Ferro- and Antiferromagnetism in a Cubic Cluster of Spins

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(Received January 8, 1962)

The Heisenberg exchange Hamiltonian has been solved exactly for a cubic array of eight spins (each with spin-$\frac{1}{2}$). Both energy eigenvalues and thermodynamic functions have been calculated. A Curie temperature can be defined and its value determined as a function of the strength of first-, second-, and third-neighbor interactions. For the antiferromagnetic state no simple definition is found for the Néel temperature. The temperature of the susceptibility maximum is determined and is plotted as a function of the strengths of the second- and third-neighbor interactions. For some values of the exchange constants, spiral-type antiferromagnetic states exist.

I. INTRODUCTION

THE exact three-dimensional solution of the Heisenberg model for ferromagnetism is not tractable for an infinite lattice. Various approximate solutions exist, some of which involve the exact solution for some small cluster of spins.[1,2] In addition, a number of solutions exist in the literature for a small number of spins in various configurations.[3] The exact treatments for the small clusters lend insight into properties of the larger system, as well as serving as the starting point for an approximate treatment of the infinite lattice problem.

This paper gives the exact solution to the Heisenberg Hamiltonian for eight spins, each with spin-$\frac{1}{2}$, located on the corners of a cube. The eigenfunctions, eigenvalues, and thermodynamic functions are calculated.

These results are applied in a subsequent article to the infinite simple cubic lattice using the Bethe-Peierls-Weiss method, (BPW). Since the basic cluster is larger than those previously used, it is more appropriate for the calculation of the effect of second- and third-neighbor interactions on the magnetic properties.

The sharp discontinuities which are indicative of the ferro- and antiferromagnetic phase transitions in the infinite crystal are not present in the small cluster of eight spins. A ferromagnetic Curie temperature T_C is defined from the temperature variation of the magnetic susceptibility. However, the antiferromagnetic Néel temperature T_N is not uniquely determined. The effect on the magnetic susceptibility of variation of the second- and third-neighbor interactions is conveniently discussed in terms of the temperature of the maximum susceptibility T_M. It is found that for some values of the interactions, "spiral"-type antiferromagnetic states[4] exist. It is also shown that regions exist where, as the temperature is lowered, ferromagnetic ordering begins, but at still lower temperatures, the system drops into the antiferromagnetic singlet state.

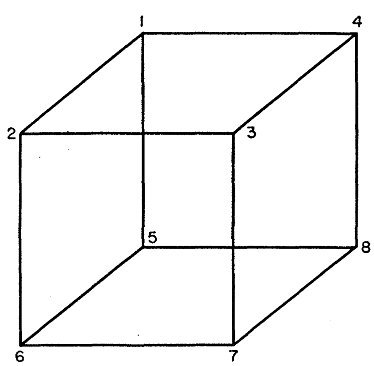


FIG. 1. Cube showing the numbering of the spins.

II. CALCULATION

The Heisenberg Hamiltonian is written

$$\mathcal{H}=-2J[\epsilon+x\mu+y\nu], \tag{1}$$

in which J is the exchange constant, x and y are proportional to the strength of next-nearest- and third-nearest-neighbor interactions, and

$$\begin{aligned}\epsilon=&\mathbf{S}_1\cdot\mathbf{S}_2+\mathbf{S}_2\cdot\mathbf{S}_3+\mathbf{S}_3\cdot\mathbf{S}_4+\mathbf{S}_4\cdot\mathbf{S}_1+\mathbf{S}_5\cdot\mathbf{S}_6+\mathbf{S}_6\cdot\mathbf{S}_7\\&+\mathbf{S}_7\cdot\mathbf{S}_8+\mathbf{S}_8\cdot\mathbf{S}_5+\mathbf{S}_1\cdot\mathbf{S}_5+\mathbf{S}_2\cdot\mathbf{S}_6+\mathbf{S}_3\cdot\mathbf{S}_7+\mathbf{S}_4\cdot\mathbf{S}_8,\\ \mu=&\mathbf{S}_1\cdot\mathbf{S}_3+\mathbf{S}_2\cdot\mathbf{S}_4+\mathbf{S}_5\cdot\mathbf{S}_7+\mathbf{S}_6\cdot\mathbf{S}_8+\mathbf{S}_1\cdot\mathbf{S}_6+\mathbf{S}_2\cdot\mathbf{S}_7\\&+\mathbf{S}_3\cdot\mathbf{S}_8+\mathbf{S}_4\cdot\mathbf{S}_5+\mathbf{S}_1\cdot\mathbf{S}_8+\mathbf{S}_2\cdot\mathbf{S}_5+\mathbf{S}_3\cdot\mathbf{S}_6+\mathbf{S}_4\cdot\mathbf{S}_7,\\ \nu=&\mathbf{S}_1\cdot\mathbf{S}_7+\mathbf{S}_2\cdot\mathbf{S}_8+\mathbf{S}_3\cdot\mathbf{S}_5+\mathbf{S}_4\cdot\mathbf{S}_6.\end{aligned} \tag{2}$$

The spin operator for the ith site $\mathbf{S}_i$ follows the numbering of the sites shown in Fig. 1.

