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APPLICATION OF THE WEISS MOLECULAR FIELD THEORY TO THE LATTICE OF THE B-SITE SPINEL

BY

WAYNE EDMUND HOLLAND, 1945-

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Approved by

H.A. Brown (advisor)   _Robert Geison_

W. J. James

ABSTRACT

The Weiss molecular field theory has been applied to the lattice of the B-site spinel. The forms of the ordering temperatures and the asymptotic Curie temperature have been determined for a sixteen-sublattice model with collinear spins. The theory has been applied to the problem of determining the exchange integrals for systems of the form $Aa_{1-x}Ab_xCr_2X_4$ and $ACr_2Xa_{4(1-y)}Xb_{4y}$. The theoretical results have been compared to the experimental data for the systems $Hg_{1-x}Cd_xCr_2S_4$, $Zn_{1-x}Cd_xCr_2Se_4$, and $CdCr_2S_{4(1-y)}Se_{4y}$ in an attempt to determine the exchange integrals.

ACKNOWLEDGEMENT

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I. INTRODUCTION

Recent investigations into the magnetic properties of spinels have been directed toward the determination of the exchange integrals by finding values that agree with the experimental data for the ordering temperature and the asymptotic Curie temperature.

One theory which gives the ordering temperature and the asymptotic Curie temperature in terms of the exchange integrals is the Weiss molecular field theory (MFT). The theory was first advanced in 1907 by Pierre Weiss. Weiss assumed that the microscopic effective field (molecular field) was proportional to the magnetization of the crystal. With the advent of quantum mechanics it was seen that the effective field theory would result if the magnetic moment of the atom was assigned an operator $\vec{\mu} = g\mu_B\vec{S}$ and an "exchange integral" was assumed present between electrons at different lattice sites.

II. REVIEW OF THE LITERATURE

Baltzer, Lehmann, and Robbins[1] have measured Θ and T_C for the spinels $CdCr_2S_4$, $CdCr_2Se_4$, and $HgCr_2S_4$. Baltzer, Wojtowicz, Robbins, and Lopatin[2] have measured Θ and T_C for these spinels and have determined the value of the nearest-neighbor (NN) exchange J and also an "average" next-nearest-neighbor (NNN) exchange K by a series expansion technique and a two-particle cluster approximation. By the same method Baltzer, Robbins, and Wojtowicz[3] have determined J and K for the systems $Hg_{1-x}Cd_xCr_2S_4$ and $Zn_{1-x}Cd_xCr_2Se_4$. Also by the same method Wojtowicz, Baltzer, and Robbins[4] have determined J and K for the system $CdCr_2S_{4(1-y)}Se_{4y}$. They have also measured Θ and T_C for this system. Brown[5] has determined J and K for this system from a B-P-W calculation.

Plumier[6] has determined the spin ordering of $ZnCr_2Se_4$ by neutron diffraction studies. Lotgering[7,8] has measured Θ and T_N for this spinel and has determined the value of the exchanges for the first-, second-, and third-nearest neighbors by a molecular field approach. Dwight and Menyuk[9] have worked on a theory for spiral spin states and have applied it to the calculation of the exchange integrals of $ZnCr_2Se_4$. Hastings and Corliss[10] have determined the spin ordering for $HgCr_2S_4$ by neutron diffraction.

III. WEISS MOLECULAR FIELD THEORY FOR THE B-SITE SPINEL

A. Definition of the B-site Spinel

The general chemical formula of the spinel is AB_2X_4. In the simple spinels the B ions are trivalent metal ions and the A ions are divalent metal ions. The X ions can be anions of the chalcogenide group. Solid solutions of the simple spinels also occur; we refer to these as systems.

The anions, which are large compared to the cations, form essentially a face-centered cubic (fcc) lattice. The smallest cubic unit cell contains eight molecules, that is 32 anions. The cations (A, B) occupy interstitial positions, of which there are two different types. In one the cation is surrounded by four oxygen ions located at the corners of a tetrahedron. Such an interstice is called a tetrahedral, or A, site. In the other the cation is surrounded by six anions placed at the vertices of an octahedron; this is called an octahedral, or B, site. Eight A sites and 16 B sites are filled per unit cell.

If the 16 B sites are occupied by trivalent cations and the eight A sites are occupied by divalent cations, the structure is said to be normal. If, in addition, only the B ions have a permanent magnetic moment (the A ions can be diamagnetic), the spinel is said to be a B-site spinel.

B. Systems to be Considered

In this paper we will consider B-site systems $(Aa_{1-x}Ab_xCr_2X_4, 0 \le x \le 1)$ in which the A-site cation is varied between one type of cation (Aa) and another (Ab) and systems $(ACr_2Xa_{4(1-y)}Xb_{4y}, 0 \le y \le 1)$ in which the anion is varied from one type (Xa) to another (Xb). In both cases the B-site cation is the Cr^{3+} ion with a spin eigenvalue 3/2.

C. NNN Interactions and Division of the Lattice

The B-site lattice of the spinel consists of four fcc sublattices, each displaced a distance of one-fourth of a cube face diagonal of the cubic unit cell.[*] The primitive unit cell has a basis of four atoms, one from each of the four fcc sublattices.[†] The lattice structure is such that if only B-B NN superexchange interactions are considered, then there are no interactions between atoms on the same sublattice. However, as Anderson has pointed out,[11] a perfect short range order with only NN interactions does not necessarily lead to long range antiferromagnetic order. Lotgering[7] has found that antiferromagnetic interactions of about five percent of the strength of the

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[*]The fcc sublattices have the following bases:
1.   0 0 0; 1/2 1/2 0; 0 1/2 1/2; 1/2 0 1/2
2.   1/4 0 3/4; 3/4 1/2 3/4; 1/4 1/2 1/4; 3/4 0 1/4
3.   1/4 1/4 0; 3/4 3/4 0; 1/4 3/4 1/2; 3/4 1/4 1/2
4.   0 1/4 3/4; 1/2 3/4 3/4; 0 3/4 1/4; 1/2 1/4 1/4

[†]Due to symmetry there are several possible primitive unit cells.

ferromagnetic NN interactions suffice to prevent ferro-
magnetism. Dwight and Menyuk[8] have found that an adequate
characterization of the exchange energy requires the con-
sideration of five distinct NNN interactions. Hence,
we must include NNN interactions also. The inclusion of
NNN interactions necessitates, however, that we subdivide
each sublattice since in order to apply the generalized
Weiss molecular field theory we must divide each fcc sub-
lattice until there are no interactions between atoms on
the same sublattice.[12] Hence, we divide each fcc sub-
lattice into four simple cubic sublattices; the B-site
lattice then consists of 16 simple cubic sublattices.[*]

D. Derivation of the Ordering Temperature and the Asymptotic Curie Temperature

The molecular field for an atom of the ith sublattice
may be written according to Weiss theory as

$$\vec{H}_{mi} = \alpha_{11}\vec{M}_1 + \alpha_{12}\vec{M}_2 + \cdots + \alpha_{1,16}\vec{M}_{16},\tag{1}$$

where $\vec{M}_1$, $\vec{M}_2$, ..., $\vec{M}_{16}$ are the magnetizations of the
other sublattices and the α_{ij} are the molecular field
coefficients linking the ith and j^{th} sublattices. If an
external field is also applied, the total field on an
atom will be

$$\vec{H}_i = \vec{H} + \alpha_{11}\vec{M}_1 + \alpha_{12}\vec{M}_2 + \cdots + \alpha_{1,16}\vec{M}_{16}.\tag{2}$$

At thermal equilibrium the magnetization of the ith

---

[*]We have numbered these according to their order as
given in footnote (*) on page 4.

sublattice is given by[13]

$$M_1 = (1/16)Ng\mu_B SB_S(x_1) \qquad (3)$$

where

$$B_S(x_1) = \frac{2S+1}{2S} \coth \frac{2S+1}{2S} x_1 - \frac{1}{2S} \coth \frac{x_1}{2S} \qquad (4)$$

and where

$$x_1 = \frac{Sg\mu_B}{kT} H_1 . \qquad (5)$$

Here N is the total number of atoms with a permanent dipole moment per unit volume, S is the spin eigenvalue, g is the gyromagnetic ratio (g = 2), k is Boltzmann's constant, T is the temperature, and μ_B is the Bohr magneton.

