood and N. W. Dalton, Proc. Phys. Soc. (London) **87**, 755 (1966).
[14] N. W. Dalton and D. W. Wood, Phys. Rev. **138**, A779 (1965).
[15] N. W. Dalton, Proc. Phys. Soc. (London) **88**, 659 (1966).
[16] In a recent publication [Mol. Phys. **11**, 551 (1966)], Pirnie *et al.* have added one more term to the expansion (1).

TABLE I. Estimates of the Curie points $J_1S^2/kT_c(\alpha)$ for the fcc lattice. In the case $S=\infty$ the values recorded are $J_1/kT_c(\alpha)$.

α	$S=\frac{1}{2}$	$S=1$	$S=\frac{3}{2}$	$S=2$	$S=\frac{5}{2}$	$S=3$	$S=\infty$
0	0.0616	0.0843	0.0980	0.107	0.114	0.119	0.157
0.1	0.0573	0.0789	0.0917	0.101	0.107	0.112	0.148
0.2	0.0537	0.0742	0.0864	0.0948	0.101	0.105	0.139
0.3	0.0506	0.0700	0.0817	0.0897	0.0955	0.0999	0.132
0.4	0.0478	0.0664	0.0776	0.0853	0.0908	0.0950	0.125
0.5	0.0454	0.0632	0.0740	0.0813	0.0866	0.0906	0.120
0.6	0.0433	0.0603	0.0707	0.0777	0.0828	0.0866	0.114
0.7	0.0414	0.0578	0.0677	0.0744	0.0793	0.0830	0.110
0.8	0.0397	0.0554	0.0650	0.0715	0.0761	0.0797	0.105
0.9	0.0381	0.0533	0.0625	0.0687	0.0732	0.0767	0.101
1.0	0.0367	0.0513	0.0602	0.0662	0.0706	0.0739	0.0977

The values of $J_1S^2/kT_c(\alpha)$ obtained for these lattices are listed in Tables I, II, and III for values of α in the range 0 (nearest-neighbor model) to 1 (equivalent-neighbor model),[17] and for spin values $S=\frac{1}{2}$, 1, $\frac{3}{2}$, 2, $\frac{5}{2}$, 3, and ∞. In the latter case the values recorded are $J_1/kT_c(\alpha)$. The convergence of the singularities in the sequence of Padé approximants to $(d/dK_1)(\ln\chi_0)$, and of the ratios of successive terms in χ_0 is very good for $S\geq 1$, and particularly so for $\alpha\geq\frac{1}{4}$. We expect that the errors in the estimates recorded in Tables I, II, and III will not exceed 1%.

In Fig. 1 we plot the variation of $T_c(\alpha)/T_c(0)$ for the extreme cases $S=\frac{1}{2}$ and $S=\infty$; the curves for intermediate spin values fall in between the two shown for a given lattice. The variation of $T_c(\alpha)/T_c(0)$ with α for $0\leq\alpha\leq 1$ is almost linear for all spin values, and the linear approximation

$$T_c(\alpha)/T_c(0)=1+m_1(S)\alpha \qquad (2)$$

ensures agreement to within 1% for $0<\alpha<0.7$, and to within 2% for values of α between 0.7 and 1, with the results in Tables I, II, and III. The values of $m_1(S)$ for the three lattices are listed in Table IV.

We have also examined the behavior of $T_c(\alpha, S)$ for $\alpha<0$, where the second-neighbor exchange integral J_2 is antiferromagnetic in sign. This region has been extensively studied using molecular-field theory,[18–19] spin-wave theory,[20] and first-order Green's-function treatments.[21–23] Smart[18] has examined the four cases arising from both positive and negative J_1 and J_2 using a molecular-field treatment for the fcc and bcc lattices, and has obtained the stable low-temperature spin configurations in each case. To overcome the inadequacy of mean field theory in the computation of the free energy, Smart proposed that the spin configuration relating to the largest critical point has the lowest free energy, thus obtaining the stable configurations and the variation of the critical temperature with α for each of the four cases. In the present case ($J_1>0$, $J_2<0$) a changeover in the spin configuration occurs

TABLE II. Estimates of the Curie points $J_1S^2/kT_c(\alpha)$ for the bcc lattice. In case of the $S=\infty$, the values recorded are $J_1/kT_c(\alpha)$.

