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Application of the Weiss molecular field theory to the lattice of the B-Site spinel

Wayne Edmund Holland

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

BY

WAYNE EDMUND HOLLAND, 1945-

A

THESIS

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[Signatures]
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 \( \text{Aa}_{1-x}\text{Ab}_x\text{Cr}_2\text{X}_4 \) and \( \text{ACr}_2\text{Xa}_4(1-y)\text{Xb}_{4y} \). The theoretical results have been compared to the experimental data for the systems \( \text{Hg}_{1-x}\text{Cd}_x\text{Cr}_2\text{S}_4 \), \( \text{Zn}_{1-x}\text{Cd}_x\text{Cr}_2\text{Se}_4 \), and \( \text{CdCr}_2\text{S}_4(1-y)\text{Se}_{4y} \) 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 $\mu = g\mu_B \mathbf{S}$ 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 \(\Theta\) and \(T_C\) for the spinels \(\text{CdCr}_2\text{S}_4\), \(\text{CdCr}_2\text{Se}_4\), and \(\text{HgCr}_2\text{S}_4\). Baltzer, Wojtowicz, Robbins, and Lopatin\(^2\) have measured \(\Theta\) 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 \(\text{Hg}_{1-x}\text{Cd}_x\text{Cr}_2\text{S}_4\) and \(\text{Zn}_{1-x}\text{Cd}_x\text{Cr}_2\text{Se}_4\). Also by the same method Wojtowicz, Baltzer, and Robbins\(^4\) have determined \(J\) and \(K\) for the system \(\text{CdCr}_2\text{S}_4(1-y)\text{Se}_4y\). They have also measured \(\Theta\) 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 \(\text{ZnCr}_2\text{Se}_4\) by neutron diffraction studies. Lotgering\(^7,\,8\) has measured \(\Theta\) 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 \(\text{ZnCr}_2\text{Se}_4\). Hastings and Corliss\(^10\) have determined the spin ordering for \(\text{HgCr}_2\text{S}_4\) by neutron diffraction.
A. Definition of the B-site Spinel

The general chemical formula of the spinel is $\text{AB}_2\text{X}_4$. 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
\((Aa_{1-x}Ab_xCr_2X_4, 0 \leq x \leq 1)\) in which the A-site cation is varied between one type of cation \((Aa)\) and another \((Ab)\) and systems \((ACr_2Xa_{4(1-y)}Xb_4y, 0 \leq y \leq 1)\) 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, a perfect short range order with only NN interactions does not necessarily lead to long range antiferromagnetic order. Lotgering has found that antiferromagnetic interactions of about five percent of the strength of the

---

*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 ferromagnetism. Dwight and Menyuk\textsuperscript{8} have found that an adequate characterization of the exchange energy requires the consideration 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 sublattice until there are no interactions between atoms on the same sublattice.\textsuperscript{12} Hence, we divide each fcc sublattice 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 \textsuperscript{i}th sublattice may be written according to Weiss theory as

\[
\vec{H}_m = a_{11}\vec{M}_1 + a_{12}\vec{M}_2 + \ldots + a_{1,16}\vec{M}_{16},
\]

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

\[
\vec{H}_1 = \vec{H} + a_{11}\vec{M}_1 + a_{12}\vec{M}_2 + \ldots + a_{1,16}\vec{M}_{16}.
\]

At thermal equilibrium the magnetization of the \(i\)th

*We have numbered these according to their order as given in footnote (*) on page 4.
sublattice is given by\(^1\text{3}\)
\[
M_1 = (1/16)NgB_S S_S(x_1)
\]
(3)

where
\[
B_S(x_1) = \frac{2S+1}{2S} \coth \frac{2S+1}{2S} x_1 - \frac{1}{2S} \coth \frac{x_1}{2S}
\]
and where
\[
x_1 = \frac{Sg\mu_B}{kT} H_1.
\]

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

Also, equation (2) reduces to
\[
H_1 = \hat{H} + \alpha_{11}M_1 + \alpha_{12}M_2 + \ldots + \alpha_{1,16}M_{16}
\]
(7)
since \(\hat{H}\) and \(\hat{H}_1\) are parallel in the paramagnetic region.

