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## Exchange Interactions in Ferromagnetic Chromium Chalcogenide Spinels

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Transition-metal spinels with magnetic ions solely on the octahedral sites have been the subject of many investigations. The properties of such spinels had always been found to be dominated by antiferromagnetic interactions. In this paper we describe the properties of a group of spinels in which ferromagnetic interactions are found to predominate. The compounds  $\text{CdCr}_2\text{S}_4$ ,  $\text{CdCr}_2\text{Se}_4$ ,  $\text{HgCr}_2\text{S}_4$ , and  $\text{HgCr}_2\text{Se}_4$  have been prepared and found to be ferromagnetic with Curie temperatures of 84.5, 129.5, 36.0, and 106°K, respectively. With the exception of  $\text{HgCr}_2\text{S}_4$ , which becomes metamagnetic below 25°K, all these materials remain ferromagnetic down to 4.2°K. These materials are also unique in that they are good electrical insulators in addition to being ferromagnets. A theoretical treatment is presented which correlates the high-temperature susceptibility with the Curie temperature and which provides a determination of the exchange interactions. The six nearest-neighbor interactions are treated by the high-temperature expansion technique of Rushbrooke and Wood, while the 30 more-distant-neighbor interactions are treated within the two-particle-cluster approximation of Callen and Callen. The analysis of the data indicates that the distant-neighbor interactions play a very important role in the determination of the type of magnetic order observed in the chalcogenide spinels.

### INTRODUCTION

THE nature of the magnetic exchange interactions in compounds having the spinel structure has been a subject of continuing interest. Up to the present time experimental and theoretical treatments have almost exclusively been concerned with systems in which antiferromagnetic interactions are predominant. We now report on an investigation of a group of spinel compounds having magnetic properties dominated by strong ferromagnetic interactions. Consideration is first given to spinel compounds in which, although antiferromagnetic interactions are predominant, some ferromagnetic interactions are to be suspected. An experimental study of a family of spinel compounds is then presented. In these compounds the ferromagnetic interactions are so strong as to overwhelm the usual antiferromagnetic interactions, so that ferromagnetism is observed.<sup>1,2</sup> Finally, we discuss the possible exchange-interaction linkages and present a theoretical treatment which permits the determination of the different exchange interactions from the experimental data.

<sup>1</sup> P. K. Baltzer, H. W. Lehmann, and M. Robbins, *Phys. Rev. Letters* **15**, 493 (1965).

<sup>2</sup> N. Menyuk, K. Dwight, R. J. Arnott, and A. Wold, *J. Appl. Phys.* **37**, 1387 (1966).

### PREDOMINANCE OF ANTIFERROMAGNETIC INTERACTIONS

We are particularly concerned with a special subclass of transition metal compounds having the spinel crystal structure. This subclass of compounds is characterized by having all the *B* sites (octahedral sites) occupied by magnetic ions (preferably one kind) and all the *A* sites (tetrahedral sites) occupied by a nonmagnetic (diamagnetic) ion. The presence of ferromagnetic interactions in a compound dominated by antiferromagnetic interactions is indicated by the value of  $\theta$  in the Curie-Weiss law for the paramagnetic susceptibility,  $\chi_M = C_M(T - \theta)^{-1}$ . As will be shown later, ferromagnetic interactions can make the  $\theta$  large and positive, while simultaneously the antiferromagnetic interactions can still be strong enough to produce an antiferromagnetic ordered ground state at low temperatures.

In Table I we summarize magnetic and crystallographic data, both previously reported and new, on compounds in which antiferromagnetic interactions dominate in producing the low-temperature ground state. Magnetic studies of all these compounds at low temperatures indicate that they are all antiferromagnets in spite of the fact that the Curie-Weiss  $\theta$ , obtained from high temperature susceptibility measurements, vary

TABLE I. Magnetic and crystallographic properties of antiferromagnetic spinels.

Composition	Lattice parameter $a$ , Å	$u$ parameter	Néel temp. $T_N$ , °K	Curie-Weiss $\theta$ , °K
MgV <sub>2</sub> O <sub>4</sub>	8.413 <sup>a</sup>	0.385 <sup>a</sup>	45 <sup>b</sup>	-750 <sup>b</sup>
ZnV <sub>2</sub> O <sub>4</sub>	8.410	...	...	-600 <sup>c</sup>
ZnMnCrO <sub>4</sub>	8.35	...	...	-268
CdMnCrO <sub>4</sub>	8.620	...	...	-95
ZnCr <sub>2</sub> O <sub>4</sub>	8.328	0.387	16 <sup>b</sup>	-392 <sup>d</sup>
CdCr <sub>2</sub> O <sub>4</sub>	8.596	0.396	9 <sup>e</sup>	-83 <sup>f</sup>
MgCr <sub>2</sub> O <sub>4</sub>	8.333 <sup>g</sup>	0.385	15 <sup>b</sup>	-350 <sup>b</sup>
ZnCr <sub>2</sub> S <sub>4</sub>	9.988	0.385	<20 <sup>h</sup>	+18 <sup>h</sup>
ZnCr <sub>2</sub> Se <sub>4</sub>	10.500	0.384	20 <sup>h</sup>	+115 <sup>h</sup>
ZnFe <sub>2</sub> O <sub>4</sub>	8.416	0.380	10	-40 <sup>i</sup>
CdFe <sub>2</sub> O <sub>4</sub>	8.704	0.386	...	-22.2
GeFe <sub>2</sub> O <sub>4</sub>	8.411 <sup>j</sup>	0.375 <sup>j</sup>	10 <sup>b</sup>	-15 <sup>b</sup>
GeCo <sub>2</sub> O <sub>4</sub>	8.317 <sup>k</sup>	0.375 <sup>k</sup>	20 <sup>b</sup>	+90 <sup>b</sup>
GeNi <sub>2</sub> O <sub>4</sub>	8.221 <sup>k</sup>	0.375 <sup>k</sup>	16 <sup>b</sup>	0 <sup>b</sup>

<sup>a</sup> Reference 3.<sup>b</sup> Reference 8.<sup>c</sup> W. Rüdorff and B. Reuter, *Z. Anorg. Allgem.* **253**, 177 (1947).<sup>d</sup> Previously reported to be -350 in Ref. 8.<sup>e</sup> Reference 2.<sup>f</sup> Independently reported to be -88 in Ref. 2.<sup>g</sup> E. J. W. Verwey and E. L. Heilmann, *J. Chem. Phys.* **15**, 174 (1947).<sup>h</sup> Reference 9.<sup>i</sup> A. Arrott and J. E. Goldman, *Bull. Am. Phys. Soc.* **30**, 62 (1955).<sup>j</sup> A. Durif-Varambon *et al.*, *Ann. Chim.* **1**, 525 (1956).<sup>k</sup> F. C. Romeijn, *Philips Res. Rept.* **8**, 304, 321 (1953).

from large negative to large positive values. Neutron-diffraction studies<sup>3-6</sup> have confirmed antiferromagnetism in ZnFe<sub>2</sub>O<sub>4</sub>, ZnCr<sub>2</sub>O<sub>4</sub>, GeNi<sub>2</sub>O<sub>4</sub>, MgV<sub>2</sub>O<sub>4</sub>, and ZnCr<sub>2</sub>Se<sub>4</sub>. The fact that antiferromagnetic order does occur and that very complex spin configurations are required to explain the data are both significant in the light of Anderson's<sup>7</sup> theoretical considerations. He has shown that the nearest-neighbor *B-B* exchange interactions alone cannot produce any long-range antiferromagnetic order on the *B* sites. All of the experimental and theoretical results mentioned above point to the conclusion that it is not sufficient to consider just the nearest-neighbor *B-B* interactions, but one must take more distant interactions into account. Blasse and Fast<sup>8</sup> have suggested that the interactions *B-X-A-X-B* are the important next-nearest interactions. Lotgering<sup>9</sup> has suggested the interactions *B-X-X-B*, while Bertaut<sup>5</sup> proposes even more distant interactions.