α	$S=\frac{1}{2}$	$S=1$	$S=\frac{3}{2}$	$S=2$	$S=\frac{5}{2}$	$S=3$	$S=\infty$
0	0.0978	0.132	0.152	0.166	0.176	0.183	0.241
0.1	0.0890	0.121	0.140	0.153	0.162	0.168	0.222
0.2	0.0817	0.112	0.129	0.141	0.150	0.156	0.205
0.3	0.0757	0.104	0.120	0.131	0.139	0.145	0.191
0.4	0.0705	0.0968	0.112	0.123	0.131	0.136	0.179
0.5	0.0661	0.0909	0.106	0.116	0.123	0.128	0.168
0.6	0.0623	0.0857	0.0996	0.109	0.116	0.122	0.159
0.7	0.0589	0.0812	0.0944	0.103	0.110	0.116	0.152
0.8	0.0559	0.0771	0.0897	0.0983	0.105	0.110	0.145
0.9	0.0532	0.0734	0.0854	0.0937	0.0997	0.105	0.138
1.0	0.0508	0.0701	0.0816	0.0895	0.0952	0.100	0.133

[17] C. Domb and N. W. Dalton, Proc. Phys. Soc. (London) **89**, 859 (1966); *ibid.* **89**, 873 (1966).
[18] J. S. Smart, Phys. Rev. **86**, 968 (1952).
[19] D. ter Haar and M. E. Lines, Phil. Trans. Roy. Soc. London **A254**, 521 (1962).
[20] D. ter Haar and M. E. Lines, Phil. Trans. Roy. Soc. London **A255**, 1 (1962).
[21] R. Tahir-Kheli and H. S. Jarrett, Phys. Rev. **135**, A1096 (1964).
[22] M. E. Lines, Phys. Rev. **135**, A1336 (1964).
[23] R. Tahir-Kheli, H. B. Callen, and H. S. Jarrett, J. Phys. Chem. Solids **27**, 23 (1966).

TABLE III. Estimates of the Curie points $J_1S^2/kT_c(\alpha)$ for the sc lattice. In the case of $S=\infty$ the values recorded are $J_1/kT_c(\alpha)$.

α	$S=\frac{1}{2}$	$S=1$	$S=\frac{3}{2}$	$S=2$	$S=\frac{5}{2}$	$S=3$	$S=\infty$
0	0.138	0.188	0.214	0.237	0.251	0.261	0.342
0.1	0.108	0.147	0.169	0.185	0.197	0.206	0.270
0.2	0.0882	0.121	0.140	0.154	0.164	0.171	0.225
0.3	0.0744	0.103	0.119	0.132	0.140	0.146	0.194
0.4	0.0645	0.0895	0.104	0.115	0.122	0.128	0.169
0.5	0.0571	0.0793	0.0921	0.102	0.109	0.114	0.150
0.6	0.0513	0.0715	0.0828	0.0919	0.0979	0.102	0.136
0.7	0.0466	0.0650	0.0753	0.0837	0.0892	0.0934	0.124
0.8	0.0427	0.0597	0.0691	0.0769	0.0820	0.0858	0.114
0.9	0.0395	0.0552	0.0639	0.0712	0.0759	0.0794	0.106
1.0	0.0367	0.0514	0.0594	0.0663	0.0706	0.0739	0.0998

TABLE IV. Estimates of $m_1(S)$ in (2).

	$S=\frac{1}{2}$	$S=1$	$S=\frac{3}{2}$	$S=2$	$S=\frac{5}{2}$	$S=3$	$S=\infty$
fcc	0.690	0.655	0.640	0.630	0.625	0.620	0.615
bcc	0.940	0.900	0.880	0.870	0.860	0.845	0.835
sc	2.80	2.70	2.65	2.62	2.58	2.56	2.49

TABLE V. Estimates of the Curie points $J_1S^2/kT_c(\alpha)$ for the fcc lattice with $\alpha<0$. In the case $S=\infty$, the values recorded are $J_1/kT_c(\alpha)$.