Substitution of equation (6) into equation (7) yields
\[
M_1 = \frac{Ng^2\mu_B^2S(S+1)}{48kT} (\hat{H} + \alpha_{11}M_1 + \ldots + \alpha_{1,16}M_{16})
\]
(8)
or

\[ M_1 = \frac{C_M}{16T} (H + \sum_{j=1}^{16} \alpha_{1j} M_j) \]  \hspace{1cm} (9)

where

\[ C_M = \frac{N_S^2 \mu_B^2 S(S+1)}{3k} \]  \hspace{1cm} (10)

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

\[ M = \sum_{i=1}^{16} M_i = \frac{C_M}{16T} (16H + \sum_{i=1}^{16} \sum_{j=1}^{16} \alpha_{1j} M_j) \]  \hspace{1cm} (11)

or

\[ M = \frac{C_M}{16T} (16H + \sum_{j=1}^{16} M_j (\sum_{i=1}^{16} \alpha_{1j})). \]  \hspace{1cm} (12)

The sum \( \sum_{i=1}^{16} \alpha_{1j} \) 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 \( \alpha_0 \)) can be factored from the summation, leaving

\[ M = \frac{C_M}{16T} (16H + \alpha_0 \sum_{j=1}^{16} M_j) \]  \hspace{1cm} (13)

\[ = \frac{C_M}{16T} (16H + \alpha_0 M). \]

Solving for \( M \), we find

\[ M = C_M H / (T - \frac{C_M}{16} \alpha_0). \]  \hspace{1cm} (14)

Hence, the susceptibility is

\[ \chi = M / H = C_M / (T - \frac{C_M}{16} \alpha_0). \]  \hspace{1cm} (15)

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

\[ \Theta = \frac{C_M}{16} \alpha_0. \]  \hspace{1cm} (16)
The magnetization equations are also valid in the vicinity of $T_N$ and $T_C$. With $H = 0$ these equations become

$$M_1 = \frac{C}{16T} \sum_{j=1}^{16} \alpha_{ij} M_j$$

(17)

or

$$0 = -\frac{16T}{C} M_1 + \sum_{j=1}^{16} \alpha_{ij} M_j.$$

(18)

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

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

(19)

E. Exchange Interactions for the B-site Spinel

Following Baltzer et al., 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. $\alpha_{ij} = n_1D_1 + \ldots + n_5D_5$, where the $n_a$ represent the number of the $a^{th}$ type of interactions between an atom in the $i^{th}$ sublattice and those in the $j^{th}$ sublattice.

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

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

etc.
This yields for the magnetization equations

\[
M_1 = \frac{C_M}{16T} \left( 2(D_3 + D_4)(M_2 + M_3 + M_4) \right. \\
\left. + 2D_2(M_6 + M_7 + M_{11} + M_{12} + M_{14} + M_{16}) \right) \\
+ (D_1 + 2D_5)(M_5 + M_8 + M_9 + M_{10} + M_{13} + M_{15}) \\
M_2 = \frac{C_M}{16T} \left( 2(D_3 + D_4)(M_1 + M_3 + M_4) \right. \\
\left. + 2D_2(M_5 + M_8 + M_{11} + M_{12} + M_{13} + M_{15}) \right) \\
+ (D_1 + 2D_5)(M_6 + M_7 + M_9 + M_{10} + M_{14} + M_{16}) \\
\text{etc.}
\]

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

\[
\begin{array}{cccccccccccccccccccc}
R & T' & R & R & U & S & S & U & U & S & U & S & U \\
R & R & T' & R & U & S & S & U & U & U & S & S & S & U & S \\
R & R & R & T' & S & U & U & S & U & U & S & S & S & U & S \\
S & U & U & S & T' & R & R & R & S & U & S & S & U & S & U \\
U & S & S & S & U & R & T' & R & R & U & S & S & S & S & U & U \\
U & S & S & S & U & R & T' & R & S & U & S & U & S & U & S & S \\
S & U & U & S & R & R & T' & U & S & S & U & S & U & S & U & S \\
S & S & U & U & S & S & U & S & U & T' & R & R & R & S & U & U \\
S & S & U & U & S & U & S & R & T' & R & R & U & S & S & U \\
U & U & S & S & S & U & S & U & R & T' & R & U & S & S & U \\
U & U & S & S & S & U & S & R & R & T' & S & U & U & S & U \\
\end{array}
\]

\[(20)\]

\[= 0\]
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

\[
\begin{align*}
T_1 &= \frac{C}{16} (6D_1 + 12D_2 + 6D_3 + 6D_4 + 12D_5), \quad 1 \text{ root} \\
T_2 &= \frac{C}{16} (-2D_1 - 4D_2 + 6D_3 + 6D_4 - 4D_5), \quad 3 \text{ roots} \\
T_3 &= \frac{C}{16} (2D_1 - 4D_2 - 2D_3 - 2D_4 + 4D_5), \quad 6 \text{ roots} \\
T_4 &= \frac{C}{16} (-2D_1 + 4D_2 - 2D_3 - 2D_4 - 4D_5), \quad 6 \text{ roots}
\end{align*}
\]