It was in connection with a previous study<sup>10</sup> that we prepared Zn[CrMn]O<sub>4</sub> and Cd[CrMn]O<sub>4</sub> and measured the paramagnetic properties given in Table I. The most significant aspect of these data are the very large

<sup>3</sup> R. Plumier and A. Tardieu, *Compt. Rend.* **257**, 3858 (1963).<sup>4</sup> L. Corliss and J. M. Hastings, *Rev. Mod. Phys.* **25**, 114 (1953).<sup>5</sup> E. F. Bertaut *et al.*, *J. Phys. Radium* **25**, 516 (1964).<sup>6</sup> R. Plumier, *Compt. Rend.* **260**, 3348 (1965); *J. Appl. Phys.* **37**, 964 (1966).<sup>7</sup> P. W. Anderson, *Phys. Rev.* **102**, 1008 (1956).<sup>8</sup> G. Blasse and J. F. Fast, *Philips Res. Rept.* **18**, 393 (1963).<sup>9</sup> F. K. Lotgering, in *Proceedings of the International Conference on Magnetism, Nottingham, England, 1964* (The Institute of Physics and The Physical Society, London, 1965), p. 533.<sup>10</sup> P. K. Baltzer and E. Lopatin, in *Proceedings of the International Conference on Magnetism, Nottingham, England, 1964* (The Institute of Physics and The Physical Society, London, 1965), p. 564.

differences in the measured  $\theta$  for the two similar compounds. The only other difference observed was a 3½% difference in lattice dimensions. The problem of understanding the observed properties of ZnCrMnO<sub>4</sub> and CdCrMnO<sub>4</sub> is complicated by the occurrence of two kinds of magnetic ions (Cr<sup>3+</sup> and Mn<sup>3+</sup>) on the *B* sites. Therefore, the compounds ZnCr<sub>2</sub>O<sub>4</sub> and CdCr<sub>2</sub>O<sub>4</sub> were also prepared and studied. The crystallographic and magnetic properties of these compounds are also shown in Table I, and again we see a great difference in the  $\theta$  values.

### PREDOMINANCE OF FERROMAGNETIC INTERACTIONS

The above study of ZnCr<sub>2</sub>O<sub>4</sub> and CdCr<sub>2</sub>O<sub>4</sub> was followed by the preparation and study of the system of compounds *ACr<sub>2</sub>X<sub>4</sub>*, where *A* = Cd or Hg, and *X* = S or Se (corresponding tellurium compounds could not be made). The details of synthesis and x-ray analysis for these compounds are given in Appendices A and B, respectively. All the compounds were prepared as single phase spinels (within the normal limitations of x-ray diffraction) and all the Cr<sup>3+</sup> ions were found to occupy the *B* sites and all the Cd<sup>2+</sup> or Hg<sup>2+</sup> ions were found to occupy the *A* sites. A summary of the crystallographic and magnetic properties is given in Table II. (These data represent a refinement over those reported previously.<sup>1</sup>) The magnetic properties were measured on compacted powder samples using a vibrating sample magnetometer. The magnetic moments reported in

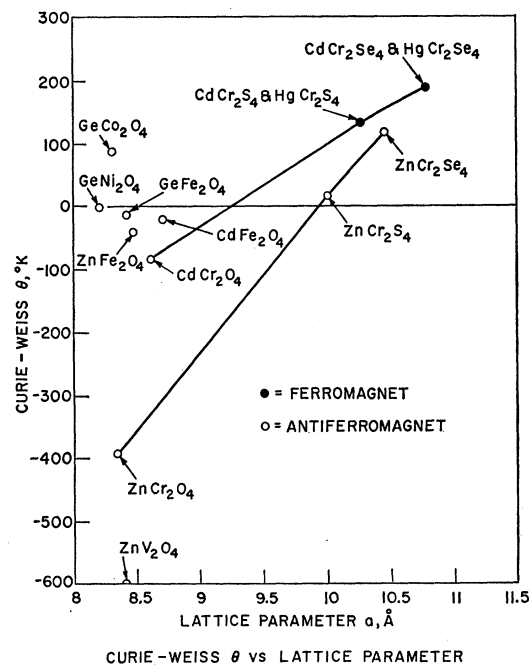


Fig. 1. Relationship between Curie-Weiss  $\theta$  and lattice parameter  $a$  for cubic spinels having all octahedral sites occupied by one kind of magnetic ion and tetrahedral sites occupied by non-magnetic ions.

TABLE II. Magnetic and crystallographic properties of ferromagnetic spinels.

Composition	Lattice parameter Å	$u$ parameter	Magnetic moment (4.2°K) $\mu_B$ /molecule	Curie temp. $T_c$ , °K	Curie-Weiss $\theta$ , °K	Curie constant $C_M$	$\frac{\theta}{T_c}$
CdCr <sub>2</sub> S <sub>4</sub>	10.244	0.390	5.15	84.5	152	3.70	1.80
CdCr <sub>2</sub> Se <sub>4</sub>	10.755	0.390	5.62	129.5	204	3.82	1.57
HgCr <sub>2</sub> S <sub>4</sub>	10.237	0.390	5.35	36.0	142	3.62	3.94
HgCr <sub>2</sub> Se <sub>4</sub>	10.753	0.390	5.64	106	200	3.79	1.89

Table II all were obtained at an applied field of 10 000 Oe and lie between the values of 5.15 and 5.64  $\mu_B$ /molecule. Such a high moment indicates an essentially ferromagnetic spin configuration, but the departures from the theoretical value of 6  $\mu_B$ /molecule for ferromagnetic Cr<sup>3+</sup> ions are not understood. Up to 5% departures from theoretical moment could be due to second phases not detectable by x-ray diffraction. Greater departures such as we observe could be due to spiral configurations superimposed upon the ferromagnetic one.

The Curie temperatures given in Table II were obtained from data both above and below the ordering temperature, as described in Appendix C. The Curie-Weiss  $\theta$  and Curie constant  $C_M$  were obtained from plots of inverse susceptibility up to 750°K. The Curie constants are all close to the spin-only value 3.75. The  $\theta$  values are all large and positive, indicating a preponderance of ferromagnetic interactions. However, there is a great range in corresponding Curie temperatures and in the resulting ratios  $\theta/T_c$ . These properties and their significance are considered further in the discussion section. Comparing the values of  $\theta$  and lattice parameter  $a$  in Table II, one sees an obvious correlation. It is in fact instructive to plot  $\theta$  and  $a$  values from both Tables I and II and connect data on compounds having the same cations, as shown in Fig. 1. It is immediately

seen, comparing the data for CdCr<sub>2</sub>X<sub>4</sub> and ZrCr<sub>2</sub>X<sub>4</sub>, that the major difference is that the cadmium compounds have a more positive  $\theta$  (this observation has also been made in Ref. 2). The high-temperature paramagnetic data for CdCr<sub>2</sub>X<sub>4</sub> and HgCr<sub>2</sub>X<sub>4</sub> are essentially identical. The general trend of more positive  $\theta$  with increasing lattice parameter seen in Fig. 1 is somewhat beclouded by the variation of the  $u$  parameter. In general, for a given set of cations,  $u$  was found to decrease with increasing  $a$ . The  $u$  parameters of the CdCr<sub>2</sub>X<sub>4</sub> were consistently higher than those of the corresponding ZnCr<sub>2</sub>X<sub>4</sub> compounds.

As indicated, both in Table II and Fig. 1, we have found CdCr<sub>2</sub>S<sub>4</sub>, CdCr<sub>2</sub>Se<sub>4</sub>, HgCr<sub>2</sub>S<sub>4</sub>, and HgCr<sub>2</sub>Se<sub>4</sub> to be ferromagnetic. The magnetization curves of these compounds at 4.2°K are shown in Fig. 2. The demagnetizing field associated with the sample shape appears to be the only factor inhibiting the magnetization of CdCr<sub>2</sub>S<sub>4</sub>, CdCr<sub>2</sub>Se<sub>4</sub>, and HgCr<sub>2</sub>Se<sub>4</sub>, which is characteristic of compounds having a very low magnetic anisotropy. A low anisotropy would be consistent with the fact that the Cr<sup>3+</sup> ion has an essentially zero-orbital moment. However, the magnetization curve of HgCr<sub>2</sub>S<sub>4</sub> in Fig. 2 is strongly S-shaped. To test for large anisotropy effects in HgCr<sub>2</sub>S<sub>4</sub>, the field was reversed and no hysteresis effects were found, indicating that this compound also has a very low anisotropy.