Although there is no spontaneous ordering above the critical temperature, a small magnetization is induced by an applied field. For usual values of the applied field the Brillouin function can be replaced by the first term in the series expansion in x, i.e. $B_S(x) = ((S + 1)/3S)x$. Then

$$M_1 = \frac{Ng^2\mu_B^2 S(S+1)}{48kT} H_1 . \qquad (6)$$

Also, equation (2) reduces to

$$H_1 = H + \alpha_{11}M_1 + \alpha_{12}M_2 + \cdots + \alpha_{1,16}M_{16} \qquad (7)$$

since $\vec{H}$ and $\vec{M}_1$ are parallel in the paramagnetic region. Substitution of equation (6) into equation (7) yields

$$M_1 = \frac{Ng^2\mu_B^2 S(S+1)}{48kT} (H + \alpha_{11}M_1 + \cdots + \alpha_{1,16}M_{16}) \qquad (8)$$

or

$$M_i = \frac{C_M}{16T} (H + \Sigma_{j=1}^{16} \alpha_{ij} M_j) \tag{9}$$

where

$$C_M = \frac{Ng^2 \mu_B^2 S(S+1)}{3k}. \tag{10}$$

By adding the magnetization equations (equations (9)) we find

$$M = \Sigma_{i=1}^{16} M_i = \frac{C_M}{16T} (16H + \Sigma_{i=1}^{16} \Sigma_{j=1}^{16} \alpha_{ij} M_j) \tag{11}$$

or

$$M = \frac{C_M}{16T} (16H + \Sigma_{j=1}^{16} M_j (\Sigma_{i=1}^{16} \alpha_{ij})). \tag{12}$$

The sum $\Sigma_{i=1}^{16} \alpha_{ij}$ is the same for every j since every B-site atom has the same number and type of NN and NNN interactions. Hence, the sum (we will call it α_0) can be factored from the summation, leaving

$$M = \frac{C_M}{16T} (16H + \alpha_0 \Sigma_{j=1}^{16} M_j)$$
$$= \frac{C_M}{16T} (16H + \alpha_0 M). \tag{13}$$

Solving for M, we find

$$M = C_M H/(T - \frac{C_M}{16} \alpha_0). \tag{14}$$

Hence, the susceptibility is

$$\chi = \frac{M}{H} = C_M/(T - \frac{C_M}{16} \alpha_0). \tag{15}$$

By comparison with the Curie-Weiss law $\chi = C_M/(T - \Theta)$ we find that

$$\Theta = \frac{C_M}{16} \alpha_0. \tag{16}$$

The magnetization equations are also valid in the vicinity of T_N and T_C. With $H = 0$ these equations become

$$M_i = \frac{C_M}{16T} \Sigma^{16}_{j=1} \alpha_{ij} M_j \tag{17}$$

or

$$0 = -\frac{16T}{C_M} M_i + \Sigma^{16}_{j=1} \alpha_{ij} M_j. \tag{18}$$

For non-trivial solutions (i.e. non-zero magnetizations) the determinant of the coefficients must be zero.

$$\begin{vmatrix} -\frac{16T}{C_M} & \alpha_{12} & \alpha_{13} & \cdots \\ \alpha_{21} & -\frac{16T}{C_M} & \alpha_{23} & \cdots \\ \alpha_{31} & \alpha_{32} & -\frac{16T}{C_M} & \cdots \\ \cdots & \cdots & \cdots & \end{vmatrix} = 0 \tag{19}$$

E. Exchange Interactions for the B-site Spinel

Following Baltzer et al.,[2] we have considered five different types of interactions to be important. (See figures 1 and 2.) These are the interactions between an atom and its first-, second-, third- (two types), and fourth-nearest neighbors. The hypothetical interaction paths are illustrated in figure 2.

Assuming random distribution of the A-site cations, the probability that any particular one is of type Aa is 1-x, and the probability that it is of type Ab is x. Similarly, the probability that the anion is of type Xa or Xb is 1-y and y, respectively. From figure 2 the six
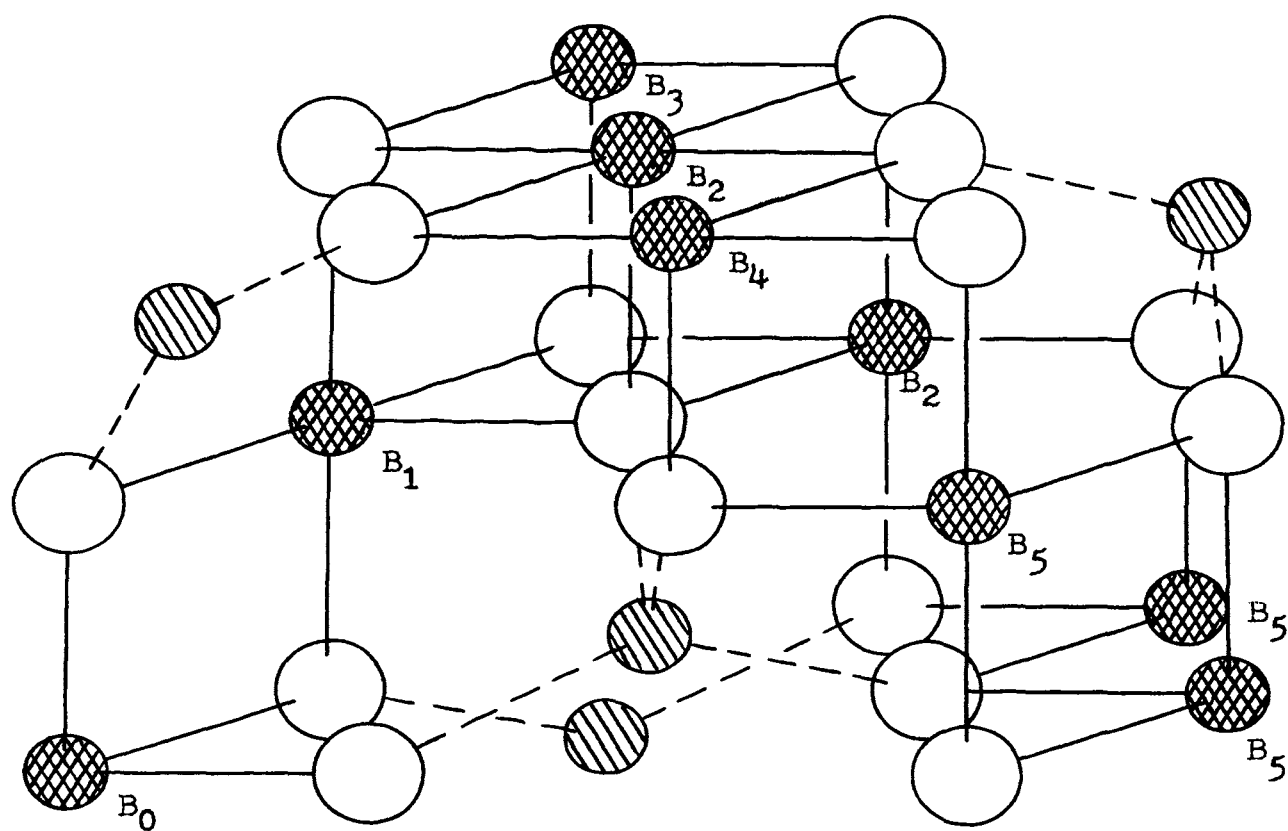
Figure 1. Portion of the spinel lattice showing nearest to fourth-nearest B-B neighbors. The large ions are the anions. The small lined ions are the A-site cations. The small cross-hatched ions are the B-site cations.
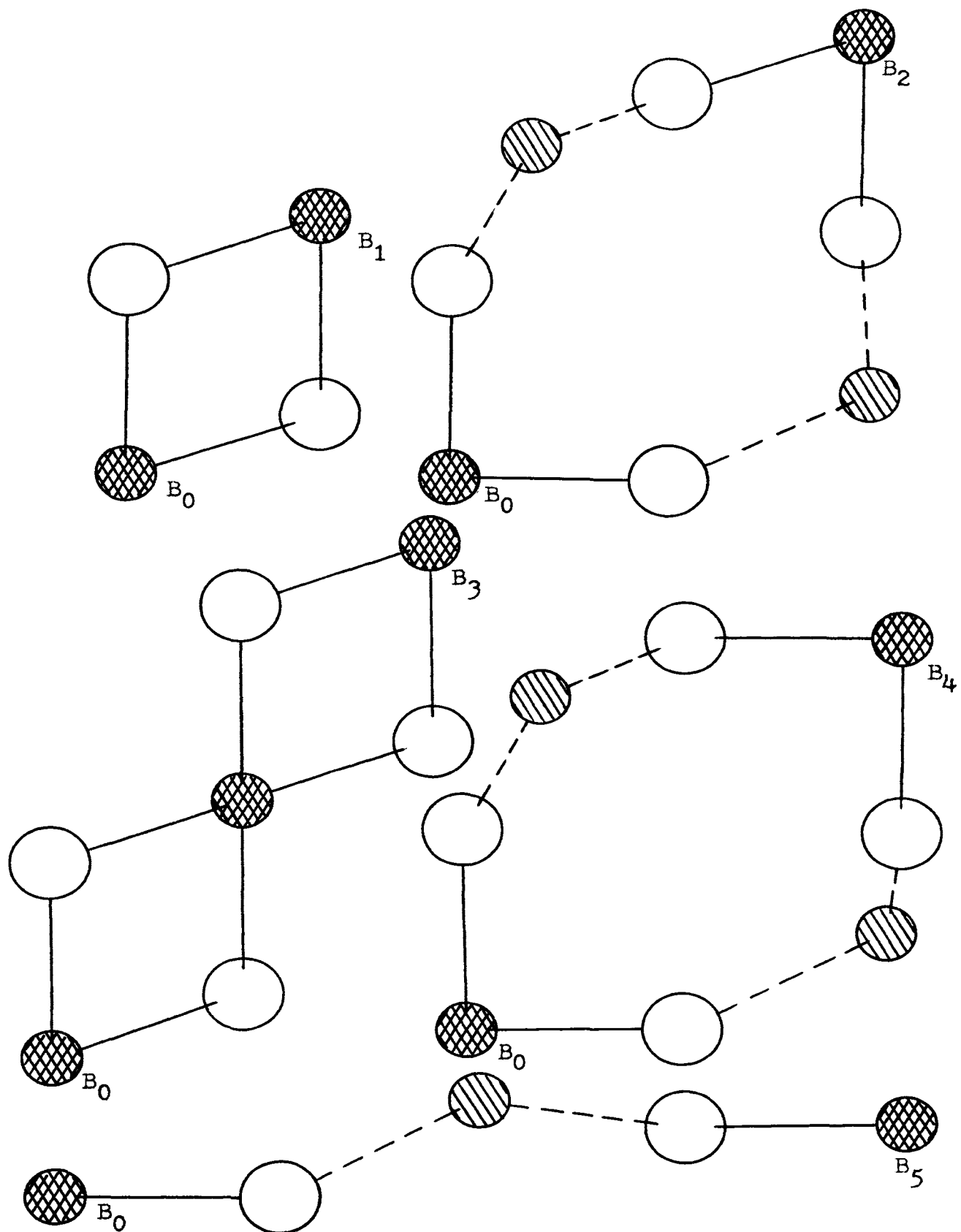
Figure 2. Interaction paths for the B-site spinel.