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.

\[
\begin{align*}
T_1 &= \begin{cases}
2D_1 + D_3 + D_4 > 0 \\
D_1 + 4D_2 + 2D_3 + 2D_4 + 2D_5 > 0 \\
D_1 + D_2 + D_3 + D_4 + 2D_5 > 0 \\
-D_1 - 2D_2 - 2D_5 > 0
\end{cases} \\
T_2 &= \begin{cases}
-D_1 - 2D_2 - 2D_5 > 0 \\
-D_1 + 2D_3 + 2D_4 - 2D_5 > 0 \\
-D_1 + D_3 + D_4 > 0 \\
-D_1 - 4D_2 - 2D_3 - 2D_4 - 2D_5 > 0
\end{cases} \\
T_3 &= \begin{cases}
D_1 - 2D_3 - 2D_4 + 2D_5 > 0 \\
D_1 - 2D_2 + 2D_5 > 0 \\
-D_1 - D_2 - D_3 - D_4 - 2D_5 > 0
\end{cases} \\
T_4 &= \begin{cases}
D_2 - D_3 - D_4 > 0 \\
-D_1 + 2D_2 - 2D_5 > 0
\end{cases}
\]

(22)
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 $\Theta = \frac{C}{n} \sum J_i/k$. 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 configuration is superimposed on an essentially ferromagnetic
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 $T_1 = 0$ 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 $i$th sublattice interacts in the same manner with $n$ neighboring ions on the $j$th sublattice. The total exchange energy will be

$$E_{ij} = -2J_{ij} \frac{\gamma_n}{n^2} \langle \vec{S}_i \cdot \vec{S}_j \rangle$$

(23)

The dipole moment of the neighboring ions is just the sum of the individual dipole moments $\vec{m}_j = gS_j \frac{\mu_B}{h}$, i.e. just

$$\vec{m}_j = \frac{e\mu_B}{h} \sum_{j=1}^{n} \hat{S}_j$$

(24)

By definition the intensity of the magnetization is given by

$$\vec{M}_j = \frac{N_4}{n} \vec{m}_j$$

(25)
where $N_j$ is the number of magnetic ions per unit volume on the $j^{th}$ sublattice. Combining equations (23), (24), and (25), we find the result

$$E_{1j} = -\frac{2J_{1j}}{\mu_B^2} \frac{n}{N_j} \langle \vec{\mu}_1 \cdot \vec{M}_j \rangle \quad (26)$$

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

$$E_{1j} = -\alpha_{1j} \langle \vec{\mu}_1 \cdot \vec{M}_j \rangle \quad (27)$$

Comparison of these two equations yields

$$\alpha_{1j} = \frac{2nJ_{1j}}{N_j \mu_B^2} \quad (28)$$

A similar calculation involving two different types of interactions with exchange integrals $J_{1ja}$ and $J_{1jb}$ yields

$$\alpha_{1j} = \frac{2}{N_j \mu_B^2} \left( n_a J_{1ja} + n_b J_{1jb} \right) \quad (29)$$

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

$$D_{1j} = \frac{2}{N_j \mu_B^2} J_{1j} = \frac{32}{N \mu_B^2} J_{1j} \quad (30)$$
IV. INTERACTIONS FOR SYSTEMS WITH VARYING A-SITE CATIONS

Let us consider a system \((\text{Aa}_{1-x}\text{Ab}_x\text{Cr}_2\text{X}_4)\) 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

\[
D_1 = \frac{32}{N g^2 \mu_B^2} J_0 \quad (31)
\]

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 \(\text{Ab}\), \(J_3\) if both are of type \(\text{Aa}\), and \(J_2\) if one is of type \(\text{Aa}\) and one is of type \(\text{Ab}\). Considering the probabilities \(1-x\) and \(x\) that the A-site cation will be of type \(\text{Aa}\) and \(\text{Ab}\), respectively, \(D_2\) can be written

\[
D_2 = \frac{32}{N g^2 \mu_B^2} (x^2 J_1 + 2x(1-x)J_2 + (1-x)^2 J_3) \quad (32)
\]

Similarly, the other interaction strengths can be written

\[
D_3 = \frac{32}{N g^2 \mu_B^2} J_4 \quad (33)
\]

\[
D_4 = \frac{32}{N g^2 \mu_B^2} (x^2 J_5 + 2x(1-x)J_6 + (1-x)^2 J_7) \quad (34)
\]

\[
D_5 = \frac{32}{N g^2 \mu_B^2} (x J_8 + (1-x)J_9) \quad (35)
\]
Making use of these expressions and the definition of $C_M$ (equation (10)), the solutions of the determinant can be written