A plot of the magnetization and the inverse susceptibility versus temperature for CdCr<sub>2</sub>Se<sub>4</sub> is shown in

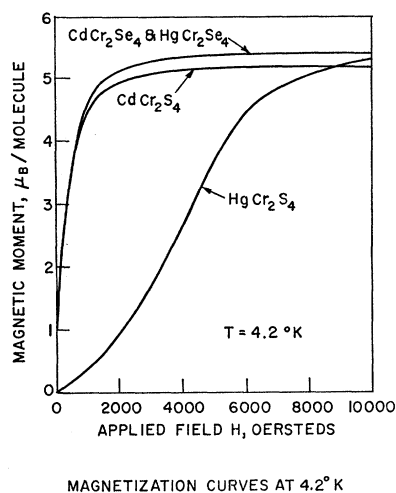


FIG. 2. Magnetic moment as a function of applied field for CdCr<sub>2</sub>S<sub>4</sub>, CdCr<sub>2</sub>Se<sub>4</sub>, HgCr<sub>2</sub>S<sub>4</sub>, and HgCr<sub>2</sub>Se<sub>4</sub> at 4.2°K.

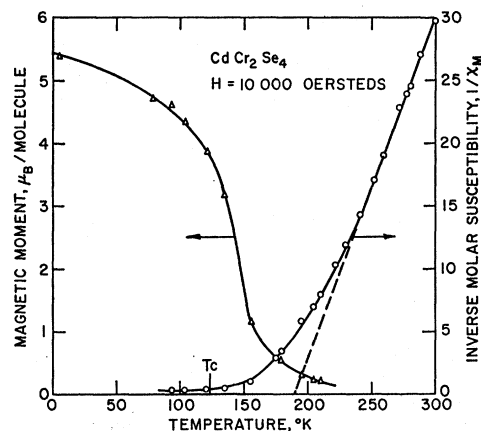


FIG. 3. Magnetic moment and inverse susceptibility as a function of temperature for CdCr<sub>2</sub>Se<sub>4</sub> in an applied field of 10 000 Oe.

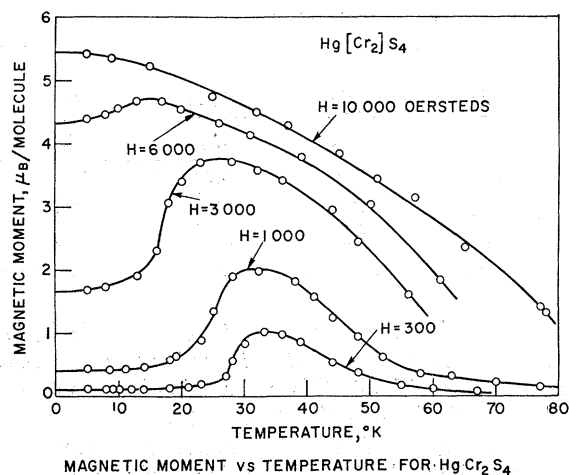


FIG. 4. Magnetic moment as a function of temperature for  $\text{HgCr}_2\text{S}_4$  in several different applied fields.

Fig. 3. This behavior is typical of that observed for all three ferromagnets,  $\text{CdCr}_2\text{S}_4$ ,  $\text{CdCr}_2\text{Se}_4$ , and  $\text{HgCr}_2\text{Se}_4$ . The nonlinear behavior of  $1/\chi$  near the Curie point is similar to that observed by Blasse and Fast, and Lotgering<sup>8,9</sup> for antiferromagnetic spinels having a positive Curie-Weiss  $\theta$ . The nonlinear  $1/\chi$  for the ferromagnets together with the large difference between Curie-Weiss  $\theta$  and Curie temperature are considered in the discussion section.

Just as the magnetization curve for  $\text{HgCr}_2\text{S}_4$  in Fig. 2 is anomalous, so also is the dependence of the magnetization on temperature, shown in Fig. 4. At high fields a typical ferromagnetic moment-versus-temperature curve is observed. However, at progressively lower fields, some kind of transition occurs at a temperature which increases with decreasing field. Magnetization curves have also been obtained for  $\text{HgCr}_2\text{S}_4$  at elevated temperatures, as shown in Fig. 5. At 27 and 32°K we obtain readily saturated magnetization curves, typical of a low-anisotropy ferromagnet, but at 24, 13, and 4.2°K we observe the S-shaped magnetization curves characteristic of metamagnets.<sup>11-14</sup> A metamagnetic material is one which can be converted from an antiferromagnetic state into a ferromagnetic one by application of a magnetic field. We have concluded that the properties of  $\text{HgCr}_2\text{S}_4$  indicate metamagnetism below 25°K and ferromagnetism for temperatures between 25°K and the Curie temperature.

The result that ferromagnetism can occur in the spinel lattice, although new to us, was actually first indicated by unpublished work in 1941. Stegemann<sup>15</sup> prepared  $\text{CdCr}_2\text{S}_4$  and measured the susceptibility at 195, 293,

<sup>11</sup> M. K. Wilkinson *et al.*, Phys. Rev. **113**, 497 (1959).

<sup>12</sup> R. B. Flippen, J. Appl. Phys. **35**, 1047 (1964).

<sup>13</sup> R. C. Sherwood *et al.*, J. Appl. Phys. **35**, 1049 (1964).

<sup>14</sup> I. S. Jacobs and P. E. Lawrence, J. Appl. Phys. **35**, 996 (1964).

<sup>15</sup> K. Stegemann, doctoral thesis, Technische Hochschule, Berlin, 1941 (unpublished).

and 425°K, from which he found a value of  $\theta = +130^\circ$ . Stegemann, on the basis of the molecular field result that  $\theta = T_c$  for a ferromagnet, concluded that  $\text{CdCr}_2\text{S}_4$  would be ferromagnetic below 130°K. The significance of this work went unnoticed for 24 years. It is therefore interesting that Menyuk *et al.* have also recently and independently discovered<sup>2</sup> that  $\text{CdCr}_2\text{S}_4$  and  $\text{CdCr}_2\text{Se}_4$  are ferromagnetic.

The electrical properties of several of these compounds have also been studied and are reported

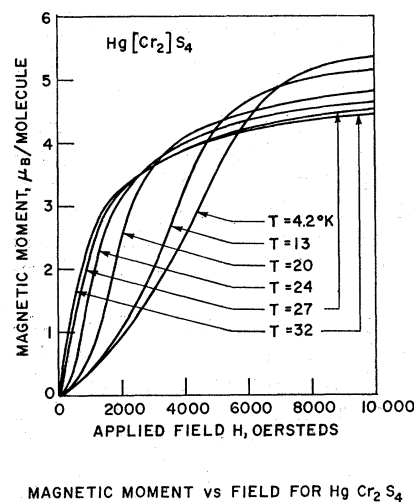


FIG. 5. Magnetic moment as a function of applied field for  $\text{HgCr}_2\text{S}_4$  at several different temperatures.

separately.<sup>1,16</sup> In brief, the compounds  $\text{CdCr}_2\text{S}_4$  and  $\text{CdCr}_2\text{Se}_4$  are found to be semiconductors which have essentially the same conductivity of  $5 \times 10^{-4} (\Omega \text{ cm})^{-1}$  at room temperature. At 77°K the conductivities of  $\text{CdCr}_2\text{S}_4$  and  $\text{CdCr}_2\text{Se}_4$  are quite different, being  $3.5 \times 10^{-10} (\Omega \text{ cm})^{-1}$  and  $6.7 \times 10^{-5} (\Omega \text{ cm})^{-1}$ , respectively. Hall and Seebeck coefficient measurements have also been made which indicate that the samples are nearly compensated semiconductors and have high mobilities for transition-metal compounds. These transport properties are in sharp contrast to those observed in the past for most ferromagnets and also to those for the ferrimagnetic spinels. In most ferromagnets a metallic type of conductivity is observed. In the ferrimagnetic spinels a low mobility ( $10^{-3} \text{ cm}^2/\text{V sec}$ ) is observed and a hopping mechanism appears to hold, while we observe a rather high mobility (about  $7 \text{ cm}^2/\text{V sec}$ ) and a band mechanism appears to hold.