NN interactions are seen to be independent of the A-site cation composition and quadratically dependent on the anion composition. The 12 B_0-B_2 and six B_0-B_4 interactions are seen to depend quadratically on the A-site composition and quartically on the anion composition. The six B_0-B_3 interactions are seen to be independent of the A-site cation composition and to have a quartic dependence on the anion composition. The 12 B_0-B_5 interactions are seen to be linearly dependent on the A-site cation composition and quadratically dependent on the anion composition.

F. Molecular Field Coefficients

Each of the five interactions B_0-B_1, B_0-B_2, B_0-B_3, B_0-B_4, B_0-B_5 can be represented by an interaction strength D_1, D_2, D_3, D_4, D_5 such that the molecular field coefficient between two sublattices is equal to the sum of the products of the interaction strength and the number of interactions of this type, i.e. $\alpha_{ij} = n_1 D_1 + \ldots + n_5 D_5$, where the n_a represent the number of the ath type of interactions between an atom in the ith sublattice and those in the jth sublattice.

The molecular field coefficients can be determined by inspection of the lattice. For example, we find

$$\alpha_{12} = 2(D_3 + D_4)$$
$$\alpha_{13} = 2(D_3 + D_4)$$
$$\alpha_{14} = 2(D_3 + D_4)$$
$$\alpha_{15} = D_1 + 2D_5 \qquad \text{etc.}$$

This yields for the magnetization equations

$$M_1 = \frac{C_M}{16T} (\; 2(D_3 + D_4)(M_2 + M_3 + M_4)$$
$$+ 2D_2(M_6 + M_7 + M_{11} + M_{12} + M_{14} + M_{16})$$
$$+ (D_1 + 2D_5)(M_5 + M_8 + M_9 + M_{10} + M_{13} + M_{15}))$$
$$M_2 = \frac{C_M}{16T} (\; 2(D_3 + D_4)(M_1 + M_3 + M_4)$$
$$+ 2D_2(M_5 + M_8 + M_{11} + M_{12} + M_{13} + M_{15})$$
$$+ (D_1 + 2D_5)(M_6 + M_7 + M_9 + M_{10} + M_{14} + M_{16}))$$

etc.

Substituting these results into the determinant (equation (19)), we find

$$
\begin{vmatrix}
T' & R & R & R & S & U & U & S & S & S & U & U & S & U & S & U \\
R & T' & R & R & U & S & S & U & S & S & U & U & U & S & U & S \\
R & R & T' & R & U & S & S & U & U & U & S & S & S & U & S & U \\
R & R & R & T' & S & U & U & S & U & U & S & S & U & S & U & S \\
S & U & U & S & T' & R & R & R & S & U & S & U & S & S & U & U \\
U & S & S & U & R & T' & R & R & U & S & U & S & S & S & U & U \\
U & S & S & U & R & R & T' & R & S & U & S & U & U & U & S & S \\
S & U & U & S & R & R & R & T' & U & S & U & S & U & U & S & S \\
S & S & U & U & S & U & S & U & T' & R & R & R & S & U & U & S \\
S & S & U & U & U & S & U & S & R & T' & R & R & U & S & S & U \\
U & U & S & S & S & U & S & U & R & R & T' & R & U & S & S & U \\
U & U & S & S & U & S & U & S & R & R & R & T' & S & U & U & S \\
S & U & S & U & S & S & U & U & S & U & U & S & T' & R & R & R \\
U & S & U & S & S & S & U & U & U & S & S & U & R & T' & R & R \\
S & U & S & U & U & U & S & S & U & S & S & U & R & R & T' & R \\
U & S & U & S & U & U & S & S & S & U & U & S & R & R & R & T' \\
\end{vmatrix} = 0 \qquad (20)
$$

where $T' = -16T/C_M$, $R = 2(D_3 + D_4)$, $S = D_1 + 2D_5$, $U = 2D_2$. The four independent solutions of this determinant are

$$T_1 = \frac{C_M}{16}(6D_1 + 12D_2 + 6D_3 + 6D_4 + 12D_5), \text{ 1 root}$$

$$T_2 = \frac{C_M}{16}(-2D_1 - 4D_2 + 6D_3 + 6D_4 - 4D_5), \text{ 3 roots}$$

$$T_3 = \frac{C_M}{16}(2D_1 - 4D_2 - 2D_3 - 2D_4 + 4D_5), \text{ 6 roots}$$

$$T_4 = \frac{C_M}{16}(-2D_1 + 4D_2 - 2D_3 - 2D_4 - 4D_5), \text{ 6 roots}$$

(21)

G. Ordering Temperature in Terms of Interaction Strengths

According to the theory just developed, the ordering temperature must be the highest of the four in order to minimize energy. Hence, if the interaction strengths are known, we can determine which solution corresponds to the ordering temperature. The necessary conditions for each solution to represent the ordering temperature are given below.

$$T_1 \begin{cases} 2D_1 + D_3 + D_4 > 0 \\ D_1 + 4D_2 + 2D_3 + 2D_4 + 2D_5 > 0 \\ D_1 + D_2 + D_3 + D_4 + 2D_5 > 0 \end{cases}$$

$$T_2 \begin{cases} -D_1 - 2D_2 - 2D_5 > 0 \\ -D_1 + 2D_3 + 2D_4 - 2D_5 > 0 \\ -D_1 + D_3 + D_4 > 0 \end{cases}$$

(22)

$$T_3 \begin{cases} -D_1 - 4D_2 - 2D_3 - 2D_4 - 2D_5 > 0 \\ D_1 - 2D_3 - 2D_4 + 2D_5 > 0 \\ D_1 - 2D_2 + 2D_5 > 0 \end{cases}$$

$$T_4 \begin{cases} -D_1 - D_2 - D_3 - D_4 - 2D_5 > 0 \\ D_2 - D_3 - D_4 > 0 \\ -D_1 + 2D_2 - 2D_5 > 0 \end{cases}$$

Note that the D's are dependent on ion composition and
that the ordering can change from one form to another
with a change in the composition. The conditions above
are represented in figure 3, which gives the form of the
ordering temperature for every combination of interaction
strengths.

H. Comparison of Theoretical and Experimental Results

An n-sublattice decomposition leads to n roots for
the determinant. One of these roots (here given by T_1) is
always proportional to the sum of all exchange integrals
for an atom $\Theta = \frac{C_M}{n} \Sigma n_i J_i / k$. The MFT also yields the
result that the highest root is the ordering temperature
because this minimizes the magnetic contribution to the
free energy. Hence, $T_C = \Theta$ for the simple ferromagnetic
substance with large, positive NN exchange. However, this
result does not agree with the experimental evidence. The
Curie temperature is usually lower than the asymptotic
Curie temperature. With a four-sublattice decomposition
two solutions to the determinant are found--a single,
ferromagnetic root T_1 and a triple, antiferromagnetic root
T_2. With a 16-sublattice decomposition two additional
roots T_3 and T_4 are found; each has a multiplicity of six.