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

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

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

\[
T_4 = \frac{5}{2k} (x^2(4J_1 - 8J_2 + 4J_3 - 2J_5 + 4J_6 - 2J_7) \\
+ x(8J_2 - 8J_3 + 4J_6 + 4J_7 - 4J_8 + 4J_9) \\
+ (-2J_0 + 4J_3 - 2J_4 - 2J_7 - 4J_9))
\]
V. EXCHANGE INTEGRALS FOR THE SYSTEM Hg$_{1-x}$Cd$_x$Cr$_2$S$_4$

The system Hg$_{1-x}$Cd$_x$Cr$_2$S$_4$ has been found to be ferromagnetic$^{1,2,15}$ throughout the range of $x$ except for the compound HgCr$_2$S$_4$, 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

\begin{align*}
a &= -46.6^\circ K \\
b &= 54.6^\circ K \\
c &= 144.0^\circ K \\
d &= -28.8^\circ K \\
e &= 77.3^\circ K \\
f &= 36.0^\circ K
\end{align*}

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 $\Theta$ 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 \(\text{Hg}_1-x\text{Cd}_x\text{Cr}_2\text{S}_4\), \(\text{CdCr}_2\text{S}_4\), \(\text{CdCr}_2\text{Se}_4\), \(\text{ZnCr}_2\text{Se}_4\), \(\text{Hg}_{1-x}\text{Cd}_x\text{Cr}_2\text{S}_4\), \(\text{CdCr}_2\text{S}_4(1-y)\text{Se}_4y\), \(\text{Zn}_{1-x}\text{Cd}_x\text{Cr}_2\text{Se}_4\). 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.
Figure 5. Diagram of hypothetical interaction paths and corresponding exchange integral number for the system Hg$_1$Cd$_x$Cr$_2$S$_4$. For the system Zn$_{1-x}$Cd$_x$Cr$_2$Se$_4$ merely replace Hg by Zn.
be solved for all the unknown J's. However, it was possible 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 experimental data was matched by a linear curve.)

\[
\begin{align*}
T_C = T_2 & \\
J_1 - 2J_2 + J_3 &= -0.4^\circ K \\
2(J_2 - J_3) + (J_8 - J_9) &= -0.6^\circ K \\
J_4 + J_5 &= 6.8^\circ K \\
J_4 + J_6 &= 6.6^\circ K \\
J_4 + J_7 &= 4.2^\circ K \\
J_0 + 2J_9 + 2J_3 &= 5.4^\circ K \\
\end{align*}
\]

\[
\begin{align*}
T_C = T_3 & \\
J_1 - 2J_2 + J_3 &= 0 \\
2(J_2 - J_3) + (J_6 - J_7) &= -2.3^\circ K \\
J_4 + J_5 &= 0.8^\circ K \\
J_5 - 2J_6 + J_7 &= 0 \\
J_8 - J_9 &= 2.6^\circ K \\
J_0 + 2J_9 &= 9.2^\circ K \\
\end{align*}
\]

\[
\begin{align*}
T_C = T_4 & \\
J_1 &= 6.8^\circ K \\
J_2 &= 6.6^\circ K \\
J_3 &= 4.2^\circ K \\
J_5 - 2J_6 + J_7 &= 1.3^\circ K \\
(J_6 - J_7) + (J_8 - J_9) &= -3.0^\circ K \\
J_0 + 2J_9 + J_4 + J_7 &= 1.2^\circ K \\
\end{align*}
\]

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.\textsuperscript{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
\[ \phi = T_1 = \frac{5}{2k} (6J_0 + 36K) \]
\[ T_2 = \frac{5}{2k} (-2J_0 + 4K) \]
\[ T_3 = \frac{5}{2k} (2J_0 - 4K) \]
\[ T_4 = \frac{5}{2k} (-2J_0 - 4K) \]

For the spinels HgCr\(_2\)S\(_4\) and CdCr\(_2\)S\(_4\) this yielded

<table>
<thead>
<tr>
<th></th>
<th>HgCr(_2)S(_4)</th>
<th>CdCr(_2)S(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(J_0/k)</td>
<td>(K/k)</td>
</tr>
<tr>
<td>(T_C = T_2)</td>
<td>-3.0°K</td>
<td>2.1</td>
</tr>
<tr>
<td>(T_C = T_3)</td>
<td>7.8</td>
<td>0.3</td>
</tr>
<tr>
<td>(T_C = T_4)</td>
<td>-15.6</td>
<td>4.2</td>
</tr>
</tbody>
</table>

