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EXCHANGE INTERACTIONS IN SEMICONDUCTING CHALCOGENIDES WITH NORMAL SPINEL STRUCTURE FROM AN EXPERIMENTAL POINT OF VIEW

F. K. LOTGERING

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Résumé. — On passe en revue les propriétés magnétiques et les structures magnétiques obtenues par diffraction des neutrons à 4 °K pour différents composés spinelle normaux. Les problèmes qui se posent lors de la détermination des paramètres d’interaction sont discutés et des valeurs estimées sont données dans les tableaux I, II et III.

Abstract. — A review is given of magnetic data and spin configurations, observed at 4 °K using neutron diffraction, of normal spinels. The problems arising in a determination of the interaction parameters are discussed and values estimated are given in tables I, II and III.

Table I

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ground state (neutron diffr.)</th>
<th>( \theta ) (°K)</th>
<th>( T_c ) (°K)</th>
<th>( M(4°K) ) (µB/mol)</th>
<th>( J(BXB) ) (k)</th>
<th>( J(AXB) ) (k)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(^{2+})Cr(^{3+})O(_4)</td>
<td>unknown</td>
<td>-380</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[2, 19, 27]</td>
</tr>
<tr>
<td>Mg(^{2+})Cr(^{3+})O(_4)</td>
<td>complex antiferrom.</td>
<td>-350</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[38, 30, 43]</td>
</tr>
<tr>
<td>Mn(^{2+})Cr(^{3+})O(_4)</td>
<td>ferrimagn.</td>
<td>-310</td>
<td>-</td>
<td>1.2</td>
<td>-(10 to 15)</td>
<td>-(5 to 10)</td>
<td>[2, 9, 13]</td>
</tr>
<tr>
<td>Fe(^{2+})Cr(^{3+})O(_4) (*)</td>
<td>spiral</td>
<td>-400</td>
<td>-</td>
<td>0.8</td>
<td>-(10 to 15)</td>
<td>-(10 to 15)</td>
<td>[3, 44]</td>
</tr>
<tr>
<td>Co(^{2+})Cr(^{3+})O(_4)</td>
<td></td>
<td>-650</td>
<td>-</td>
<td>0.14</td>
<td>-(20 to 30)</td>
<td>( \pm ) 20</td>
<td>[4, 25, 13]</td>
</tr>
<tr>
<td>Cu(^{2+})Cr(^{3+})O(_4) (*)</td>
<td>Yafet-Kittel</td>
<td>-135 (**)</td>
<td>-</td>
<td>0.5</td>
<td>( \pm ) 10</td>
<td>( \pm ) 10</td>
<td>[4, 26]</td>
</tr>
<tr>
<td>Mg(^{2+})Mn(^{3+})O(_4) (*)</td>
<td>antiferrom. structure unknown</td>
<td>450</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[4, 16]</td>
</tr>
<tr>
<td>Zn(^{2+})Mn(^{3+})O(_4) (*)</td>
<td>unknown</td>
<td>-450</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[4, 47, 16]</td>
</tr>
<tr>
<td>Mn(^{2+})Fe(^{3+})O(_4) (*)</td>
<td></td>
<td>-530</td>
<td>-</td>
<td>1.6</td>
<td>-(15 to 20)</td>
<td>-(5 to 10)</td>
<td>[4, 16, 48]</td>
</tr>
<tr>
<td>Mn(^{2+})V(^{3+})O(_4)</td>
<td>Yafet-Kittel</td>
<td>-56 (**)</td>
<td>-</td>
<td>2.1</td>
<td>( \pm ) 5</td>
<td>( \pm ) 10</td>
<td>[5, 10, 11]</td>
</tr>
<tr>
<td>Co(^{2+})V(^{3+})O(_4)</td>
<td></td>
<td>-145 (**)</td>
<td>-</td>
<td>1.3</td>
<td>-(30 to 40)</td>
<td>( \pm ) 15</td>
<td>[5, 10]</td>
</tr>
</tbody>
</table>

(*) Tetragonal distorted at \( T = 0 \) (except FeCr\(_2\)O\(_4\), which is orthorhombic) : interaction parameters are mean values (compare reference [12]).
(**) The use of \( T_c \) introduces an unknown statistical error in \( J_{AB} \) and \( J_{BB} \) but does not enter into the ratio \( J_{BB}/J_{AB} \).