An ordering that is not strictly ferromagnetic or
antiferromagnetic (spins aligned antiparallel) cannot in
general be described by a small number of sublattices.
Hence, for the spinels considered--where a spiral configu-
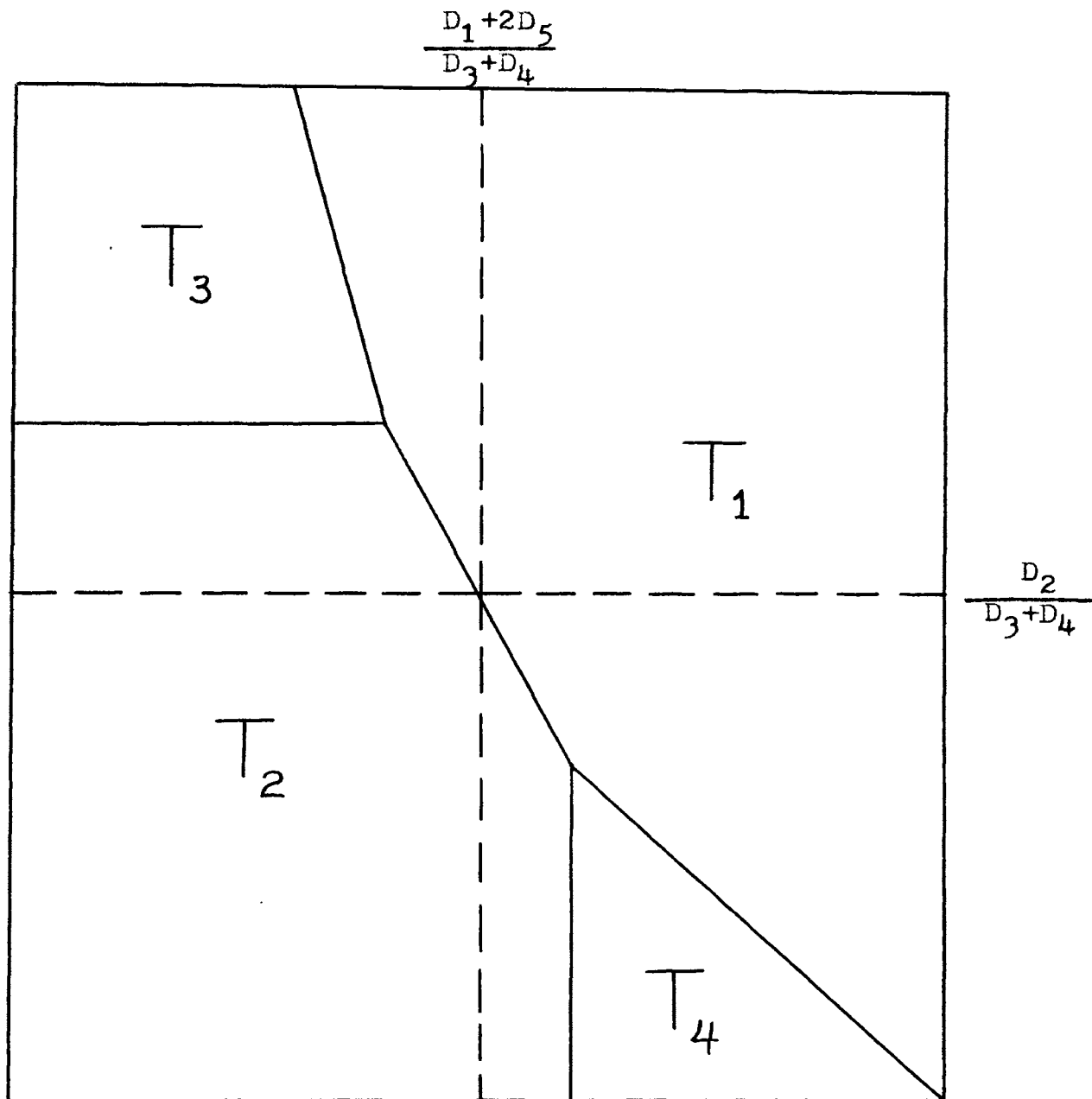ration is superimposed on an essentially ferromagnetic

$$\frac{D_1 + 2D_5}{D_3 + D_4}$$

T_3

T_1

$$\frac{D_2}{D_3 + D_4}$$

T_2

T_4

Figure 3. Regions where T_1, T_2, T_3, and T_4 are the largest of the four.

ordering--the new roots arising from the increased decomposition may possibly provide a good approximation to the ordering temperature. For these spinels the NN exchange J_0 is thought to be large and positive. Hence T_3 is seen to be the most likely choice for T_C since it would be lower than $T_1 = \Theta$ but still positive and since T_2 and T_3 would be negative if the NN interaction is the largest. In this light we will ignore a strict application of the molecular field theory and make the ad hoc assumption that the ordering temperature of the systems considered can be expressed by T_2, T_3, or T_4.

I. Relationship of Molecular Field Coefficients and Exchange Integrals

The molecular field coefficients can be directly related to the exchange integrals. Let us suppose that a magnetic ion on the ith sublattice interacts in the same manner with n neighboring ions on the jth sublattice. The total exchange energy will be[14]

$$E_{ij} = - 2J_{ij} \; \Sigma^n_{j=1} \; \frac{\langle \vec{S}_1 \cdot \vec{S}_j \rangle}{\hbar^2} \tag{23}$$

The dipole moment of the neighboring ions is just the sum of the individual dipole moments $\vec{\mu}_j = g\vec{S}_j \mu_B / \hbar$, i.e. just

$$\vec{m}_j = \frac{g\mu_B}{\hbar} \; \Sigma^n_{j=1} \; \vec{S}_j \tag{24}$$

By definition the intensity of the magnetization is given by

$$\vec{M}_j = \frac{N}{n} \vec{m}_j \tag{25}$$

where N_j is the number of magnetic ions per unit volume on the jth sublattice. Combining equations (23), (24), and (25), we find the result

$$E_{ij} = - \frac{2J_{ij}}{g^2 \mu_B^2} \frac{n}{N_j} \langle \vec{\mu}_1 \cdot \vec{M}_j \rangle \qquad (26)$$

The energy of a dipole $\vec{\mu}_1$ in a hypothetical molecular field $\vec{M}_j$ due to the magnetization of these same ions is

$$E_{ij} = - \alpha_{ij} \langle \vec{\mu}_1 \cdot \vec{M}_j \rangle \qquad (27)$$

Comparison of these two equations yields

$$\alpha_{ij} = \frac{2nJ_{ij}}{N_j g^2 \mu_B^2} \qquad (28)$$

A similar calculation involving two different types of interactions with exchange integrals J_{ija} and J_{ijb} yields

$$\alpha_{ij} = \frac{2}{N_j g^2 \mu_B^2} (n_a J_{ija} + n_b J_{ijb}) \qquad (29)$$

This suggests that the interaction strengths can be written (where $N_1 = N/16$)

$$D_{ij} = \frac{2}{N_j g^2 \mu_B^2} J_{ij} = \frac{32}{N g^2 \mu_B^2} J_{ij} \qquad (30)$$