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\(_2\)S\(_4\) by the B-F-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\(_2\)S\(_4\) and \(J_0/k = 13°K\) and \(K/k = -0.6°K\) for HgCr\(_2\)S\(_4\). 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

\[ J_0 = 13.9°K \]
\[ J_1 - 2J_2 + J_3 = 0 \]
\[2(J_2 - J_3) + (J_6 - J_7) = -2.4^\circ K\]
\[2J_3 + J_4 + J_7 = 0.8^\circ K\]
\[J_5 - 2J_6 + J_7 = 0\]
\[J_8 = 0.2^\circ K\]
\[J_9 = -2.4^\circ K\]
VI. EXCHANGE INTEGRALS FOR THE SYSTEM $\text{Zn}_1-x\text{Cd}_x\text{Cr}_2\text{Se}_4$

The system $\text{Zn}_1-x\text{Cd}_x\text{Cr}_2\text{Se}_4$ has been found to be ferromagnetic for the range $x = 0.35$ to 1 and antiferromagnetic for the range $x = 0$ to 0.35. Neutron diffraction studies have shown the spinel $\text{ZnCr}_2\text{Se}_4$ to have a helical spin configuration below the Neel temperature.

The Curie temperature $T_C$ is linear in the range $x = 0.35$ to 1, and the Neel temperature $T_N$ is approximately constant over the entire range $x = 0$ to 0.35. The asymptotic Curie temperature $\Theta$ 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

<table>
<thead>
<tr>
<th></th>
<th>$T_N$</th>
<th>$T_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$T_2$</td>
<td>$T_3$</td>
</tr>
<tr>
<td>II</td>
<td>$T_2$</td>
<td>$T_4$</td>
</tr>
<tr>
<td>III</td>
<td>$T_3$</td>
<td>$T_2$</td>
</tr>
<tr>
<td>IV</td>
<td>$T_3$</td>
<td>$T_4$</td>
</tr>
<tr>
<td>V</td>
<td>$T_4$</td>
<td>$T_2$</td>
</tr>
<tr>
<td>VI</td>
<td>$T_4$</td>
<td>$T_3$</td>
</tr>
</tbody>
</table>

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.\textsuperscript{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 experimental parameters are

\[
\begin{align*}
a &= 89^\circ K \\
b &= 115^\circ K \\
c &= 0 \\
d &= 20^\circ K \\
e &= 152.5^\circ K \\
f &= -23^\circ K
\end{align*}
\]

Equating coefficients with those in equations (36) we have six equations in ten unknowns for each case plus the conditions \( J_2 = \frac{1}{2}(J_1 + J_3) \) and \( J_6 = \frac{1}{2}(J_5 + J_7) \). We cannot solve for all the \( J \)'s; however, we can solve for the combinations given in the table below.

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>( J_1 )</td>
<td>(-5.3^\circ K)</td>
<td>9.9</td>
<td>(-2.5)</td>
<td>9.9</td>
<td>4.4</td>
<td>4.4</td>
</tr>
<tr>
<td>( J_2 )</td>
<td>(-1.8)</td>
<td>5.3</td>
<td>(-1.0)</td>
<td>5.3</td>
<td>3.7</td>
<td>3.7</td>
</tr>
<tr>
<td>( J_3 )</td>
<td>1.6</td>
<td>0.8</td>
<td>0.5</td>
<td>0.8</td>
<td>2.9</td>
<td>2.9</td>
</tr>
<tr>
<td>( J_4 + J_5 )</td>
<td>4.4</td>
<td>4.4</td>
<td>9.9</td>
<td>(-15.0)</td>
<td>9.9</td>
<td>(-15.0)</td>
</tr>
<tr>
<td>( J_4 + J_6 )</td>
<td>3.7</td>
<td>3.7</td>
<td>5.3</td>
<td>(-7.3)</td>
<td>5.3</td>
<td>(-7.3)</td>
</tr>
<tr>
<td>( J_4 + J_7 )</td>
<td>2.9</td>
<td>2.9</td>
<td>0.8</td>
<td>0.3</td>
<td>0.8</td>
<td>0.3</td>
</tr>
<tr>
<td>( J_8 - J_9 )</td>
<td>9.1</td>
<td>(-6.9)</td>
<td>1.5</td>
<td>1.5</td>
<td>(-3.1)</td>
<td>9.1</td>
</tr>
<tr>
<td>( J_0 + 2J_9 )</td>
<td>1.5</td>
<td>3.2</td>
<td>5.8</td>
<td>5.8</td>
<td>1.1</td>
<td>1.5</td>
</tr>
</tbody>
</table>

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\textsubscript{2}Se\textsubscript{4} this yields
For CdCr$_2$Se$_4$ 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$_x$Cr$_2$Se$_4$. 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 $J_9 = -7.7^\circ K k$. 

