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Application of the Weiss Molecular Field Theory to the B-Site Spinel¹⁾

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A molecular field treatment of the B-site spinel was used to determine the ordering temperatures and the asymptotic Curie temperature in terms of the exchange integrals. The theory was developed from a 16-sublattice model and took into account interactions between an atom and its nearest to fourth-nearest neighbors. Experimental values of the ordering temperatures and the asymptotic Curie temperature were then used to determine the exchange integrals for the systems $\text{Hg}_{1-x}\text{Cd}_x\text{Cr}_2\text{S}_4$, $\text{CdCr}_2\text{S}_{4(1-y)}\text{Se}_{4y}$, and $\text{Zn}_{1-x}\text{Cd}_x\text{Cr}_2\text{Se}_4$.

Die Molekularfeldtheorie von B-Spinellen wurde benutzt, um die Ordnungstemperaturen und die asymptotische Curie-Temperatur durch die Austauschintegrale auszudrücken. Die Theorie benutzt ein Modell mit 16 Untergittern und berücksichtigt Wechselwirkungen bis zu viertnächsten Nachbarn. Aus den experimentellen Werten der Ordnungstemperaturen und der asymptotischen Curie-Temperatur der Systeme $\text{Hg}_{1-x}\text{Cd}_x\text{Cr}_2\text{S}_4$, $\text{CdCr}_2\text{S}_{4(1-y)}\text{Se}_{4y}$ und $\text{Zn}_{1-x}\text{Cd}_x\text{Cr}_2\text{Se}_4$ werden die Austauschintegrale für diese Systeme bestimmt.

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. If only the B ions have a permanent magnetic moment, the spinel is said to be a B-site spinel. Solid solutions of the simple spinels also occur; we refer to these as systems.

In this paper we will consider B-site systems ($\text{Aa}_{1-x}\text{Ab}_x\text{Cr}_2\text{X}_4$, $0 \leq x \leq 1$) in which the A-site cation is varied between one type of cation (Aa) and another (Ab), and systems ($\text{ACr}_2\text{Xa}_{4(1-y)}\text{Xb}_{4y}$, $0 \leq y \leq 1$) 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 $3/2$.

The B-site lattice of the spinel consists of four f.c.c. sublattices, each displaced a distance of one-fourth of a cube face diagonal of the cubic unit cell.³⁾ The primitive unit cell has a basis of four atoms, one from each of the four f.c.c. sublattices.⁴⁾ The lattice structure is such that if only B-B nearest-neighbor (NN) superexchange interactions are considered, then there are no interactions between atoms on the same sublattice. However, as Anderson has pointed

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³⁾ The f.c.c. sublattices have the following bases:

1. $0\ 0\ 0$; $\frac{1}{2}\ \frac{1}{2}\ 0$; $0\ \frac{1}{2}\ \frac{1}{2}$; $\frac{1}{2}\ 0\ \frac{1}{2}$;
2. $\frac{1}{4}\ \frac{1}{4}\ 0\ \frac{3}{4}$; $\frac{3}{4}\ \frac{1}{2}\ \frac{3}{4}$; $\frac{1}{4}\ \frac{1}{2}\ \frac{1}{4}$; $\frac{3}{4}\ 0\ \frac{1}{4}$;
3. $\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}\ 0$; $\frac{3}{4}\ \frac{3}{4}\ 0$; $\frac{1}{4}\ \frac{3}{4}\ \frac{1}{4}$; $\frac{3}{4}\ \frac{1}{4}\ \frac{1}{4}$;
4. $0\ 0\ \frac{1}{4}\ \frac{3}{4}$; $\frac{1}{2}\ \frac{1}{2}\ \frac{3}{4}$; $0\ \frac{3}{4}\ \frac{1}{4}$; $\frac{1}{2}\ \frac{1}{4}\ \frac{1}{4}$.