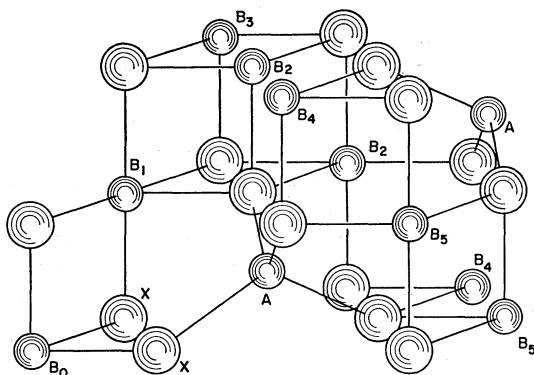
## CRYSTAL STRUCTURE

Before considering the experimental results described above, let us first look at the spinel lattice, and in particular the  $B$  sublattice. A portion of the spinel structure for the generalized compound  $A[B_2]X_4$  is shown in Fig. 6. The ion  $B_1$  at a distance  $(a/4)2^{1/2}$  is

<sup>16</sup> H. W. Lehmann and M. Robbins, J. Appl. Phys. **37**, 1389 (1966).

one of six equivalent nearest neighbors to the ion  $B_0$ . These nearest neighbors can interact either directly via overlap of their electronic wave functions or indirectly at right angles through the intermediate anions  $X$ . The ion  $B_2$  at a distance  $(a/4)6^{1/2}$  is one of 12 equivalent second nearest neighbors to  $B_0$ . The ions  $B_3$  and  $B_4$  both at a distance  $(a/4)8^{1/2}$  are representative of two sets of six equivalent third nearest-neighbors to  $B_0$ . These two sets of third nearest neighbors are not equivalent to each other, which is most readily shown by the fact that there is an intermediate  $B$ -site ion ( $B_1$ ) between  $B_3$  and  $B_0$ , whereas this is not true for  $B_4$  and  $B_0$ . The ion  $B_5$  at a distance  $(a/4)10^{1/2}$  is one of 12 equivalent fourth nearest-neighbors.

It is noteworthy that all the 30 interactions,  $B_0-B_2$ ,  $B_0-B_4$ , and  $B_0-B_5$  can be considered to occur by the same extended superexchange path,  $B_0-X-A-X-B_i$ , whereas the interaction  $B_0-B_3$  is much more complex. It therefore appears possible, in any theoretical treatment of the interactions between the  $B$ -site ions, that the 30 interactions  $B_0-X-A-X-B_2$ ,  $B_0-X-A-X-B_4$ , and  $B_0-X-A-X-B_5$  will all be commensurate in strength and equal in the first approximation. The six interactions  $B_0-B_3$  are distinctly unique and will be neglected in the following discussion. This would greatly simplify the



PORTION OF SPINEL LATTICE SHOWING NEAREST TO 4th - NEAREST B-B NEIGHBORS

FIG. 6. Portion of the lattice structure of a spinel having the general formula  $A[B_2]X_4$ . The figure shows the geometrical relationships among the 1st through 4th nearest  $B$ - $B$  neighbors as described in the text.

problem by reducing the number of unknowns. It should be emphasized that the great number of  $B_0-X-A-X-B_i$  interactions could well outweigh the small number of stronger nearest-neighbor interactions. In addition, these long-range interactions would be expected to depend strongly on the  $A$ -site cation; indeed, the data on the Curie-Weiss  $\theta$  in Table I show a remarkable sensitivity to the nature of the  $A$ -site cation.

The positions of the cations on the  $A$  and  $B$  sites in the spinel lattice are completely described by the lattice parameter  $a$ , and the distances between these ions all

vary linearly with  $a$ . The anion positions of the spinel lattice, however, must be described by the two parameters  $a$  and  $u$ . Gorter<sup>17</sup> has discussed the geometrical relationships of ions in spinels. One can readily calculate the variation in the bond angles  $B-X-B$  and  $B-X-A$  as functions of the  $u$  parameter, as shown in Fig. 7. The bond angle  $B-X-B$  increases linearly through  $90^\circ$  and the angle  $B-X-A$  decreases, almost linearly, through  $125.3^\circ$  with  $u$  increasing through 0.375. The various exchange interactions in spinels could well be more influenced by these angles than by 3% changes in distances between the ions. In  $ZnCr_2O_4$  and  $CdCr_2O_4$  the Cr-O distances are the same, while the Zn-O and Cd-O distances vary directly with the size of the  $A$ -site ion, and the  $B-O-B$  angles equal  $95.6^\circ$  and  $99.9^\circ$ , and the  $B-O-A$  angles equal  $121.2^\circ$  and  $117.9^\circ$ , respectively.

### THEORETICAL DISCUSSION

Many of the magnetic properties of the spinel  $B$ -site ferromagnets can be accounted for on the basis of a Heisenberg spin Hamiltonian of the form

$$\mathcal{H} = -2J \sum_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - 2K \sum_{ik} \mathbf{S}_i \cdot \mathbf{S}_k - g\mu H_z \sum_i S_{iz}. \quad (1)$$

The sum over  $ij$  includes all nearest-neighbor pair interactions ( $B_0-B_1$ ). The number of nearest-neighbors is  $z=6$ , and the strength of the nearest-neighbor exchange  $J$  is assumed to be positive (ferromagnetic). The sum over  $ik$  includes all pair interactions of the type  $B_0-B_2$ ,  $B_0-B_4$ , and  $B_0-B_5$ . The number of next-nearest-neighbors is  $y=30$  since we assume all these interactions to have identical strength  $K$ . The sign of  $K$  may be either positive or negative. The final term is the spin Hamiltonian is the usual Zeeman energy in an external field  $H_z$ .

The Curie-Weiss parameter  $\theta$  is obtained from the leading terms in the high-temperature expansion of the inverse susceptibility. In the case of a spin Hamiltonian

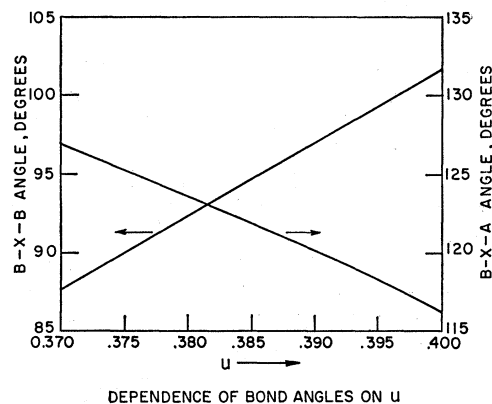


FIG. 7. Dependence of the  $B-X-B$  and  $B-X-A$  bond angles on the structure parameter  $u$  in cubic spinels,  $A[B_2]X_4$ .

<sup>17</sup> E. W. Gorter, Philips Res. Rept. 9, 295, 321, 403 (1954).