IV. INTERACTIONS FOR SYSTEMS WITH VARYING A-SITE CATIONS

Let us consider a system $(Aa_{1-x}Ab_xCr_2X_4)$ where only the A-site cation composition is varied. In this case the interaction strength D_1 (for NN interactions) is independent of the A-site cation composition since the interaction path does not include an A-site cation. Equation (30) will yield

$$D_1 = \frac{32}{Ng^2\mu_B^2} J_0 \tag{31}$$

For exchange paths involving A-site cations, a slight modification is necessary. The exchange integral will vary with the type of cation involved. For example, the B_0-B_2 interaction involves two A-site cations and the exchange integral can be called J_1 if both are of type Ab, J_3 if both are of type Aa, and J_2 if one is of type Aa and one is of type Ab. Considering the probabilities $1-x$ and x that the A-site cation will be of type Aa and Ab, respectively, D_2 can be written

$$D_2 = \frac{32}{Ng^2\mu_B^2} (x^2J_1 + 2x(1-x)J_2 + (1-x)^2J_3) \tag{32}$$

Similarly, the other interaction strengths can be written

$$D_3 = \frac{32}{Ng^2\mu_B^2} J_4 \tag{33}$$

$$D_4 = \frac{32}{Ng^2\mu_B^2} (x^2J_5 + 2x(1-x)J_6 + (1-x)^2J_7) \tag{34}$$

$$D_5 = \frac{32}{Ng^2\mu_B^2} (xJ_8 + (1-x)J_9) \tag{35}$$

Making use of these expressions and the definition of C_M (equation (10)), the solutions of the determinant can be written

$$T_1 = \frac{5}{2k} (x^2(12J_1 - 24J_2 + 12J_3 + 6J_5 - 12J_6 + 6J_7)$$
$$+ x(24J_2 - 24J_3 + 12J_6 - 12J_7 + 12J_8 - 12J_9)$$
$$+ (6J_0 + 12J_3 + 6J_4 + 6J_7 + 12J_9))$$

$$T_2 = \frac{5}{2k} (x^2(-4J_1 + 8J_2 - 4J_3 + 6J_5 - 12J_6 + 6J_7)$$
$$+ x(-8J_2 + 8J_3 + 12J_6 - 12J_7 - 4J_8 + 4J_9)$$
$$+ (-2J_0 - 4J_3 + 6J_4 + 6J_7 - 4J_9))$$

$$T_3 = \frac{5}{2k} (x^2(-4J_1 + 8J_2 - 4J_3 - 2J_5 + 4J_6 - 2J_7)$$
$$+ x(-8J_2 + 8J_3 - 4J_6 + 4J_7 + 4J_8 - 4J_9)$$
$$+ (2J_0 - 4J_3 - 2J_4 - 2J_7 + 4J_9))$$

$$T_4 = \frac{5}{2k} (x^2(4J_1 - 8J_2 + 4J_3 - 2J_5 + 4J_6 - 2J_7)$$
$$+ x(8J_2 - 8J_3 - 4J_6 + 4J_7 - 4J_8 + 4J_9)$$
$$+ (-2J_0 + 4J_3 - 2J_4 - 2J_7 - 4J_9))$$

(36)

V. EXCHANGE INTEGRALS FOR THE SYSTEM $Hg_{1-x}Cd_xCr_2S_4$

The system $Hg_{1-x}Cd_xCr_2S_4$ has been found to be ferro-magnetic[1,2,15] throughout the range of x except for the compound $HgCr_2S_4$, which is thought to have a spiral structure.[1,10]

The experimental curves for $\Theta(x)$ and $T_C(x)$ can be approximated by a quadratic polynomial in x, say

$$\Theta(x) = ax^2 + bx + c$$

$$T_C(x) = dx^2 + ex + f$$

The coefficients for the experimental data[3] were calculated to be

$$a = -46.6^\circ K \qquad\qquad d = -28.8^\circ K$$

$$b = 54.6^\circ K \qquad\qquad e = 77.3^\circ K$$

$$c = 144.0^\circ K \qquad\qquad f = 36.0^\circ K$$

For the $\Theta(x)$ curve, the coefficients can be set equal to those determined for T_1 from equation (36). This yields three equations in the ten unknown exchange integrals.

The proper form for T_C was assumed to be one of T_2, T_3, or T_4 since the asymptotic Curie temperature Θ was given by T_1, and from the experimental data $\Theta \neq T_C$. Since it was not known which was the proper choice, each was tried in turn. The coefficients d, e, and f were set equal to those for T_2, T_3, and T_4. Each case yielded three more equations in the ten unknowns, which with those for $\Theta(x)$ gave a total of six equations in ten unknowns for each case. Clearly, the equations could not

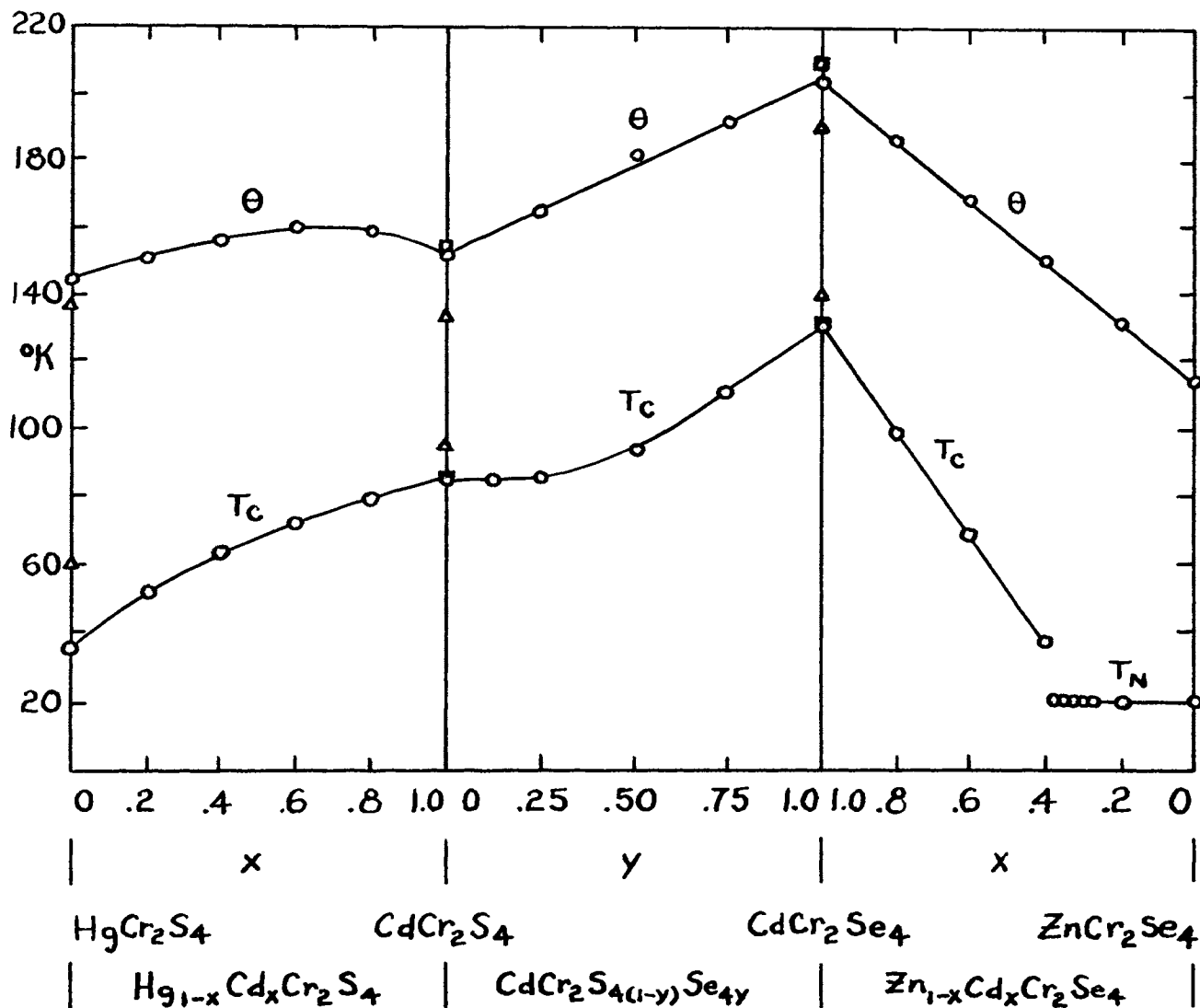Figure 4. Experimental data for the systems $Hg_{1-x}Cd_xCr_2S_4$, $CdCr_2S_{4(1-y)}Se_{4y}$, $Zn_{1-x}Cd_xCr_2Se_4$. The circular data points are from references 3 and 4. The square data points are from reference 15, and the triangular data points are from reference 1.

NN (B$_0$-B$_1$)

J_0

NNN

B$_0$-B$_2$

Cd○◇○Cd   Cd○◇○Hg   Hg○◇○Hg
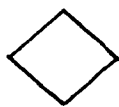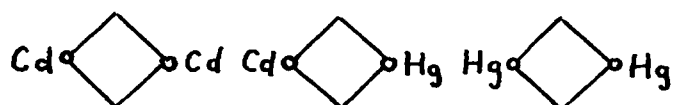
J_1 J_2 J_3

B$_0$-B$_3$

J_4

B$_0$-B$_4$

Cd○◇○Cd   Cd○◇○Hg   Hg○◇○Hg

J_5 J_6 J_7

B$_0$-B$_5$

Cd   Hg
 R   R

J_8 J_9

Figure 5. Diagram of hypothetical interaction paths and corresponding exchange integral number for the system $Hg_{1-x}Cd_xCr_2S_4$. For the system $Zn_{1-x}Cd_xCr_2Se_4$ merely replace Hg by Zn.