⁴⁾ Due to symmetry there are several possible primitive unit cells.

out [1], a perfect short range order with only NN interactions does not necessarily lead to long range antiferromagnetic order. Lotgering [2] has found that antiferromagnetic interactions of about 5% of the strength of the ferromagnetic NN interactions suffice to prevent ferromagnetism. Dwight and Menyuk [3] have found that an adequate characterization of the exchange energy requires the consideration of five distinct next-nearest neighbor (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 f.c.c. sublattice until there are no interactions between atoms on the same sublattice [4]. Hence, we divide each f.c.c. sublattice into four simple cubic sublattices; the B-site lattice then consists of 16 simple cubic sublattices.

A 16-sublattice molecular field treatment of the B-site spinel lattice leads to the determinant

$$\begin{vmatrix} A & B & C & D \\ B & A & D & C \\ C & D & A & B \\ D & C & B & A \end{vmatrix} = 0,$$

where

$$A = \begin{pmatrix} T' & R & R & R \\ R & T' & R & R \\ R & R & T' & R \\ R & R & R & T' \end{pmatrix}, \quad B = \begin{pmatrix} S & U & U & S \\ U & S & S & U \\ U & S & S & U \\ S & U & U & S \end{pmatrix},$$

$$C = \begin{pmatrix} S & S & U & U \\ S & S & U & U \\ U & U & S & S \\ U & U & S & S \end{pmatrix}, \quad D = \begin{pmatrix} S & U & S & U \\ U & S & U & S \\ S & U & S & U \\ U & S & U & S \end{pmatrix},$$

and where $T' = 2kT/5$, $R = 2(J_3 + J_4)$, $S = J_1 + 2J_5$, $U = 2J_2$. Here J_1, J_2, J_3, J_4 , and J_5 are the exchange integrals between an atom and its first-, second-, third- (two types, exchange integrals J_3 and J_4), and fourth-nearest neighbors. The exchange integrals J_1 through J_5 correspond, respectively, to those for the B_0-B_1 through B_0-B_5 exchanges of Baltzer et al. [5]. The solutions to the determinant are

$$T_1 = \frac{5}{2k} (6J_1 + 12J_2 + 6J_3 + 6J_4 + 12J_5),$$

$$T_2 = \frac{5}{2k} (-2J_1 - 4J_2 + 6J_3 + 6J_4 - 4J_5),$$

$$T_3 = \frac{5}{2k} (2J_1 - 4J_2 - 2J_3 - 2J_4 + 4J_5),$$

$$T_4 = \frac{5}{2k} (-2J_1 + 4J_2 - 2J_3 - 2J_4 - 4J_5).$$

Since there were too many exchange integrals to evaluate with the data available,

all exchanges except the nearest-neighbor exchanges were assumed to be of equal strength with an exchange integral K . The solutions to the determinant reduce to

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

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

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

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

where J is the nearest-neighbor exchange.

The expression for T_1 can be seen to be that for the asymptotic Curie temperature. The molecular field theory yields the result that the highest root is the ordering temperature since 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 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 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_4 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 , noting that the appearance of the additional roots T_3 and T_4 is a direct result of the additional sublattices required.

It was found that the experimental data of Baltzer et al. [5] and Wojtowicz et al. [6] could be matched for the spinels HgCr_2S_4 , CdCr_2S_4 , and CdCr_2Se_4 for the values of J/k and K/k given in Table 1. They have determined the values 13, 11.8, and 14 °K for J/k and -0.6 , -0.33 , and -0.1 °K for K/k for these spinels.

The best agreement between experiment and our theory can be obtained by assuming T_3 to represent T_C . With this assumption the systems $\text{Hg}_{1-x}\text{Cd}_x\text{Cr}_2\text{S}_4$ and $\text{CdCr}_2\text{S}_{4(1-y)}\text{Se}_{4y}$ can be matched to a satisfactory degree with integrals J and K that we vary linearly with the composition variables x or y as

$$J(x) = (1 - x) J_0 + x J_1.$$

Table 1

Values of exchange integrals consistent with experimental values of θ and T_C for the spinels HgCr_2S_4 , CdCr_2S_4 , and CdCr_2Se_4