<table>
<thead>
<tr>
<th></th>
<th>CdCr$_2$Se$_4$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_C = T_2$</td>
<td>$J_0/k$</td>
<td>$K/k$</td>
</tr>
<tr>
<td></td>
<td>$-16.1^\circ K$</td>
<td>$4.9$</td>
</tr>
<tr>
<td>$T_C = T_3$</td>
<td>$22.9$</td>
<td>$-1.5$</td>
</tr>
<tr>
<td>$T_C = T_4$</td>
<td>$-45.8$</td>
<td>$9.9$</td>
</tr>
</tbody>
</table>
We now consider systems \((\text{ACr}_2\text{X}_a(1-y)\text{X}_b4_y)\) where the anion is varied. By procedures analogous to those of Section IV we can write the interaction strengths

\[
D_1 = \frac{32}{\sqrt{Ng}^2} \left( y^2 J_1 + 2y(1-y)J_2 + (1-y)^2 J_3 \right) \tag{38}
\]

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

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

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

\[
D_5 = \frac{32}{\sqrt{Ng}^2} \left( y^2 J_{25} + 2y(1-y)J_{26} + (1-y)^2 J_{27} \right) \tag{42}
\]

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 \(\text{A}_{a_1-x}\text{AB}_x\text{Cr}_2\text{X}_b\). \(J_3\) is the only exchange integral when \(y = 0\); it corresponds to \(J_0\) for the systems \(\text{A}_{a_1-x}\text{AB}_x\text{Cr}_2\text{X}_a\).