The eigenfunctions of Eq. (1) can be classified according to the total spin S, the z component of the total spin M_S, and the irreducible representation of the cubic group. Table I contains a complete list of symmetry types and energy eigenvalues for the cubic cluster.[5] The notation for the representations is such that a vector transforms as Γ_4^-. If the root λ is double or triple valued, the representation occurs two or three times, respectively; e.g., there are three states with $S=0$ and

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

[1] H. A. Brown and J. M. Luttinger, Phys. Rev. **100**, 685 (1955). This paper contains references to much of the literature on the subject.

[2] J. S. Smart, J. Phys. Chem. Solids **20**, 41 (1961).

[3] R. Orbach, Phys. Rev. **115**, 1181 (1959); L. F. Mattheiss, *ibid.* **123**, 1209 (1961).

[4] T. A. Kaplan, Phys. Rev. **116**, 888 (1959); J. Villain, J. Phys. Chem. Solids **11**, 303 (1959); A. Yoshimori, J. Phys. Soc. Japan **14**, 807 (1959).

[5] A tabulation of wave functions and matrix elements is contained in Massachusetts Institute of Technology Lincoln Laboratory Technical Report-254 (unpublished).

symmetry Γ_1^+. The spectrum for $x=y=0$ is shown in Fig. 2.

For a given value of the total spin S the center of gravity of the energy levels $E_{\mathrm{C.G.}}$ is given by the sum rule

$$E_{\mathrm{C.G.}}=-2\left[\sum_{i<j} J_{ij}\right]\left[S(S+1)-\tfrac{3}{4}N\right]/\left[N(N-1)\right], \quad (3)$$

in which N is the number of spins (each with spin-$\frac{1}{2}$) and J_{ij} is the exchange constant between sites i and j. Equation (3) represents a convenient check of the calculated energy eigenvalues. The Heisenberg approximation for ferromagnetism[6] corresponds to calculating the partition function using Eq. (3) for the energy eigenvalues.

In calculations of the infinite lattice,[1] the values of the ferromagnetic Curie temperature T_C and the antiferromagnetic Néel temperature T_N are related to characteristic features of the susceptibility χ vs temperature T. The Curie law susceptibility is given by

TABLE I. Spin, symmetry type, and energy eigenvalues for the cubic cluster of eight spins.

Spin	Representation	Eigenvalue $[\lambda=E/(-2J)]$
4	Γ_1^+	$\lambda=3+3x+y$
3	Γ_4^-	$\lambda=2+x$
	Γ_5^+	$\lambda=1+x+y$
	Γ_2^-	$\lambda=3x$
2	Γ_3^+	$\lambda=\frac{1}{2}(1-x)\pm\frac{1}{2}[(1-x)^2+4(1-y)^2]^{\frac{1}{2}}$
	Γ_5^+	$\lambda=\pm[(1-x)^2+(1-y)^2-(1-x)(1-y)]^{\frac{1}{2}}$
	Γ_1^+	$\lambda=-(1-x)\pm[4(1-x)^2+(1-y)^2-3(1-x)(1-y)]^{\frac{1}{2}}$
	Γ_5^-	$\lambda=1-x$
	Γ_4^-	$\lambda=-1+x$
	Γ_3^-	$\lambda=0$
1	Γ_4^-	$\lambda^3+2\lambda^2(1+x+y)+\lambda(-2+7x+5y+3xy-x^2)$ $+(-2+2y+4x^2+6xy-2x^3)=0$
	Γ_4^+	$\lambda=-\frac{1}{2}(1+3x)\pm\frac{1}{2}[5-2x+x^2+4y^2-8y]^{\frac{1}{2}}$
	Γ_2^-	$\lambda=-2+x-y\pm[4-7x-y+4x^2+y^2-xy]^{\frac{1}{2}}$
	Γ_5^+	$\lambda=-\frac{1}{2}(3+x)\pm\frac{1}{2}[5-10x+9x^2-8xy+4y^2]^{\frac{1}{2}}$
	Γ_5^-	$\lambda=-2x$
	Γ_3^-	$\lambda=-1-x$
0	Γ_1^+	$\lambda^3+\lambda^2(5+x+3y)+\lambda(-1+18x+14y-9x^2+6xy-y^2)$ $+3(-9+3x+5y+3x^2+6xy-y^2-3x^3$ $-3x^2y+3xy^2-y^3)=0$
	Γ_3^+	$\lambda=-(1+2x)\pm[2-2x+x^2-2y+y^2]^{\frac{1}{2}}$
	Γ_1^-	$\lambda=-3x$
	Γ_5^+	$\lambda=-(1+x+y)$
	Γ_5^-	$\lambda=-2-x$