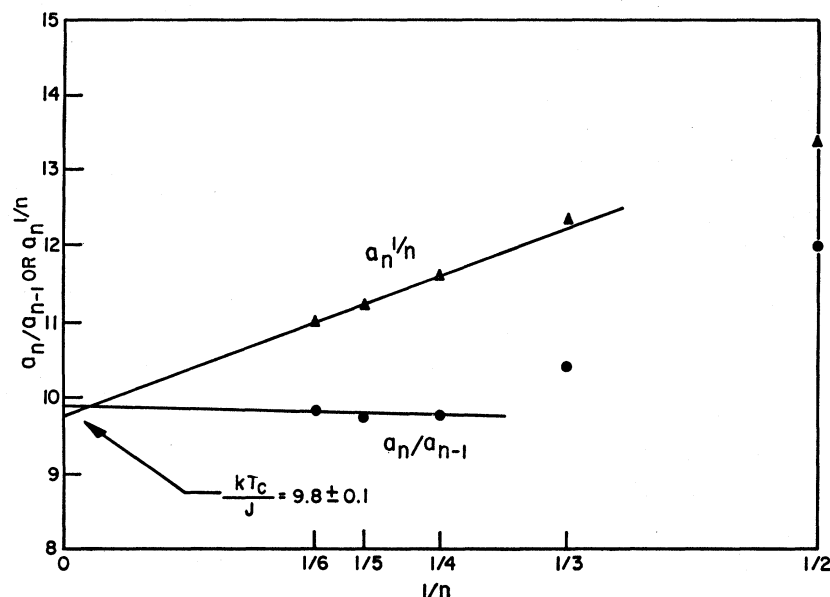


FIG. 8. Graphical determination of the reduced Curie temperature by the extrapolation of the sequences  $\{a_n^{1/n}\}$  and  $\{a_n/a_{n-1}\}$  as described in the text.

of the present form, the required result is<sup>18</sup>

$$\theta = \frac{2}{3}S(S+1)(z(J/k) + y(K/k)), \quad (2)$$

where  $S$  is the spin and  $k$  is Boltzmann's constant. In our particular example of  $\text{Cr}^{3+}$  ( $S = \frac{3}{2}$ ) on the spinel  $B$  sites we obtain

$$\theta = 15(J/k)(1 + 5K/J). \quad (3)$$

The Curie temperature is obtained from the high-temperature expansion of the susceptibility using two different methods. The first method follows the extrapolation technique of Rushbrooke and Wood.<sup>19</sup> For the special case of  $K=0$ , the procedure is straightforward. First, we evaluate the coefficients  $a_n$  in the series expansion for the susceptibility,

$$\chi_M = (C_M/T) \sum_n a_n (J/kT)^n.$$

Formulas for the first seven coefficients have been derived<sup>19</sup> for arbitrary spin and general lattice structure. In our example  $S = \frac{3}{2}$ , and the structure parameters (in the notation of Ref. 19) have the values  $z=6$ ,  $p_1=2$ ,  $p_2=2$ ,  $p_3=0$ ,  $p_4=2$ ,  $q=0$ , and  $r=2$ . The results for  $a_0$  through  $a_6$  are 1, 15, 180, 1876.5, 18 333.625, 178 613.400, and 1 771 183.58, respectively. The Curie temperature is then obtained by computing the sequences  $\{a_n^{1/n}\}$  and  $\{a_n/a_{n-1}\}$ , plotting as a function of  $1/n$ , and extrapolating to  $1/n=0$ . The extrapolations in this example are shown in Fig. 8, the result being  $kT_c/J = 9.8 \pm 0.1$ . In addition, this procedure was also carried out for  $S=2$ ,  $\frac{5}{2}$ , and 3, where the extrapolations were even more smooth and regular. The results for  $kT_c/J$  were 16.0, 23.6, and 32.8, respectively. These

values along with that for  $S = \frac{3}{2}$  are plotted as functions of  $S(S+1)$  in Fig. 9. As had been previously observed by Rushbrooke and Wood<sup>19</sup> for the sc, bcc, and fcc lattices, a linear dependence of the Curie point on  $S(S+1)$  is found. The strict adherence to a linear dependence on  $S(S+1)$  thus provides a greater degree of confidence in the accuracy of the desired  $S = \frac{3}{2}$  point.

The second method of obtaining the Curie temperature involves the use of the powerful Padé-approximant technique.<sup>20</sup> In this method the Curie point is determined by locating the singularities in the Padé approximants to the high-temperature susceptibility series. Starting with the series expansions described above we have computed the  $[2,3]$  and  $[2,4]$  Padé approximants to the susceptibility for  $S = \frac{3}{2}$ ; the results obtained for the Curie temperature  $kT_c/J$  are 9.74 and 9.77, respectively. This procedure was repeated for  $S=2$ ,  $\frac{5}{2}$ , and 3: the Curie points obtained from the  $[2,4]$  Padé approximants were 16.1, 23.7, and 33.0, respectively. All of these determinations are in excellent agreement with the above extrapolated values and increase our reliance in the accuracy of our results. Combining the values obtained from the two independent procedures we find (for  $S = \frac{3}{2}$ )  $kT_c/J = 9.8 \pm 0.1$ . Combining this result with the general formula for  $\theta$ , Eq. (3), yields  $\theta/T_c = 1.53 \pm 0.02$  ( $K=0$ ).

The calculation of the Curie point for finite  $K$  can, in principle, be accomplished in the same manner as described above; general formulas for the coefficients in the susceptibility series appropriate to our assumed spin Hamiltonian have been derived.<sup>18,21</sup> The computa-

<sup>18</sup> P. J. Wojtowicz and R. I. Joseph, Phys. Rev. 135, A1314 (1964).

<sup>19</sup> G. S. Rushbrooke and P. J. Wood, Mol. Phys. 1, 257 (1958).

<sup>20</sup> For a review of Padé approximants see G. A. Baker, Jr., in *Advances in Theoretical Physics*, edited by K. A. Brueckner (Academic Press Inc., New York, 1965), Vol. 1, p. 1. Many further references are made to the use of Padé approximants in the Ising and Heisenberg problems.

<sup>21</sup> K. Pirnie and P. J. Wood, Phys. Letters 17, 241 (1965).

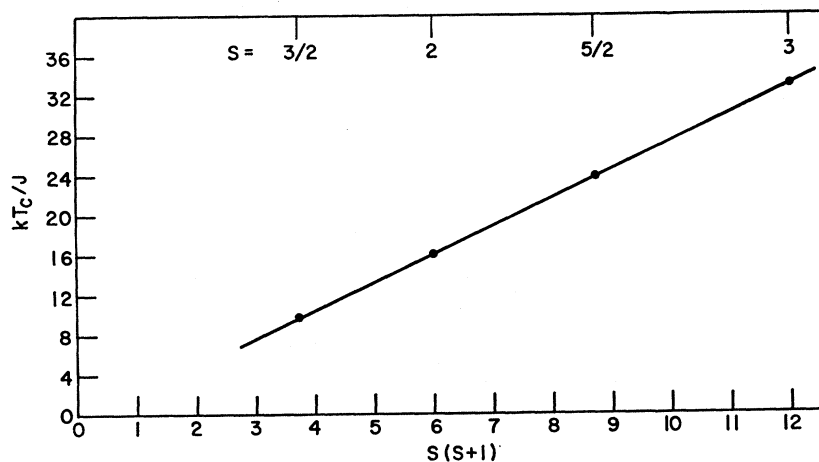


FIG. 9. Reduced Curie temperatures of nearest-neighbor spinel *B*-site ferromagnets as a function of  $S(S+1)$ .

tion, however, requires a detailed knowledge of the lattice statistics [the value of the  $p_n(\alpha; \beta\gamma \dots)$  in the notation of Ref. 18] for the particular structure under study. The task of determining the values of the structure parameters is greatly complicated by the large number of next nearest neighbors ( $y=30$ ), and is a matter of continuing current investigation. In the meantime we will have to be content with a less accurate approximation.