α	$S=1$	$S=\frac{3}{2}$	$S=2$	$S=\frac{5}{2}$	$S=3$	$S=\infty$
0	0.0843	0.0980	0.107	0.114	0.119	0.157
−0.1	0.0906	0.104	0.116	0.123	0.129	0.169
−0.2	0.0979	0.113	0.123	0.130	0.135	0.174
−0.3	0.106	0.123	0.134	0.142	0.148	0.193
−0.4	0.116	0.135	0.147	0.155	0.162	0.212
−0.5	...	0.148	0.162	0.172	0.179	0.233
−0.6	...	...	0.179	0.190	0.199	0.259
−0.7	...	...	...	...	...	0.292
−0.8	...	...	...	...	...	0.330

TABLE VI. Estimates of the Curie points $J_1S^2/kT_c(\alpha)$ for the bcc lattice with $\alpha<0$. In the case of $S=\infty$, the values recorded are $J_1/kT_c(\alpha)$.

α	$S=1$	$S=\frac{3}{2}$	$S=2$	$S=\frac{5}{2}$	$S=3$	$S=\infty$
0	0.132	0.152	0.166	0.176	0.183	0.241
−0.1	0.146	0.168	0.183	0.194	0.201	0.265
−0.2	0.163	0.187	0.203	0.215	0.249	0.293
−0.3	0.185	0.212	0.229	0.242	0.283	0.329
−0.4	0.212	0.243	0.263	0.277	0.329	0.383
−0.5	...	0.287	0.309	0.325	...	0.529

between ferromagnetic ordering and antiferromagnetic ordering of the second kind at a value of $\alpha=\alpha^*$, which is spin-independent, and at nonzero values of $T_c(\alpha^*)=T_N(\alpha^*)$.

Tahir-Kheli and Jarret[21] have computed the $T_c(\alpha, S)$-versus-α curves for the bcc and fcc ferromagnets using a first-order Green's-function treatment, and find that $T_c(\alpha)\to 0$ with an infinite slope as $\alpha\to\alpha^*$. The low-temperature phases of the fcc antiferromagnet have also been examined by Lines[22] using the random-phase approximation (RPA), and this has been extended to the bcc and sc lattices by Tahir Kheli *et al.*[23] These authors again adopt the T_c criterion to obtain the stable spin configurations and proceed to calculate the $T_N(\alpha)$ and $T_c(\alpha)$-versus-α curves for the various phases, obtaining the same α^* as molecular-field theory, but with $T_c(\alpha^*)=T_N(\alpha^*)=0$, and both functions having an infinite slope at α^*. The values of α^* obtained in this approximation are -1, -0.68, and -0.25 for the fcc, bcc, and sc lattices, respectively.

Following Smart's interpretation of molecular-field

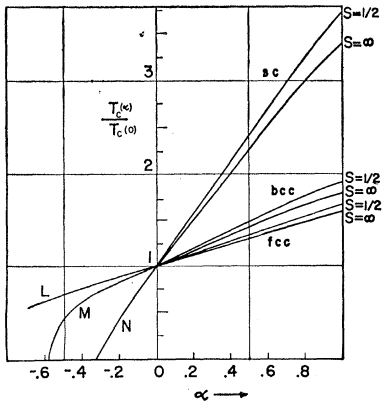

FIG. 1. Variation of the Curie points of the sc, bcc, and fcc lattices with the strength of the second-neighbor interaction. The curves L, M, and N correspond to the fcc, bcc, and sc lattices, respectively, for the case $S=\infty$.

theory and the RPA results, we expect that for a given lattice and spin value, $T_c(\alpha, S)$ as derived from series expansions will have a singular point on the negative α axis where $T_c(\alpha^*, S)\to 0$ as $\alpha\to\alpha^*(S)$.

Unfortunately at low spin values the series expansions quickly become erratic as α increases negatively and it has not been possible to obtain reliable estimates of the critical points in the neighborhood of α^*. In this region the convergence of the Padé approximant singularities rapidly breaks down. This behavior sets in usually at values of $T_c(\alpha)/T_c(0)$ which are too high for the curves to be extrapolated to $\alpha^*(S)$. The situation with regard to convergence improves steadily for large spin values, and in the limiting case $S=\infty$, we have been able to construct the $T_c(\alpha)/T_c(0)$ versus α curves close to α^* for the bcc and sc lattices. The values of $\alpha^*(S=\infty)$ obtained from Fig. 1 are -0.58 ± 0.01 and -0.33 ± 0.01 for the bcc and sc lattices, respectively.