By substituting these expressions for the interaction strengths, the solutions for the determinant can be written in terms of the exchange integrals.
\[ T_1 = \frac{5}{2k} (x^4 (12(J_4 - 4J_5 + 2(J_6+J_7+J_8) - 4J_9 + J_{10}) \\
+ 6(J_{11} - 4J_{12} + 2(J_{13}+J_{14}+J_{15}) - 4J_{16} + J_{17}) \\
+ 6(J_{18} - 4J_{19} + 2(J_{20}+J_{21}+J_{22}) - 4J_{23} + J_{24}) \\
+ x^3 (12(4J_5 - 4(J_6+J_7+J_8) + 12J_9 - 4J_{10}) \\
+ 6(4J_{12} - 4(J_{13}+J_{14}+J_{15}) + 12J_{16} - 4J_{17}) \\
+ 6(4J_{19} - 4(J_{20}+J_{21}+J_{22}) + 12J_{23} - 4J_{24}) \\
+ x^2 (6(J_1 - 2J_2 + J_3) \\
+ 12(2(J_6+J_7+J_8) - 12J_9 + 6J_{10}) \\
+ 6(2(J_{13}+J_{14}+J_{15}) - 12J_{16} + 6J_{17}) \\
+ 6(2(J_{20}+J_{21}+J_{22}) - 12J_{23} + 6J_{24}) \\
+ 12(J_{25} - 2J_{26} + J_{27}) \\
+ x(6(2J_2 - 2J_3) \\
+ 12(4J_9 - 4J_{10}) \\
+ 6(4J_{16} - 4J_{17}) \\
+ 6(4J_{23} - 4J_{24}) \\
+ 12(2J_{26} - 2J_{27})) \\
+ (6(J_3) \\
+ 12(J_{10}) \\
+ 6(J_{17}) \\
+ 6(J_{24}) \\
+ 12(J_{27})) \\) \]
\( T_2 = \frac{S}{2K} \left( x^4 (-4J_4 - 4J_5 + 2(J_6 + J_7 + J_8) - 4J_9 + J_{10}) \right. \\
+ 6(J_{11} - 4J_{12} + 2(J_{13} + J_{14} + J_{15}) - 4J_{16} + J_{17}) \\
+ 6(J_{18} - 4J_{19} + 2(J_{20} + J_{21} + J_{22}) - 4J_{23} + J_{24}) \right) \\
\left. + x^3 (-4(4J_5 - 4(J_6 + J_7 + J_8) + 12J_9 - 4J_{10}) \\
+ 6(4J_{12} - 4(J_{13} + J_{14} + J_{15}) + 12J_{16} - 4J_{17}) \\
+ 6(4J_{19} - 4(J_{20} + J_{21} + J_{22}) + 12J_{23} - 4J_{24}) \right) \\
\left. + x^2 (-2(J_1 - 2J_2 + J_3) \\
- 4(2(J_6 + J_7 + J_8) - 12J_9 + 6J_{10}) \\
+ 6(2(J_{13} + J_{14} + J_{15}) - 12J_{16} + 6J_{17}) \\
+ 6(2J_{20} + J_{21} + J_{22}) - 12J_{23} + 6J_{24}) \\
- 4(J_{25} - 2J_{26} + J_{27}) \right) \\
\left. + x (-2(2J_2 - 2J_3) \\
- 4(4J_9 - 4J_{10}) \\
+ 6(4J_{16} - 4J_{17}) \\
+ 6(4J_{23} - 4J_{24}) \\
- 4(2J_{26} - 2J_{27}) \right) \\
\left. + (-2(J_3) \\
- 4(J_{10}) \\
+ 6(J_{17}) \\
+ 6(J_{24}) \\
- 4(J_{27}) \right) \)
\[ T_3 = \frac{5}{2k} x^4 \left( -4(J_4 + 4J_5 + 2(J_6 + J_7 + J_8) - 4J_9 + J_{10}) \right. \]
\[ \left. - 2(J_{11} - 4J_{12} + 2(J_{13} + J_{14} + J_{15}) - 4J_{16} + J_{17}) \right. \]
\[ \left. - 2(J_{18} - 4J_{19} + 2(J_{20} + J_{21} + J_{22}) - 4J_{23} + J_{24}) \right) \]
\[ + x^3 \left( -4(4J_5 - 4(J_6 + J_7 + J_8) + 12J_9 - 4J_{10}) \right. \]
\[ \left. - 2(4J_{12} - 4(J_{13} + J_{14} + J_{15}) + 12J_{16} - 4J_{17}) \right. \]
\[ \left. - 2(4J_{19} - 4(J_{20} + J_{21} + J_{22}) + 12J_{23} - 4J_{24}) \right) \]
\[ + x^2 \left( 2(J_1 - 2J_2 + J_3) \right. \]
\[ \left. - 4(2(J_6 + J_7 + J_8) - 12J_9 + 6J_{10}) \right. \]
\[ \left. - 2(2(J_{13} + J_{14} + J_{15}) - 12J_{16} + 6J_{17}) \right. \]
\[ \left. - 2(2(J_{20} + J_{21} + J_{22}) - 12J_{23} + 6J_{24}) \right. \]
\[ + 4(J_{25} - 2J_{26} + J_{27}) \]  \hspace{1cm} (45) \]
\[ + x \left( 2J_2 - 2J_3 \right) \]
\[ - 4(4J_9 - 4J_{10}) \]
\[ - 2(4J_{16} - 4J_{17}) \]
\[ - 2(4J_{23} - 4J_{24}) \]
\[ + 4(2J_{26} - 2J_{27}) \]}
\[ + \left( 2(J_3) \right. \]
\[ \left. - 4(J_{10}) \right. \]
\[ \left. - 2(J_{17}) \right. \]
\[ \left. - 2(J_{24}) \right. \]
\[ + 4(J_{27}) \)
\[ T_4 = \frac{5}{2k} \left( x^4 \left( 4(J_4 - 4J_5 + 2(J_6 + J_7 + J_8) - 4J_9 + J_{10}) \right. \right. \\
\left. \left. - 2(J_{11} - 4J_{12} + 2(J_{13} + J_{14} + J_{15}) - 4J_{16} + J_{17}) \right. \right. \\
\left. \left. - 2(J_{18} - 4J_{19} + 2(J_{20} + J_{21} + J_{22}) - 4J_{23} + J_{24}) \right) \\
\left. \right. + \left( 4(J_5 - 4(J_6 + J_7 + J_8) + 12J_9 - 4J_{10}) \right) \right. \\
\left. \right. - 2(4J_{12} - 4(J_{13} + J_{14} + J_{15}) + 12J_{16} - 4J_{17}) \right. \\
\left. \right. - 2(4J_{19} - 4(J_{20} + J_{21} + J_{22}) + 12J_{23} - 4J_{24}) \\
\left. \right) \right. \\
\left. \right. + x^3 \left( 4(J_5 - 4(J_6 + J_7 + J_8) + 12J_9 - 4J_{10}) \right. \\
\left. \right. - 2(4J_{12} - 4(J_{13} + J_{14} + J_{15}) + 12J_{16} - 4J_{17}) \right. \\
\left. \right. - 2(4J_{19} - 4(J_{20} + J_{21} + J_{22}) + 12J_{23} - 4J_{24}) \\
\left. \right) \right. \\
\left. \right. + x^2 \left( -2(J_1 - 2J_2 + J_3) \right. \\
\left. \right. + 4(2(J_6 + J_7 + J_8) - 12J_9 + 6J_{10}) \right. \\
\left. \right. - 2(2(J_{13} + J_{14} + J_{15}) - 12J_{16} + 6J_{17}) \right. \\
\left. \right. - 2(2(J_{20} + J_{21} + J_{22}) - 12J_{23} + 6J_{24}) \right. \\
\left. \right. - 4(J_{25} - 2J_{26} + J_{27}) \right) \\
\left. \right) \right. \\
\left. \right. + x \left( -2(2J_2 - 2J_3) \right. \\
\left. \right. + 4(4J_9 - 4J_{10}) \right. \\
\left. \right. - 2(4J_{16} - 4J_{17}) \right. \\
\left. \right. - 2(4J_{23} - 4J_{24}) \right. \\
\left. \right. - 4(2J_{26} - 2J_{27}) \right) \right. \\
\left. \right. + \left( -2(J_3) \right. \\
\left. \right. + 4(J_{10}) \right. \\
\left. \right. - 2(J_{17}) \right. \\
\left. \right. - 2(J_{24}) \right. \\
\left. \right. - 4(J_{27}) \right) \right) \]
VIII. EXCHANGE INTEGRALS FOR THE SYSTEM CdCr$_2$S$_4$(1-y)Se$_4$y