The Curie temperature in cases where both  $J$  and  $K$  are finite is treated as follows: Since the Hamiltonian, Eq. (1), is a linear function of  $J$  and  $K$ , the Curie temperature can be decomposed into a product of two factors:

$$T_c(J, K) = T_c(J, 0) f(K/J). \quad (4)$$

The first factor is the Curie temperature for  $K=0$  (the result described above), while the second factor describes the variation of the Curie temperature with the ratio of the second-to-first-neighbor interaction strengths,  $K/J$ ;  $f(0)=1$ . For  $T_c(J, 0)$  we will use the series-expansion value of  $9.8 J/k$ , while  $f(K/J)$  will be computed within the two-particle cluster approximation of Callen and Callen.<sup>22</sup> Approaches of this kind, utilizing the series expansion estimate for  $T_c(J, 0)$  and the molecular field theory for the computation of  $f(K/J)$ , have proved successful in the cases of europium sulphide<sup>23</sup> and yttrium iron garnet.<sup>24</sup> By using the more correct statistical treatment of the two-particle cluster theory, even greater accuracy can be expected in the computation of  $f(K/J)$ . The two-particle cluster equations for the calculation of the Curie temperature and the  $f(K/J)$  as functions of  $S$ ,  $z$ ,  $y$ ,  $J$ , and  $K$  are presented in Eqs. (20) and (45) of Ref. 22, and will not be reproduced here. Solutions to these equations were obtained on an RCA-601 electronic computer for  $S=3/2$ ,  $z=6$ ,  $y=30$  and many values of the ratio  $K/J$ . The result of combining these solutions with the series

expansion determination of  $T_c(J, 0)$  is displayed in Fig. 10. Here we have plotted the reduced Curie temperature  $kT_c(J, K)/J$ , and the reduced Curie-Weiss parameter  $k\theta/J$  as functions of  $K/J$ . The ratio of  $\theta$  to  $T_c$  is plotted as a function of  $K/J$  in Fig. 11. The dashed portions of the curves are estimates based on extrapolations from the computer solutions represented by the solid lines. Physical solutions of the two-particle cluster equations are unobtainable in this region of small  $T_c$  because of a basic inability of the two-particle cluster theory to account for long-range spin-wave correlation in the low-temperature range.<sup>25</sup>

A number of important features emerge from these calculations. As anticipated, small values of  $K/J$  have a profound effect on  $T_c$  and  $\theta$ . In particular, for small negative values of  $K/J$  the Curie point drops drastically, becoming zero in the vicinity of  $K/J = -0.05$ . For values of  $K/J$  less than  $-0.05$  we find that it is possible to have ferromagnetism disappear while  $\theta$  is still strongly positive. The existence of antiferromagnets having positive  $\theta$  is thus explained within this model. Furthermore, when  $K/J$  approaches  $-0.05$  the magnitude of  $\theta/T_c$  is seen to rise sharply. A large value of  $\theta/T_c$  in a ferromagnet thus presages the impending breakdown of the ferromagnetic order by the second-neighbor antiferromagnetic interactions. Note that  $\text{HgCr}_2\text{S}_4$  with  $\theta/T_c = 3.94$  is a metamagnet showing antiferromagnetic-ferromagnetic transitions at low temperatures. For positive values of  $K/J$  the ratio of  $\theta/T_c$  is a slowly varying function having a minimum of 1.22 at about  $K/J = 1.0$ ;  $\theta/T_c$  never does reach the value 1 as is predicted by the molecular field treatment which grossly oversimplifies the problem.

The results shown in Figs. 10 and 11 have been used to obtain a semiquantitative determination of the exchange interaction parameters for the spinel *B*-site ferromagnets. Using the experimental values of  $\theta$  and  $T_c$  given in Table II, we find the values of  $J/k$  and  $K/k$

<sup>22</sup> H. B. Callen and E. Callen, Phys. Rev. 136, A1675 (1964).

<sup>23</sup> S. H. Charap and E. L. Boyd, Phys. Rev. 133, A811 (1964).

<sup>24</sup> P. J. Wojtowicz, Phys. Rev. (to be published).

<sup>25</sup> H. B. Callen and E. Callen, J. Phys. Soc. Japan 20, 1980 (1965).

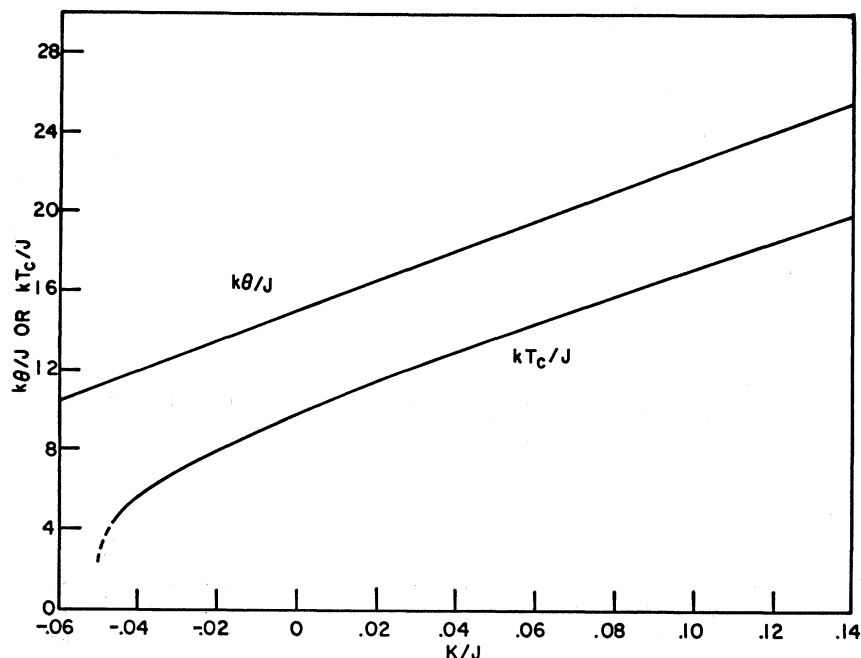


FIG. 10. Reduced Curie-Weiss  $\theta$  and reduced Curie temperature as functions of the ratio of exchange interaction parameters  $K/J$ .

listed in Table III. The uncertainties in these numbers, from combined experimental and theoretical sources, are estimated to be of the order of 10% (perhaps 25% in the case of  $\text{HgCr}_2\text{S}_4$ ). We expect to improve these values as more complete experiments and more reliable theories become available.

In setting down the Hamiltonian, Eq. (1), we assumed that  $J$  was definitely positive. This assumption is in keeping with the expectations of Kanamori,<sup>26</sup> who predicted on symmetry grounds that the  $90^\circ$  superexchange between octahedrally coordinated  $3d^3$  ions would be ferromagnetic. The large Cr-Cr separation ( $\geq 3.63 \text{ \AA}$ ) excludes direct overlap of the chromium orbitals. The neglect of direct exchange interactions is then consistent with the lack of metallic conductivity.<sup>16</sup> An analysis of the magnetization of ferrimagnetic  $\text{MnCr}_2\text{S}_4$  by Menyuk *et al.*<sup>27</sup> also suggests the existence of a positive  $J$  in the chromium sulfide and selenide spinels. Having adopted this assumption concerning  $J$ , we find the sign of  $K$  to be negative in all cases, Table III. It is possible, of course, that the signs of  $J$  and  $K$

could be opposite to those given here. We cannot, unfortunately, investigate this case (large positive  $K$  and small negative  $J$ ) quantitatively. Again, the lattice statistics required in the computation of the  $a_n$  are not yet available for the  $\gamma=30$  equivalent interactions.

The magnitudes of the exchange interaction constants which we have obtained appear to form a consistent picture. Since  $J$  represents the strength of the nearest-neighbor Cr-X-Cr superexchange, we expect its value to be similar for those materials having the same anion X. Table III shows that the values of  $J$  for the sulphides as well as those for the selenides are almost the same. Furthermore, with  $K$  representing the strength of the Cr-X-A-X-Cr superexchange, we expect its value to depend on the nature of the A-site cation. Our analysis shows that the magnitudes of  $K$  for the two Hg compounds are nearly alike and two to five times larger than those for the two Cd compounds.

Finally, we compare our values of the exchange parameters with those determined by Plumier<sup>6</sup> for the antiferromagnet  $\text{ZnCr}_2\text{Se}_4$ . Using a molecular-field approach and ignoring the  $B_0$ - $B_5$  interaction, Plumier obtains the following results:  $W_0=24.9^\circ\text{K}$  (our  $J/k$ ),  $W_1=7.8^\circ\text{K}$  (our  $B_0$ - $B_2$  interaction), and  $W_2=-10.65^\circ\text{K}$  (our  $B_0$ - $B_4$  interaction). The differences between these values and those in Table III are much larger than would be expected from the replacement of Cd or Hg by Zn. We believe that the major source of these discrepancies lies in the use of the molecular-field method in the analysis of the Zn compound. Further contributions to the discrepancies surely arise from the different assumptions concerning the nature of the Hamiltonian. In our view all 30 next-nearest-neighbor interactions are important and (from structural con-

TABLE III. Values of the exchange interaction parameters in the spinel B-site ferromagnets.