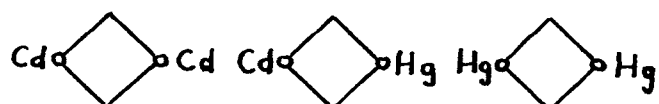be solved for all the unknown J's. However, it was pos-
sible to solve for combinations of the exchange integrals.
(In one of the cases ($T_C = T_3$) the two equations for the
x^2 term of Θ and T_C were contradictory, so the experi-
mental data was matched by a linear curve.)

$$\underline{T_C = T_2}$$

$$J_1 - 2J_2 + J_3 = -0.4^\circ K\ k$$
$$2(J_2 - J_3) + (J_8 - J_9) = -0.6^\circ K\ k$$
$$J_4 + J_5 = 6.8^\circ K\ k$$
$$J_4 + J_6 = 6.6^\circ K\ k$$
$$J_4 + J_7 = 4.2^\circ K\ k$$
$$J_0 + 2J_9 + 2J_3 = 5.4^\circ K\ k$$

$$\underline{T_C = T_3}$$

$$J_1 - 2J_2 + J_3 = 0$$
$$2(J_2 - J_3) + (J_6 - J_7) = -2.3^\circ K\ k$$
$$2J_3 + J_4 + J_7 = 0.8^\circ K\ k$$
$$J_5 - 2J_6 + J_7 = 0$$
$$J_8 - J_9 = 2.6^\circ K\ k$$
$$J_0 + 2J_9 = 9.2^\circ K\ k$$

$$\underline{T_C = T_4}$$

$$J_1 = 6.8^\circ K\ k$$
$$J_2 = 6.6^\circ K\ k$$
$$J_3 = 4.2^\circ K\ k$$
$$J_5 - 2J_6 + J_7 = 1.3^\circ K\ k$$
$$(J_6 - J_7) + (J_8 - J_9) = -3.0^\circ K\ k$$
$$J_0 + 2J_9 + J_4 + J_7 = 1.2^\circ K\ k$$

Since the NN exchange is thought to be large and
positive and those for the NNN interactions much smaller,
the proper choice is still not well identified.[2,3,5,15]
A simplifying approximation was next tried. The NNN
exchanges were approximated by a single "average" exchange
integral K. The solutions to the determinant were then

$$\Theta = T_1 = \frac{5}{2k}(6J_0 + 36K)$$

$$T_2 = \frac{5}{2k}(-2J_0 + 4K)$$

$$T_3 = \frac{5}{2k}(2J_0 - 4K)$$

$$T_4 = \frac{5}{2k}(-2J_0 - 4K)$$

(37)

For the spinels $HgCr_2S_4$ and $CdCr_2S_4$ this yielded

	$HgCr_2S_4$		$CdCr_2S_4$	
	J_0/k	K/k	J_0/k	K/k
$T_C = T_2$	$-3.0°K$	2.1	-10.0	3.4
$T_C = T_3$	7.8	0.3	15.2	-0.8
$T_C = T_4$	-15.6	4.2	-30.6	6.7

Since the value of J_0/k and K/k have already been calculated, the proper choice for T_C can be determined.
H. A. Brown[5] has found the values $J_0/k = 13.9°K$ and
$K/k = -0.7°K$ for $CdCr_2S_4$ by the B-P-W method, while
Baltzer et al.,[2] using the series expansion technique
and a two-particle cluster approximation, have found the
values $J_0/k = 11.8°K$ and $K/k = -0.3°K$ for $CdCr_2S_4$ and
$J_0/k = 13°K$ and $K/k = -0.6°K$ for $HgCr_2S_4$. The case
$T_C = T_3$ can be seen to give the closest agreement to the
previously determined values of J_0/k and K/k. Substituting
the value of J_0/k determined by Brown into the equations
above for the case $T_C = T_3$, we determined the exchange
integrals to be

$$J_0 = 13.9°K \ k$$

$$J_1 - 2J_2 + J_3 = 0$$

$$2(J_2-J_3)+(J_6-J_7) = -2.4^\circ K \; k$$

$$2J_3+J_4+J_7 = 0.8^\circ K \; k$$

$$J_5-2J_6+J_7 = 0$$

$$J_8 = 0.2^\circ K \; k$$

$$J_9 = -2.4^\circ K \; k$$

VI. EXCHANGE INTEGRALS FOR THE SYSTEM $Zn_{1-x}Cd_xCr_2Se_4$

The system $Zn_{1-x}Cd_xCr_2Se_4$ has been found to be ferro-
magnetic for the range x = 0.35 to 1 and antiferromagnetic
for the range x = 0 to 0.35.[1,3,15] Neutron diffraction
studies have shown the spinel $ZnCr_2Se_4$ to have a helical
spin configuration below the Neel temperature.[6]

The Curie temperature T_C is linear in the range
x = 0.35 to 1, and the Neel temperature T_N is approxi-
mately constant over the entire range x = 0 to 0.35. The
asymptotic Curie temperature Θ is represented by the
solution T_1, and since the experimental data shows $T_C \neq \Theta$
and $T_N \neq \Theta$, we have assumed that one of the solutions T_2,
T_3, or T_4 represents the Curie temperature while another
represents the Neel temperature. The possible cases are

	T_N	T_C
I	T_2	T_3
II	T_2	T_4
III	T_3	T_2
IV	T_3	T_4
V	T_4	T_2
VI	T_4	T_3

We then write

$$\Theta(x) = T_1 = ax + b$$

$$T_N = cx + d$$

$$T_C = ex + f$$

where we have ignored the quadratic term because the

---

experimental curves are linear.[3] (This implies directly

that $J_2 = \frac{1}{2}(J_1 + J_3)$ and $J_6 = \frac{1}{2}(J_5 + J_7)$.) The experi-

mental parameters are

$$a = 89°K \qquad c = 0 \qquad e = 152.5°K$$
$$b = 115°K \qquad d = 20°K \qquad f = -23°K$$

Equating coefficients with those in equations (36) we have

six equations in ten unknowns for each case plus the con-

ditions $J_2 = \frac{1}{2}(J_1 + J_3)$ and $J_6 = \frac{1}{2}(J_5 + J_7)$. We cannot

solve for all the J's; however, we can solve for the com-

binations given in the table below.

	I	II	III	IV	V	VI
J_1	-5.3°K	9.9	-2.5	9.9	4.4	4.4
J_2	-1.8	5.3	-1.0	5.3	3.7	3.7
J_3	1.6	0.8	0.5	0.8	2.9	2.9
J_4+J_5	4.4	4.4	9.9	-15.0	9.9	-15.0
J_4+J_6	3.7	3.7	5.3	-7.3	5.3	-7.3
J_4+J_7	2.9	2.9	0.8	0.3	0.8	0.3
J_8-J_9	9.1	-6.9	1.5	1.5	-3.1	9.1
J_0+2J_9	1.5	3.2	5.8	5.8	1.1	1.5

Again the values of the J's determined do not provide a

definite answer to the problem of determining the proper

form of T_C and T_N. Hence, we once again replace all the

NNN exchanges by an "average" exchange K. For the spinel

$CdCr_2Se_4$ this yields

	$CdCr_2Se_4$	
	J_0/k	K/k
$T_C = T_2$	$-16.1^{\circ}K$	4.9
$T_C = T_3$	22.9	-1.5
$T_C = T_4$	-45.8	9.9

For $CdCr_2Se_4$ Brown[5] has found the values $J_0/k = 17.0^{\circ}K$ and $K/k = -0.7^{\circ}K$, while Baltzer et al.[2] have found the values $J_0/k = 14.0^{\circ}K$ and $K/k = -0.1^{\circ}K$. In addition, we can calculate J_0/k and K/k for others of the ferromagnetic spinels in the system $Zn_{1-x}Cd_xCr_2Se_4$. If we extrapolate these values into the antiferromagnetic region to $x = 0$, we find that the largest of T_2, T_3, and T_4 is now given by $T_2 = 20^{\circ}K$, which agrees closely with the experimental data. The transition between T_3 and T_2 occurs at about $x = 0.2$, which compares reasonably well with the experimental value of $x = 0.35$. Hence, the best approximation to T_C and T_N are T_3 and T_2, respectively. The exchange integrals are given by case I. In addition, the value of J_0/k determined by Brown can be substituted into these combinations to yield also $J_8 = 1.4^{\circ}K$ k and $J_9 = -7.7^{\circ}K$ k.