$$\chi=\mathfrak{N}\mathcal{S}(\mathcal{S}+1)g^2\mu_B{}^2/3kT, \quad (4)$$

in which $\mathfrak{N}$ is the number of spins with spin quantum number $\mathcal{S}$, g is the spectroscopic splitting factor, and μ_B is the Bohr magneton. For a cluster of N spins, each with spin-$\frac{1}{2}$, the quantity $\mathfrak{N}\mathcal{S}(\mathcal{S}+1)$ in the paramagnetic and ferromagnetic states is $[\mathfrak{N}\mathcal{S}(\mathcal{S}+1)]_{\mathrm{para}}=\frac{3}{4}N$ and $[\mathfrak{N}\mathcal{S}(\mathcal{S}+1)]_{\mathrm{ferro}}=\frac{1}{4}N(N+2)$. Thus, the Curie law gives the slopes of the susceptibilities in the paramagnetic and ferromagnetic states as

$$[\partial\chi_{\mathrm{ferro}}/\partial(1/T)]/[\partial\chi_{\mathrm{para}}/\partial(1/T)]=(N+2)/3.$$

On the susceptibility plot, the region $2J/kT\lesssim 1$ is characterized by the smaller slope and the region $2J/kT\gtrsim 1$ by the larger slope; the intermediate region exhibits a change in slope which becomes very sharp and very large ($\propto N$) as the size of the cluster increases to the size of a macroscopic crystal. The Curie temperature T_C is identified with the maximum slope of the χ vs $1/T$ plot, as is done in the Kramers-Opechowski method.[1] Application of this argument for the macroscopic crystal is made to the finite cluster whereby the Curie temperature is again associated with the maximum slope of χ vs $1/T$ for the cluster.

[6] J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932), p. 322.

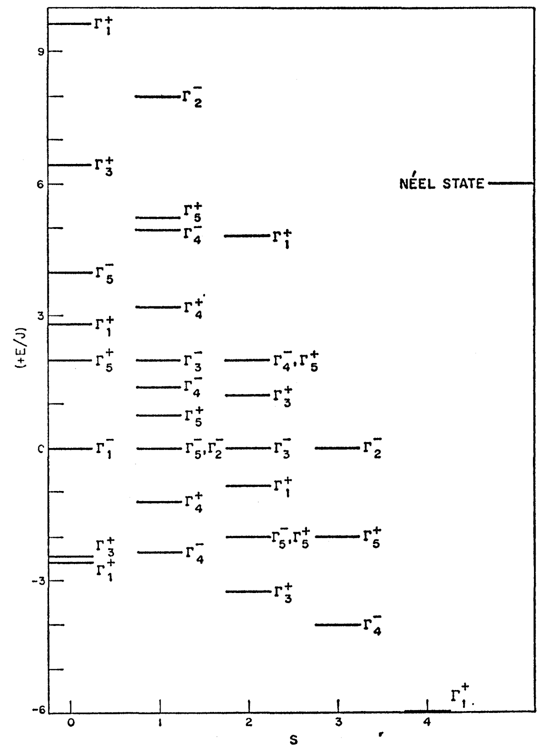
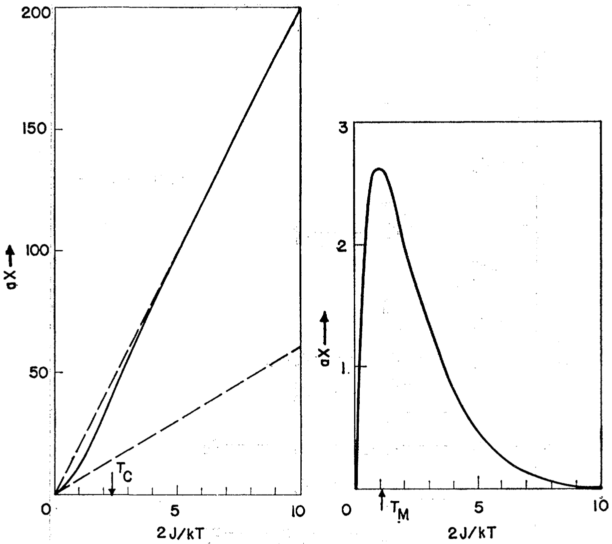


FIG. 2. Energy spectrum assuming only nearest-neighbor interactions, $x=y=0$. The spectrum is arranged according to the value of the total spin. The Néel state energy is indicated even though it is not a proper eigenstate of the system.