Compound	$J/k$ , $^\circ\text{K}$	$K/k$ , $^\circ\text{K}$
$\text{CdCr}_2\text{S}_4$	11.8	-0.33
$\text{CdCr}_2\text{Se}_4$	14.0	-0.10
$\text{HgCr}_2\text{S}_4$	13	-0.6
$\text{HgCr}_2\text{Se}_4$	15.8	-0.51

<sup>26</sup> J. Kanamori, J. Phys. Chem. Solids **10**, 87 (1959); P. W. Anderson, Solid State Phys. **14**, 203 (1963).

<sup>27</sup> N. Menyuk, K. Dwight, and A. Wold, J. Appl. Phys. **36**, 1088 (1965).



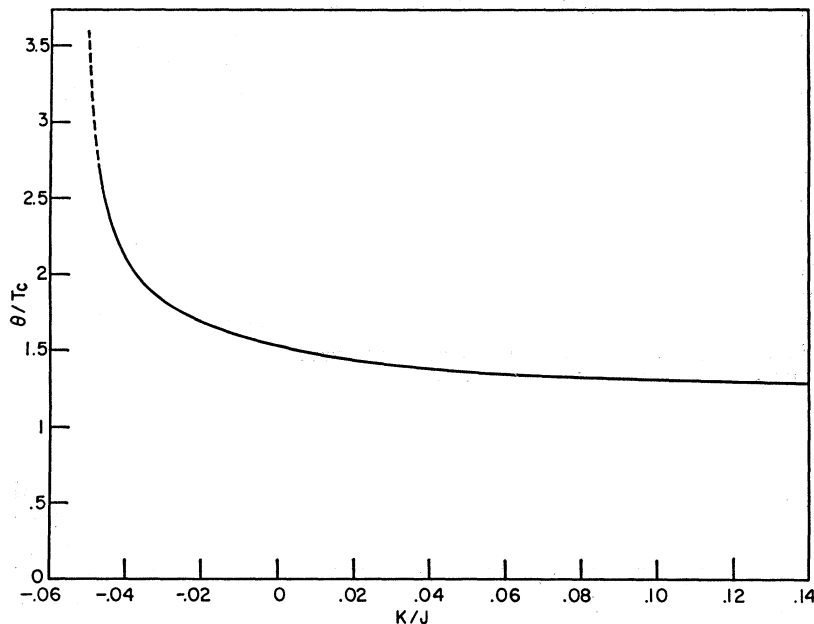


FIG. 11. The ratio  $\theta/T_c$  as a function of the ratio of exchange interaction parameters  $K/J$ .

siderations) commensurate. We have assumed all these interactions to be of strictly equal strength  $K$  in Eq. (1) only in order to keep the theory tractable. The treatment of this problem without the simplification of equal  $K$  appears prohibitively difficult.

### CONCLUSION

The fact that the materials reported here are all ferromagnetic, even though they are electrical insulators, is further evidence that the exchange mechanism for ferromagnetism does not require a high conductivity. These compounds are therefore to be added to the very small number of known electrically insulating ferromagnets. These materials further have the distinction of exhibiting the highest Curie temperatures within this class.

The large  $\theta/T_c$  ratios observed for these ferromagnets (as well as the nonlinear  $1/\chi$ -versus-temperature behavior just above the Curie temperature) are shown to arise naturally in two ways. The first source of the large departures of the  $\theta/T_c$  from unity lies in the complex statistics of the magnetic lattice as demonstrated in the work of Rushbrooke and Wood. Additional increases in the size of  $\theta/T_c$  are shown to arise from the competition between the opposing ferromagnetic and antiferromagnetic interactions. The suspected<sup>3-7</sup> strong role of distant neighbor exchange interactions in the spinel  $B$ -site antiferromagnets has therefore been found to hold in the ferromagnets as well. The 30 commensurate long-distance interactions easily dominate over the six nearest-neighbor interactions in determining the type of magnetic order.

At present we do not have a comparable theory for obtaining similar information on the exchange inter-

actions in the antiferromagnetic spinels. The principal difficulty is the inability to determine the ground-state spin configurations of the  $B$ -site antiferromagnets; these will be very sensitive to the competition between the opposing interactions and to the possible non-equivalency of the 30 more distant interactions. In addition, even if the ground states were known, the theory of the Néel points appears prohibitively difficult for this complex crystal structure. We emphasize that, in view of the results described in this paper, the application of the molecular-field approximation to the antiferromagnets would be very dangerous.

Although there seems to be little doubt that these compounds are essentially ferromagnetic, we feel that the observed departures from the theoretical moment of  $6\mu_B$  are beyond the experimental error and are significant. With the competition from the large number of antiferromagnetic next-nearest-neighbor interactions, the ground-state spin configuration could well be a ferromagnetic spiral. Neutron-diffraction investigations are clearly indicated; the large absorption of neutrons by cadmium, however, precludes the examination of the cadmium compounds.

### APPENDIX A: PREPARATION OF $\text{CdCr}_2\text{S}_4$ , $\text{CdCr}_2\text{Se}_4$ , $\text{HgCr}_2\text{S}_4$ , AND $\text{HgCr}_2\text{Se}_4$

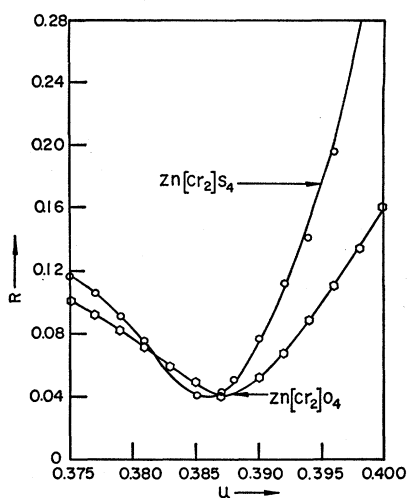
These compounds were prepared by dry-mixing the starting materials for 24 h, pressing the powder into pellets which were weighed, firing in evacuated quartz tubes, and weighing again.  $\text{CdCr}_2\text{S}_4$  and  $\text{HgCr}_2\text{S}_4$  were prepared from metallic chromium and sulfur with CdS and HgS, respectively. The samples were heated to  $800^\circ\text{C}$  at  $10\text{--}15^\circ\text{C/h}$ , then held at this temperature for 48 h, and then furnace cooled. It was necessary to re-

grind, press, and refire the  $\text{CdCr}_2\text{S}_4$  to obtain a complete reaction.  $\text{CdCr}_2\text{Se}_4$  was prepared in the same way except that at the end of the 48-h soak at  $800^\circ\text{C}$  the temperature was lowered to  $670^\circ$  for another 48 h and then furnace cooled. The  $\text{HgCr}_2\text{Se}_4$  was first fired at  $700^\circ\text{C}$  and furnace cooled. It was observed that a considerable amount of  $\text{HgSe}$  had crystallized at one end of the tube. This material was recovered and reground with the bulk of the sample, pressed and refired as before, but at  $600^\circ\text{C}$ . It was necessary to repeat this process two more times to achieve a complete reaction. In all cases, chemical analysis showed that the amount of anion (S or Se) was within 1% of theoretical.

The preparation of  $\text{CdCr}_2\text{Te}_4$  and  $\text{HgCr}_2\text{Te}_4$  was attempted using the general method described above, but with a variety of thermal treatments. It was found, however, that no reaction could be obtained under any conditions.

#### APPENDIX B: X-RAY ANALYSIS

Slow-scan x-ray diffractometer traces for the determination of the lattice parameters ( $a$  and  $u$  for the spinel structure) were obtained for all the materials using  $\text{CuK}\alpha$  radiation and a scanning speed of  $\frac{1}{3}^\circ$  per min. The integrated intensities were obtained by measuring the area under each reflection peak. Using the atomic-scattering factors (corrected for anomalous dispersion) of the ions present, calculated intensities for various values of  $u$  were obtained on the RCA-601 computer. For each assumed value of  $u$ , a minimum weighted average deviation between the calculated and observed intensities ( $R$  factor) is also obtained by an optimization of the temperature factor. The value of  $u$



X-RAY DIFFRACTION ANALYSIS OF  $\text{ZnCr}_2\text{O}_4$  AND  $\text{ZnCr}_2\text{S}_4$

FIG. 12.  $R$  factor (weighted average deviation between calculated and observed x-ray intensities) as a function of assumed values of the structure parameter  $u$  for  $\text{Zn}[\text{Cr}_2]\text{O}_4$  and  $\text{Zn}[\text{Cr}_2]\text{S}_4$ .