VII. INTERACTIONS FOR SYSTEMS WITH VARYING ANIONS

We now consider systems $(ACr_2Xa_{4(1-y)}Xb_{4y})$ where the anion is varied. By procedures analogous to those of Section IV we can write the interaction strengths

$$D_1 = \frac{32}{Ng^2\mu_B^2} (y^2 J_1 + 2y(1-y)J_2 + (1-y)^2 J_3) \tag{38}$$

$$D_2 = \frac{32}{Ng^2\mu_B^2} (y^4 J_4 + 4y^3(1-y)J_5 + 2y^2(1-y)^2(J_6+J_7+J_8) + 4y(1-y)^3 J_9 + (1-y)^4 J_{10}) \tag{39}$$

$$D_3 = \frac{32}{Ng^2\mu_B^2} (y^4 J_{11} + 4y^3(1-y)J_{12} + 2y^2(1-y)^2(J_{13}+J_{14}+J_{15}) + 4y(1-y)^3 J_{16} + (1-y)^4 J_{17}) \tag{40}$$

$$D_4 = \frac{32}{Ng^2\mu_B^2} (y^4 J_{18} + 4y^3(1-y)J_{19} + 2y^2(1-y)^2(J_{20}+J_{21}+J_{22}) + 4y(1-y)^3 J_{23} + (1-y)^4 J_{24}) \tag{41}$$

$$D_5 = \frac{32}{Ng^2\mu_B^2} (y^2 J_{25} + 2y(1-y)J_{26} + (1-y)^2 J_{27}) \tag{42}$$

Here D_1 is the NN interaction strength. J_1 is the only exchange integral when $y = 1$; hence, it corresponds to J_0 for the systems $Aa_{1-x}Ab_xCr_2Xb_4$. J_3 is the only exchange integral when $y = 0$; it corresponds to J_0 for the systems $Aa_{1-x}Ab_xCr_2Xa_4$.

By substituting these expressions for the interaction strengths, the solutions for the determinant can be written in terms of the exchange integrals.

$$
\begin{aligned}
T_1 = \frac{5}{2k} \Big(& x^4 \big(12(J_4 - 4J_5 + 2(J_6+J_7+J_8) - 4J_9 + J_{10}) \\
& + 6(J_{11} - 4J_{12} + 2(J_{13}+J_{14}+J_{15}) - 4J_{16} + J_{17}) \\
& + 6(J_{18} - 4J_{19} + 2(J_{20}+J_{21}+J_{22}) - 4J_{23} + J_{24}) \big) \\
+ & x^3 \big(12(4J_5 - 4(J_6+J_7+J_8) + 12J_9 - 4J_{10}) \\
& + 6(4J_{12} - 4(J_{13}+J_{14}+J_{15}) + 12J_{16} - 4J_{17}) \\
& + 6(4J_{19} - 4(J_{20}+J_{21}+J_{22}) + 12J_{23} - 4J_{24}) \big) \\
+ & x^2 \big(6(J_1 - 2J_2 + J_3) \\
& + 12(2(J_6+J_7+J_8) - 12J_9 + 6J_{10}) \\
& + 6(2(J_{13}+J_{14}+J_{15}) - 12J_{16} + 6J_{17}) \\
& + 6(2(J_{20}+J_{21}+J_{22}) - 12J_{23} + 6J_{24}) \\
& + 12(J_{25} - 2J_{26} + J_{27}) \big) \\
+ & x \big(6(2J_2 - 2J_3) \\
& + 12(4J_9 - 4J_{10}) \\
& + 6(4J_{16} - 4J_{17}) \\
& + 6(4J_{23} - 4J_{24}) \\
& + 12(2J_{26} - 2J_{27}) \big) \\
+ & \big(6(J_3) \\
& + 12(J_{10}) \\
& + 6(J_{17}) \\
& + 6(J_{24}) \\
& + 12(J_{27}) \big) \Big)
\end{aligned}
$$

(43)

$$
\begin{aligned}
T_2 = \tfrac{5}{2k} \big(&x^4(-4(J_4 - 4J_5 + 2(J_6+J_7+J_8) - 4J_9 + J_{10}) \\
&+ 6(J_{11} - 4J_{12} + 2(J_{13}+J_{14}+J_{15}) - 4J_{16} + J_{17}) \\
&+ 6(J_{18} - 4J_{19} + 2(J_{20}+J_{21}+J_{22}) - 4J_{23} + J_{24})) \\
+x^3(&-4(4J_5 - 4(J_6+J_7+J_8) + 12J_9 - 4J_{10}) \\
&+ 6(4J_{12} - 4(J_{13}+J_{14}+J_{15}) + 12J_{16} - 4J_{17}) \\
&+ 6(4J_{19} - 4(J_{20}+J_{21}+J_{22}) + 12J_{23} - 4J_{24})) \\
+x^2(&-2(J_1 - 2J_2 + J_3) \\
&- 4(2(J_6+J_7+J_8) - 12J_9 + 6J_{10}) \\
&+ 6(2(J_{13}+J_{14}+J_{15}) - 12J_{16} + 6J_{17}) \\
&+ 6(2(J_{20}+J_{21}+J_{22}) - 12J_{23} + 6J_{24}) \\
&- 4(J_{25} - 2J_{26} + J_{27})) \\
+ x(&-2(2J_2 - 2J_3) \\
&- 4(4J_9 - 4J_{10}) \\
&+ 6(4J_{16} - 4J_{17}) \\
&+ 6(4J_{23} - 4J_{24}) \\
&- 4(2J_{26} - 2J_{27})) \\
+ (&-2(J_3) \\
&- 4(J_{10}) \\
&+ 6(J_{17}) \\
&+ 6(J_{24}) \\
&- 4(J_{27})))
\end{aligned}
$$

$$(44)$$

$$
\begin{aligned}
T_3 = \frac{5}{2k} \, (x^4(&-4(J_4 - 4J_5 + 2(J_6{+}J_7{+}J_8) - 4J_9 + J_{10}) \\
&- 2(J_{11} - 4J_{12} + 2(J_{13}{+}J_{14}{+}J_{15}) - 4J_{16} + J_{17}) \\
&- 2(J_{18} - 4J_{19} + 2(J_{20}{+}J_{21}{+}J_{22}) - 4J_{23} + J_{24})) \\
+x^3(&-4(4J_5 - 4(J_6{+}J_7{+}J_8) + 12J_9 - 4J_{10}) \\
&- 2(4J_{12} - 4(J_{13}{+}J_{14}{+}J_{15}) + 12J_{16} - 4J_{17}) \\
&- 2(4J_{19} - 4(J_{20}{+}J_{21}{+}J_{22}) + 12J_{23} - 4J_{24})) \\
+x^2(& \ 2(J_1 - 2J_2 + J_3) \\
&- 4(2(J_6{+}J_7{+}J_8) - 12J_9 + 6J_{10}) \\
&- 2(2(J_{13}{+}J_{14}{+}J_{15}) - 12J_{16} + 6J_{17}) \\
&- 2(2(J_{20}{+}J_{21}{+}J_{22}) - 12J_{23} + 6J_{24}) \\
&+ 4(J_{25} - 2J_{26} + J_{27}) \\
+ x(& \ 2(2J_2 - 2J_3) \\
&- 4(4J_9 - 4J_{10}) \\
&- 2(4J_{16} - 4J_{17}) \\
&- 2(4J_{23} - 4J_{24}) \\
&+ 4(2J_{26} - 2J_{27})) \\
+ (& \ 2(J_3) \\
&- 4(J_{10}) \\
&- 2(J_{17}) \\
&- 2(J_{24}) \\
&+ 4(J_{27})))
\end{aligned}
\tag{45}
$$

$$
\begin{aligned}
T_4 = \frac{5}{2k} (\, x^4 (\ & 4(J_4 - 4J_5 + 2(J_6+J_7+J_8) - 4J_9 + J_{10}) \\
& - 2(J_{11} - 4J_{12} + 2(J_{13}+J_{14}+J_{15}) - 4J_{16} + J_{17}) \\
& - 2(J_{18} - 4J_{19} + 2(J_{20}+J_{21}+J_{22}) - 4J_{23} + J_{24}) \\
+ x^3 (\ & 4(4J_5 - 4(J_6+J_7+J_8) + 12J_9 - 4J_{10}) \\
& - 2(4J_{12} - 4(J_{13}+J_{14}+J_{15}) + 12J_{16} - 4J_{17}) \\
& - 2(4J_{19} - 4(J_{20}+J_{21}+J_{22}) + 12J_{23} - 4J_{24})) \\
+ x^2 (& -2(J_1 - 2J_2 + J_3) \\
& + 4(2(J_6+J_7+J_8) - 12J_9 + 6J_{10}) \\
& - 2(2(J_{13}+J_{14}+J_{15}) - 12J_{16} + 6J_{17}) \\
& - 2(2(J_{20}+J_{21}+J_{22}) - 12J_{23} + 6J_{24}) \\
& - 4(J_{25} - 2J_{26} + J_{27})) \\
+ x (& -2(2J_2 - 2J_3) \\
& + 4(4J_9 - 4J_{10}) \\
& - 2(4J_{16} - 4J_{17}) \\
& - 2(4J_{23} - 4J_{24}) \\
& - 4(2J_{26} - 2J_{27})) \\
+ \ (& -2(J_3) \\
& + 4(J_{10}) \\
& - 2(J_{17}) \\
& - 2(J_{24}) \\
& - 4(J_{27})))
\end{aligned}
$$