The identification of an antiferromagnetic Néel temperature represents a more difficult problem. In fact, the application of this model without crystalline anisotropy to an infinite lattice does not seem to yield a phase transition; this question is discussed more fully in a subsequent publication. For this reason, the temperature T_M of the susceptibility maximum is chosen as a convenient quantity to use in discussions of the antiferromagnetic state.

A plot of the susceptibility vs $1/T$ for $x=y=0$ is shown in Fig. 3 for both ferromagnetic and antiferromagnetic coupling. For convenience, the plot is presented in dimensionless form in terms of $\alpha\chi$ vs $2J/kT$, with $\alpha=6J/g^2\mu_B{}^2$. For the ferromagnetic case ($J>0$) the slope of the curve in Fig. 3(a) has the two limiting values indicated by the dashed lines. The characteristic



(a) (b)

FIG. 3. Susceptibility vs $2J/kT$ for $x=y=0$; (a) $J>0$ and (b) $J<0$. The Curie temperature and the temperature of the susceptibility maximum are indicated. See text for constant of proportionality, α.

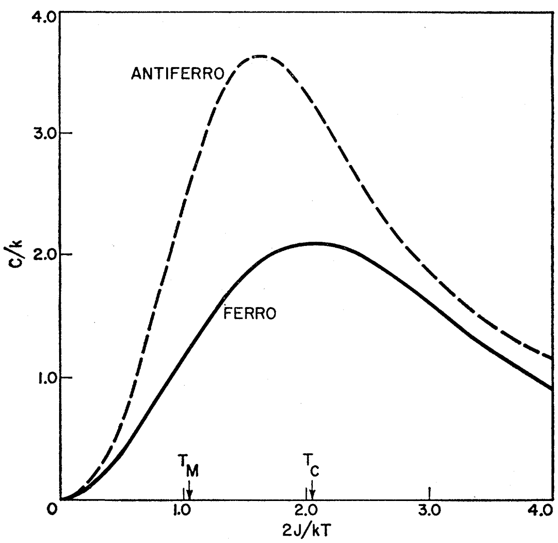


FIG. 5. Heat capacity vs $2J/kT$ for $x=y=0$. T_C and T_M as determined from the susceptibility are indicated.

temperatures T_C and T_M are determined as a function of the strength of the second- and third-neighbor interactions. These results are shown in Fig. 4.

The heat capacity is shown for the same parameters in Fig. 5. The positions of T_C and T_M as determined from the susceptibility are also indicated. It should be noted that even for the infinite lattice the maximum in the heat capacity is not simply related to the phase transitions.

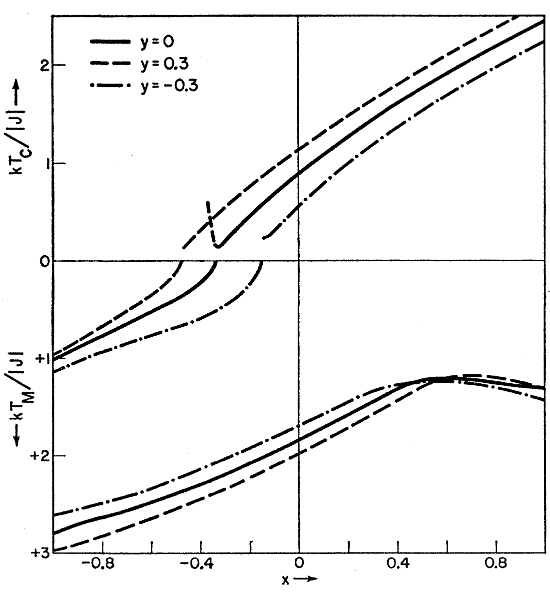


FIG. 4. T_C and T_M vs x with y as a parameter. The upper curves refer to $J>0$ and the lower curves to $J<0$.