Evidently the series expansions are locating the same α^* as mean field theory and RPA corresponding to ordering of the same kind for $\alpha<\alpha^*$, and these results are obtained without the *ad hoc* T_c criterion. Also the same behavior of $T_c(\alpha)$ near α^* as the RPA is given and with $T_c(\alpha)=0$ (points on the curves very close to the α axis have been found).

It is not possible to say at this stage whether α^* is spin-independent or not, however, the results shown in Fig. 1 do suggest that $\alpha^*(S)\geq\alpha^*(S=\infty)$. In Tables V and VI we have recorded the critical points for the bcc and fcc lattices with values of $\alpha<0$, and over a range of values for which the approximants to $(d/dK_1)(\ln\chi_0)$ locate consistent singularities on the positive real axis.

Further work relating to a review of comparisons (a) and (b) above (see Sec. I) for a number of ferromagnetic insulators is in progress and will be published elsewhere.

ACKNOWLEDGMENT

We would like to thank C. J. Elliott for helpful assistance with programming.

PHYSICAL REVIEW VOLUME 159, NUMBER 2 10 JULY 1967

^{31}P Nuclear Magnetic Resonance in the Paramagnetic State of UP*

B. A. Scott,† K. A. Gingerich,‡ and R. A. Bernheim

Department of Chemistry, Whitmore Laboratory, The Pennsylvania State University, University Park, Pennsylvania

(Received 10 February 1967)

The ^{31}P nuclear magnetic resonance was observed in the paramagnetic state of the metallic antiferromagnet, uranium monophosphide ($T_N=123$°K). The ^{31}P Knight shift measured over the temperature region 125–300°K was found to be positive, varying from $K=2$ to 4%. Linearity of the $K(T)$-versus-$\chi(T)$ relationship permitted the assignment of a ^{31}P hyperfine field as +21.6 kOe/(Bohr magneton). Using the Mott-Goodenough theory, the magnetic and electrical properties of UP are interpreted from a model in which the Fermi level lies in overlapping bands composed of phosphorus s, p states and metal $6d$-t_{2g} states.

I. INTRODUCTION

URANIUM monophosphide crystallizes in the $B1$-type NaCl structure with lattice parameter $a_0=5.590$ Å.[1] Magnetic susceptibility data obtained by Trzebiatowski and Troć[2] indicate an antiferromagnetic transition at 123°K and normal Curie-Weiss behavior above that temperature. From neutron diffraction patterns at 78°K, Sidhu, Vogelsgang, and Anderson deduced the ordering as ferromagnetic within each (001) basal plane but oppositely aligned in successive alternating layers.[3] These authors also found reasonably good agreement between theoretical and experimental magnetic form factors assuming a U^{3+} $5f^3$ electron configuration. Kanter and Kazmierowicz have reported a large positive maximum in the Hall effect at the Néel temperature, and an electrical resistivity which increases to a value of 300 $\mu\Omega$ cm up to T_N, but which remains essentially constant in the paramagnetic region.[4] In the present investigation we have examined the ^{31}P nuclear magnetic resonance in UP above the Néel point. The temperature dependence of the resonance shift combined with susceptibility data makes possible a determination of the sign and magnitude of the net hyperfine field at the phosphorus sites. The origin of the shift is then discussed within the context

* This research was supported in part by the National Institute of Health and in part by the U. S. Atomic Energy Commission Contract under Grant No. AT (30-1)-2541.

† Present address: Eastern Laboratory, E. I. du Pont de Nemours, Inc., Gibbstown, New Jersey.

‡ Present address: Battelle Memorial Institute, Columbus, Ohio.

[1] M. Heimbrecht, M. Zumbusch, and W. Biltz, Z. Anorg. Allgem. Chem. **245**, 391 (1940).

[2] W. Trzebiatowski and R. Troć, Bull. Acad. Polon. Sci. Ser. Sci. Chim. **11**, 661 (1963).

[3] S. S. Sidhu, W. Volgelsang, and K. D. Anderson, J. Phys. Chem. Solids **27**, 1197 (1966).

[4] M. A. Kanter and C. W. Kazmierowicz, Bull. Am. Phys. Soc. **9**, 633 (1964).