(46)

VIII. EXCHANGE INTEGRALS FOR THE SYSTEM $CdCr_2S_{4(1-y)}Se_{4y}$

Since the solution $T_C = T_3$ has been found to be applicable for the spinels $CdCr_2S_4$ and $CdCr_2Se_4$, we will apply this solution to the entire system $CdCr_2S_{4(1-y)}Se_{4y}$. Substituting the interaction strengths from Section VII, we can find expressions for $T_C(y)$ and $\Theta(y)$ in terms of the exchange integrals. These expressions are quartic in the parameter y, and they can be compared with quartic polynomials matched to the experimental data of Wojtowicz, Baltzer, and Robbins,[4] i.e. with

$$\Theta(y) = ay^4 + by^3 + cy^2 + dy + e$$
$$T_C(y) = fy^4 + gy^3 + hy^2 + jy + k$$

where

$a = b = c = 0$	$f = g = 0$
$d = 52°K$	$h = 22.2°K$
$e = 152°K$	$j = -4.2°K$
	$k = 33.8°K$

By comparison of coefficients of powers of y, we can derive ten equations linear in the exchange integrals. These can be solved to yield
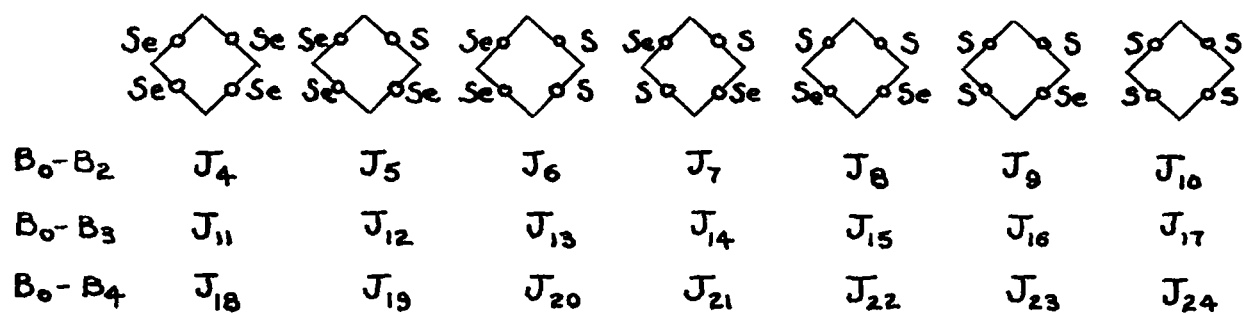
$$J_1 + 2J_{25} = 16.1°K \ k$$
$$J_2 + 2J_{26} = 13.9°K \ k$$
$$J_3 + 2J_{27} = 13.5°K \ k$$
$$2J_4 + J_{11} + J_{18} = -6.2°K \ k$$
$$2J_5 + J_{12} + J_{19} = -4.1°K \ k$$
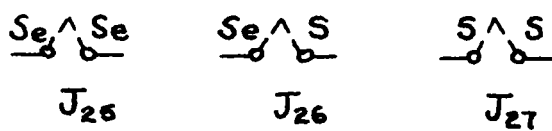$$2(J_6 + J_7 + J_8) + (J_{13} + J_{14} + J_{15}) + (J_{20} + J_{21} + J_{22}) = -8.8°K \ k$$
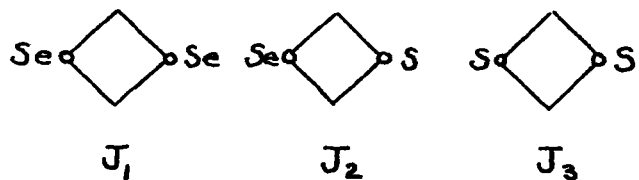
Figure 6. Diagram of hypothetical interaction paths and corresponding exchange integral number for the system $CdCr_2S_{4(1-y)}Se_{4y}$.

$$2J_9 + J_{16} + J_{22} = -2.7^\circ K \ k$$

$$2J_{10} + J_{17} + J_{24} = -3.4^\circ K \ k$$

Using the approximations

$$J_{11} = J_{18}$$

$$J_{12} = J_{19}$$

$$J_6 = J_7 = J_8, \ J_{13} = J_{14} = J_{15} = J_{20} = J_{21} = J_{22}$$

$$J_{16} = J_{23}$$

$$J_{17} = J_{24}$$

and the values

$$J_1 = 17.0^\circ K \ k$$

$$J_2 = 15.4^\circ K \ k$$

$$J_3 = 13.9^\circ K \ k$$

determined by Brown,[5] the exchange integrals for the system are determined to be

$$J_{25} = -0.5^\circ K \ k$$

$$J_{26} = -0.8^\circ K \ k$$

$$J_{27} = -0.2^\circ K \ k$$

$$J_4 + J_{11} = -3.1^\circ K \ k$$

$$J_5 + J_{12} = -2.1^\circ K \ k$$

$$J_6 + J_{13} = -1.5^\circ K \ k$$

$$J_9 + J_{16} = -1.4^\circ K \ k$$

$$J_{10} + J_{17} = -1.7^\circ K \ k$$

IX. CONCLUSION

The Weiss molecular field theory was applied to the lattice of the B-site spinel. The forms of the ordering temperatures and the asymptotic Curie temperature were found for a 16-sublattice model with collinear spins. The theory gave 16 roots, of which four were independent. The singly-occurring root T_1 was seen to be equal to the asymptotic Curie temperature. One of the others had a multiplicity of three, and the other two had a multiplicity of six. The theory was applied to the problem of determining the exchange integrals for systems of the type $Aa_{1-x}Ab_xCr_2X_4$ and $ACr_2Xa_{4(1-y)}Xb_{4y}$. An ad hoc assumption was made that the ordering temperature was given by T_2, T_3, or T_4 and not by $T_1 = T_C = \Theta$, which was not justified experimentally for the systems considered. With this assumption a number of relationships were found between exchange integrals, and the NN exchange integral and an "average" NNN exchange integral were calculated for several of the spinels.

The theory was applied to the systems $Hg_{1-x}Cd_xCr_2S_4$, $CdCr_2S_{4(1-y)}Se_{4y}$, and $Zn_{1-x}Cd_xCr_2Se_4$. There were too many exchange integrals for a formal evaluation, and the results by no means provide a definitive test of the foregoing assumption. On the other hand, there were no contradictions between theory and experiment. Even when the many NNN exchange integrals were replaced by a single "average" exchange K, the results were reasonable. The systems

considered coincided at the spinels $CdCr_2Se_4$ and $CdCr_2S_4$ (see figure 4). Additional data on related systems would be helpful in evaluating the exchange integrals. Since they would have to coincide where the systems met, additional conditions would be placed on them. Neutron diffraction evaluation of the antiferromagnetic samples would aid in determining if the lattice was sufficiently subdivided.

X. APPENDIX: SOLUTION OF THE DETERMINANT

The determinant can be solved by reducing it to a diagonal matrix. The reduction is accomplished by replacing two rows or columns of the matrix with the sum and difference of the two rows or columns. Following is one scheme for doing this; each indicated step should be performed first on rows (columns) and then on columns (rows).

	Step 1.		Step 2.		Step 3.
replace 1 by	1+2	1 by	1+3	1 by	1+9+5+13
2	2-1	2	2+4	2	2+14
3	3+4	3	3-1	3	3+11
4	4-3	4	4-2	4	4+8
5	5+6	5	5+7	5	5+13-1-9
6	6-5	6	6+8	6	6+10
7	7+8	7	7-5	7	7+15
8	8-7	8	8-6	8	8-4
9	9+10	9	9+11	9	9-1
10	10-9	10	10+12	10	10-6
11	11+12	11	11-9	11	11-3
12	12-11	12	12-10	12	12+16
13	13+14	13	13+15	13	13-5
14	14-13	14	14+16	14	14-2
15	15+16	15	15-13	15	15-7
16	16-15	16	16-14	16	16-12

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XII. VITA

Wayne Edmund Holland was born on January 26, 1945 in Kansas City, Missouri. He received his primary and secondary education in Kansas City, Missouri. He has received his college education from the University of Missouri-Kansas City in Kansas City, Missouri, and the University of Missouri-Rolla in Rolla, Missouri. He received his Bachelor of Science degree in Physics from the University of Missouri-Kansas City in Kansas City, Missouri, in June 1967.

He has been enrolled in the Graduate School of the University of Missouri-Rolla since September 1967 and has been appointed to a Research Assistantship for the periods September 1967 to June 1968 and September 1968 to June 1969 and to a Graduate Assistantship for the period September 1969 to January 1970.