	HgCr_2S_4		CdCr_2S_4		CdCr_2Se_4	
	J/k	K/k	J/k	K/k	J/k	K/k
$T_C = T_2$	-3.0	2.1	-10.0	3.4	-16.1	4.9
$T_C = T_3$	7.8	0.3	15.2	-0.8	22.9	-1.5
$T_C = T_4$	-15.6	4.2	-30.6	6.7	-45.8	9.9

This should be a reasonable first approximation for systems with varying cation concentration and has been shown [7] to be useful for systems in which the anions are substituted. Obviously, improved agreement could be obtained with quadratic dependence on composition, but this complication was considered not worth the effort.

The ferromagnetic portion of the system $\text{Zn}_{1-x}\text{Cd}_x\text{Cr}_2\text{Se}_4$ can also be matched by $T_C = T_3$. We will assume that the exchange integrals are continuous across the point of transition between the ferromagnetic and antiferromagnetic regions since the experimental data for the asymptotic Curie temperature are linear and continuous. With this assumption we note that we have determined the exchange integrals for the entire system since we need only to extrapolate J and K to $x = 0$. In the region $x = 0$ to $x = 0.2$ the largest of T_2 , T_3 , and T_4 is no longer T_3 but T_2 . The transition between T_3 and T_2 at about $x = 0.2$ compares reasonably well with the experimental value of $x = 0.35$. Hence, the ordering temperature in the antiferromagnetic region can be approximated by T_2 . The exchange integrals for the systems are shown in Fig. 1.

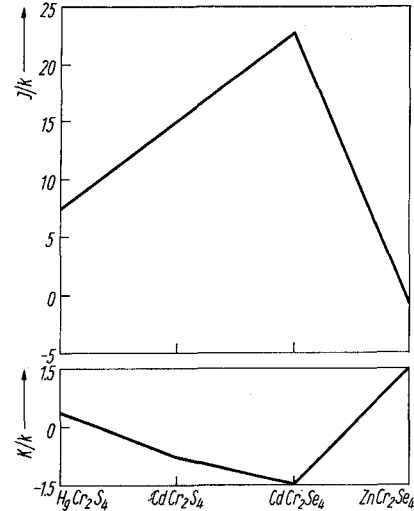


Fig. 1. Calculated values of J/k and K/k for the systems $\text{Hg}_{1-x}\text{Cd}_x\text{Cr}_2\text{S}_4$, $\text{CdCr}_2\text{S}_4(1-y)\text{Se}_4y$, and $\text{Zn}_{1-x}\text{Cd}_x\text{Cr}_2\text{Se}_4$

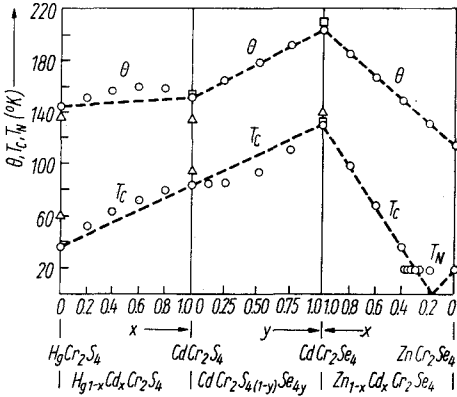


Fig. 2. Comparison of experimental values of θ , T_C , and T_N with those calculated from the molecular field theory

Fig. 2 compares the experimental values of θ and T_C and those calculated from the exchange integrals just determined. The circular data points are from Baltzer et al. [5] and from Wojtowicz et al. [6]. The square data points are from Menyuk et al. [8] and the triangular data points are from Baltzer et al. [9]. The calculated values of θ , T_C , and T_N are given by the dashed lines. Considering the approximate nature of the calculation the agreement with the data is quite satisfactory. Thus it appears that our *ad hoc* assumption about the meaning of the roots T_i may be of some value. With it, we are able to match the data reasonably well for each system with two straight lines for θ and T_C by the choice of two parameters; and these parameters have reasonable values.

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