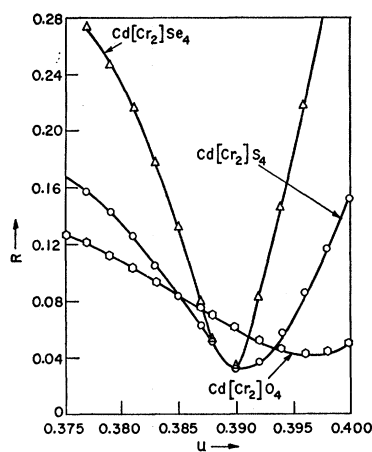


FIG. 13.  $R$  factor (weighted average deviation between calculated and observed x-ray intensities) as a function of assumed values of the structure parameter  $u$  for  $\text{Cd}[\text{Cr}_2]\text{O}_4$ ,  $\text{Cd}[\text{Cr}_2]\text{S}_4$ , and  $\text{Cd}[\text{Cr}_2]\text{Se}_4$ .

which characterizes a compound is taken as that one which gives the minimum  $R$  factor. The variation of  $R$  with assumed values of  $u$  can be seen in Figs. 12-14.

It is also possible to obtain calculated intensities for different assumed ionic distributions which can be compared to the observed intensities. Typical results of this

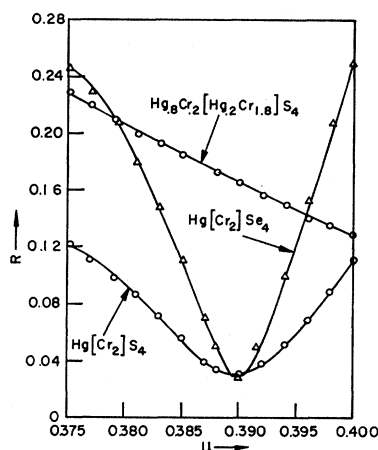


FIG. 14.  $R$  factor (weighted average deviation between calculated and observed x-ray intensities) as a function of assumed values of the structure parameter  $u$  for  $\text{Hg}[\text{Cr}_2]\text{Se}_4$  and two possible cationic distributions of  $\text{HgCr}_2\text{S}_4$ .

X-RAY DIFFRACTION ANALYSIS OF  $\text{HgCr}_2\text{S}_4$  AND  $\text{HgCr}_2\text{Se}_4$

type of calculation are also shown in Fig. 14 for  $\text{HgCr}_2\text{S}_4$  assuming the distribution  $\text{Hg}_{0.8}\text{Cr}_{0.2}[\text{Cr}_{1.8}\text{Hg}_{0.2}]\text{S}_4$ . This type of calculation verified that all of these materials are normal spinels (all the  $\text{Cr}^{3+}$  ions are on the  $B$  sites).

#### APPENDIX C: CURIE-TEMPERATURE DETERMINATION

A method, somewhat different from the usual, has been used to determine the Curie temperature of the compounds discussed in this report. The main virtue of the method is that extensive measurements at or very near to the ordering temperature are not required. Furthermore, the method is based on the latest theo-

retical treatments of the critical behavior of ferromagnets.

Recently, numerous investigators<sup>28</sup> have shown that for a Heisenberg ferromagnet, near the Curie temperature, the initial susceptibility behaves as

$$\chi_0(T) = C(T - T_c)^{-\gamma}, \quad \gamma = \frac{4}{3}.$$

Similarly, the thermal behavior of the spontaneous magnetization of a ferromagnet near the Curie temperature behaves as

$$M_0(T) = B(T_c - T)^\beta, \quad \beta = \frac{1}{3}.$$

These results should be compared to the values  $\gamma = 1$  and  $\beta = \frac{1}{2}$ , predicted by the molecular-field treatment.

Both of the above expressions for  $\chi_0$  and  $M_0$  are meant to hold only very near to the Curie temperature and for zero applied field. Nevertheless, we have found the form of these expressions useful for finite fields and for significant departures in temperature from the Curie temperature. This fact has been exploited to obtain Curie temperatures from a minimum of data.

Magnetization data were obtained, for a number of small fixed applied fields, over a temperature range centered on the expected Curie temperature. The magnetization data for a given fixed field were then used to calculate  $M^3$  and  $\chi^{-3/4}$ , which were then plotted versus temperature. A typical example is shown in Fig. 15, where the magnetization  $M$ , and  $\chi^{-1}$ , have also been shown. The plotted curves of both  $M^3$  and  $\chi^{-3/4}$  are found to be much more linear than the corresponding curves for  $M$  and  $\chi^{-1}$ . The linear portions of the  $M^3$  and  $\chi^{-3/4}$  curves also extend much closer to the Curie temperature which improved subsequent extrapolation.

The linear portions of the curves for both  $M^3$  and  $\chi^{-3/4}$  are extrapolated to the temperature axis and the intercepts averaged to yield the indicated Curie tem-

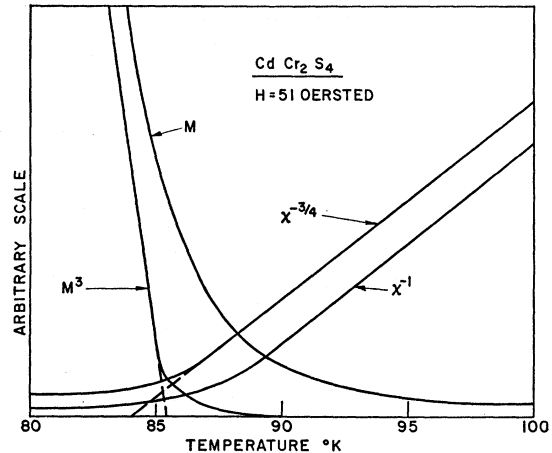


FIG. 15. Graphical determination of the Curie temperature of  $\text{CdCr}_2\text{S}_4$  by the combined extrapolation of  $M^3$  and  $\chi^{-3/4}$ . The quantities  $M$  and  $\chi^{-1}$  are also plotted for comparison.

perature for the finite field used to obtain the data. The values of the indicated Curie temperatures for the various finite fields are then extrapolated to zero field to yield the results given in Table II. The experimental fact that the indicated Curie temperatures were found to be almost independent of the finite applied field for most of the compounds studied further indicates the value of this method.

The determination of the Curie temperature for  $\text{HgCr}_2\text{S}_4$  was not so straightforward. A very strong nonlinear dependence of apparent Curie temperature on the field observed for  $\text{HgCr}_2\text{S}_4$ , is due to the fact that in this compound the competing influences of the ferromagnetic and antiferromagnetic interactions are almost equal. Similar effects in both antiferromagnets and other ferromagnets have also been observed<sup>29</sup> whenever the values of  $J$  and  $K$  lie near the transition region between antiferromagnetism and ferromagnetism. Even demagnetizing fields and interaction fields between domains can influence the measurements, and one must extrapolate to zero field from rather high fields and suffer the possibility of increased errors.

<sup>28</sup> C. Domb and M. F. Sykes, *Phys. Rev.* **128**, 168 (1962); J. Gammel, W. Marshall, and L. Morgan, *Proc. Roy. Soc. (London)* **A275**, 257 (1963); E. Callen and H. B. Callen, *J. Appl. Phys.* **36**, 1140 (1965); P. Heller and G. Benedek, *Phys. Rev. Letters* **14**, 71 (1965); M. E. Fisher, in *Proceedings of the International Conference on Magnetism, Nottingham, England, 1964* (The Institute of Physics and The Physical Society, London, 1965), p. 79.

<sup>29</sup> These results will be reported in a subsequent publication.