III. DISCUSSION

The calculation of the magnetic properties for an eight-spin cubic cluster shows several interesting features. The antiferromagnetic state of the cluster gives a reasonable approximation to the antiferromagnetic state of the infinite solid in the following aspects. The susceptibility and heat capacity have the same low- and high-temperature limits as the infinite lattice. For $x=y=0$, the susceptibility maximum of the eight-spin cluster is given by $kT_M/J=1.83$. The Bethe-Peierls-Weiss method results in a Néel temperature given by $kT_N/J=2.01$. For the macroscopic crystal, a sharp maximum in $\chi\|$ occurs at T_N. The ferromagnetic state, on the other hand, is not well represented by the small cluster. The heat capacity has the correct low- and high-temperature limits; however, the susceptibility has the correct limiting value only for the high temperature case (paramagnetic region). In addition, the Curie temperature for the cluster is given by $kT_C/J=0.90$ compared with the Bethe-Peierls-Weiss value of 1.85.

In order to investigate the number of spins required to reproduce the ferromagnetic behavior of an infinite solid, the Heisenberg approximation [i.e., assume Eq. (3) for all energy levels] was carried out for clusters of 8, 64, and 216 spins. The results for the heat capacity are shown in Fig. 6. The Curie temperature for these clusters was found from the susceptibility curves and the results are shown in Table II. A rather slow convergence is to be noted for the ferromagnetic case. To put it another way, 216 spins are too few to represent the infinite ferromagnetic lattice. Comparison with the Heisenberg approximation is not useful for the antiferromagnetic case. The Heisenberg approximation gives results for the antiferromagnetic state which get worse as N increases, i.e., $T_M \rightarrow 0$ as $N \rightarrow \infty$.

TABLE II. Values of T_C calculated in the Heisenberg approximation for cubic clusters of various numbers of spins.

N	kT_C/J
8	1.3
64	1.8
216	2.2
...	...
∞	3.0

Another interesting feature of the eight-spin cubic cluster is the existence of an antiferromagnetic state for $J>0$. For example, for $y=0$ and $x<-\frac{1}{3}$, an antiferromagnetic state exists with $J>0$, which corresponds to a "classical" spiral state,[4] i.e., nearest neighbors are mostly parallel to take advantage of positive J and next-nearest neighbors most antiparallel. An examination of the susceptibility curve in the region $y=0$ and $x\lesssim-\frac{1}{3}$ shows that the system begins to order ferromagnetically because of the greater weighting factor for the $S=4$ state, but at low temperatures, the system becomes antiferromagnetic because an $S=0$, Γ_1^+, state is lower in energy.[7] The condition on x and y for the accidental degeneracy of the $S=4$, Γ_1^+, state and an $S=0$, Γ_1^+, state is given by

$$3(1+4x_0+3x_0^2)+7y_0+12x_0y_0+2y_0^2+3x_0^2y_0+2x_0y_0^2=0. \quad (5)$$

In Fig. 4, the dashed branch of the $y=0$ curve indicates this possibility of a "high"-temperature ferromagnetic state. The $y=\pm0.3$ calculations also allow this possibility, but, for simplicity, these branches are not plotted in Fig. 4.

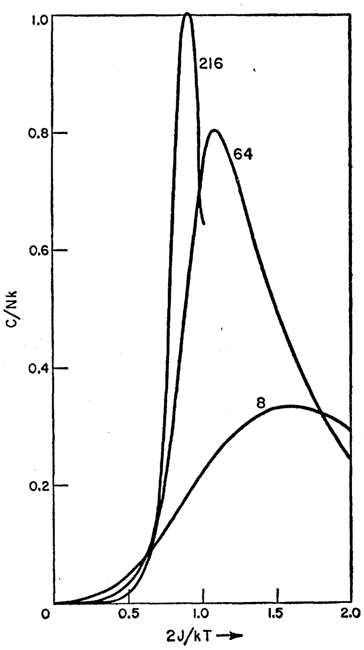


FIG. 6. Heat capacity for the ferromagnetic state in the Heisenberg approximation for cubic clusters of 8, 64, and 216 spins.

It is also possible to select values of the parameters x and y so that an $S=0$, Γ_3^+ state is the lowest antiferromagnetic state of the system for $J<0$. The classical analog to this situation is discussed in reference 4.

ACKNOWLEDGMENTS

The author has profited from discussions with Dr. G. W. Pratt, Jr., Dr. J. S. Smart, and Dr. T. A. Kaplan. He is deeply indebted to Dr. M. S. Dresselhaus for many suggestions and for programming the computation for the IBM 7090.

[7] This effect has many of the same features as that used by H. Sato and A. Arrott, Phys. Rev. **114**, 1427 (1959), to explain the magnetic behavior of some Fe-Al alloys which are ferromagnetic at high temperatures but antiferromagnetic at low temperatures.