Since the solution $T_C = T_3$ has been found to be applicable for the spinels CdCr$_2$S$_4$ and CdCr$_2$Se$_4$, we will apply this solution to the entire system CdCr$_2$S$_4$(1-y)Se$_4$y. 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,\textsuperscript{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

- $a = b = c = 0$,
- $d = 52^\circ K$,
- $e = 152^\circ K$,
- $f = g = 0$,
- $h = 22.2^\circ K$,
- $j = -4.2^\circ K$,
- $k = 33.8^\circ K$.

By comparison of coefficients of powers of $y$, we can derive ten equations linear in the exchange integrals.

These can be solved to yield

- $J_1 + 2J_{25} = 16.1^\circ K$ k
- $J_2 + 2J_{26} = 13.9^\circ K$ k
- $J_3 + 2J_{27} = 13.5^\circ K$ k
- $2J_4 + J_{11} + J_{18} = -6.2^\circ K$ k
- $2J_5 + J_{12} + J_{19} = -4.1^\circ K$ k
- $2(J_6 + J_7 + J_8 + J_{13} + J_{14} + J_{15}) + (J_{20} + J_{21} + J_{22}) = -8.8^\circ K$ k
Figure 6. Diagram of hypothetical interaction paths and corresponding exchange integral number for the system CdCr$_2$S$_4$(1-$y$)Se$_4y$. 
\[2J_9 + J_{16} + J_{22} = -2.7^\circ K\]
\[2J_{10} + J_{17} + J_{24} = -3.4^\circ K\]

Using the approximations

\[J_{11} = J_{18}\]
\[J_{12} = J_{19}\]
\[J_6 = J_7 = J_8, J_{13} = J_{14} = J_{15} = J_{20} = J_{21} = J_{22}\]
\[J_{15} = J_{23}\]
\[J_{17} = J_{24}\]

and the values

\[J_1 = 17.0^\circ K\]
\[J_2 = 15.4^\circ K\]
\[J_3 = 13.9^\circ K\]

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

\[J_{25} = -0.5^\circ K\]
\[J_{26} = -0.8^\circ K\]
\[J_{27} = -0.2^\circ K\]
\[J_{4} + J_{11} = -3.1^\circ K\]
\[J_{5} + J_{12} = -2.1^\circ K\]
\[J_{6} + J_{13} = -1.5^\circ K\]
\[J_{9} + J_{16} = -1.4^\circ K\]
\[J_{10} + J_{17} = -1.7^\circ K\]
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 $T_1 = T_C = 0$, 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$_2$Se$_4$ and CdCr$_2$S$_4$ (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).

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<td>1 by 1+9+5+13</td>
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<td>2 2+4</td>
<td>2 2+14</td>
</tr>
<tr>
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<td>5 5+13-1-9</td>
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<td>6 6+8</td>
<td>6 6+10</td>
</tr>
<tr>
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</tr>
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<td>16 16-12</td>
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XI. BIBLIOGRAPHY


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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.

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