Table II

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ground state (neutron diffr.)</th>
<th>( \theta ) (°K)</th>
<th>( T_c ) (°K)</th>
<th>( \phi ) (deg)</th>
<th>( J(BXB) ) (k)</th>
<th>( J(BXXB) ) (k)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(^{3+})Cr(^{3+})S(_4)</td>
<td>Yafet-Kittel</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>10 (**)</td>
<td>-</td>
<td>[14, 15]</td>
</tr>
<tr>
<td>Cd(^{2+})Cr(^{3+})S(_4)</td>
<td>ferromagn.</td>
<td>135</td>
<td>97</td>
<td>-</td>
<td>12 (*)</td>
<td>-0.3 (*)</td>
<td>[22, 23, 24]</td>
</tr>
<tr>
<td>Hg(^{2+})Cr(^{3+})S(_4)</td>
<td></td>
<td>140</td>
<td>22</td>
<td>( \approx ) 10</td>
<td>( \approx ) 0.5</td>
<td>-</td>
<td>[22, 23, 49]</td>
</tr>
<tr>
<td>Zn(^{2+})Cr(^{3+})Se(_4)</td>
<td>antiferrom. spiral</td>
<td>100</td>
<td>42</td>
<td>( \approx ) 10</td>
<td>( \approx ) 1</td>
<td>-</td>
<td>[21, 35]</td>
</tr>
<tr>
<td>Cd(^{2+})Cr(^{3+})Se(_4)</td>
<td>ferromagn.</td>
<td>200</td>
<td>142</td>
<td>-</td>
<td>14 (*)</td>
<td>-0.1 (*)</td>
<td>[22, 23]</td>
</tr>
<tr>
<td>Hg(^{2+})Cr(^{3+})Se(_4)</td>
<td>ferromagn.</td>
<td>190</td>
<td>120</td>
<td>-</td>
<td>16 (*)</td>
<td>-0.5 (*)</td>
<td>[22, 23]</td>
</tr>
</tbody>
</table>

(*) Values given in reference [23].
(**) See text for method of determination.
Exchange Interactions in Semiconducting Chalcogenides

I. Introduction. — After Néel’s [1] discovery of the phenomenon of ferrimagnetism in the ferrites having spinel structure, the spinel lattice continued to play an important part in the study of magnetism. This may be a consequence of two unique properties of the spinel lattice: (1) it is the most highly symmetric lattice containing two kinds of crystallographically different sites, the tetrahedral (A) sites and the octahedral (B) sites, and (2) a great variety of chemical substitutions exists for cations as well as for anions. The purpose of the present paper is to review the information about the superexchange interactions in semiconducting spinels as it appears from the magnetic data and neutron diffraction results. The discussion is restricted to simple systems containing equivalent lattice sites occupied by one kind of ions («normal» spins) because a restriction of the number of interaction parameters is necessary. For example, the number of five AB and BB nearest-neighbour interactions (M_A M_B, M_B M_A M_B M_B, M_B M_B M_B M_B) in M[M(M')]X_4 is reduced to two (M'_A M_B, M_B M_B) in M'[M(M')]X_4.

The A-site lattice consists of two f. c. c. Bravais lattices, the relative position of which is such that a site of one Bravais lattice is surrounded tetrahedrally by four sites of the other. This gives a natural division of the A lattice into the two Bravais lattices and promotes an ordering according to a simple two-sublattice model in suitable substances. The B lattice however, has a more complicated structure and consists of three other sublattices. As a consequence of this geometric difference between the A and B lattices, spin ordering in which negative BB interaction plays an essential part is more complicated (e. g. in Ge[Co_2]O_4, Mn[Cr_2]O_4) than that in which negative AA interaction is essential (e. g. in Co[Cr_2]O_4, Mn[Cr_2]S_4).

II. Ferrimagnetic, normal spinels. — Normal spinels with magnetic ions on A and B sites are:

(1) An indication of this type of interaction was recently found in In[Cr_2]S_4 [17].

Table III

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn^2+Al^3+O_4 (*)</td>
<td>6 (n)</td>
<td>-0.3</td>
<td>[37]</td>
<td>Co^2+Al^3+O_4 (*)</td>
<td>4 (n)</td>
<td>-0.4</td>
<td>[37]</td>
</tr>
<tr>
<td>Mn^2+Rh^3+O_4</td>
<td>15</td>
<td>-0.6</td>
<td>[38]</td>
<td>Co^2+Rh^3+O_4</td>
<td>27</td>
<td>-3</td>
<td>[38]</td>
</tr>
<tr>
<td>Mn^2+Ga^3+O_4 (*)</td>
<td>33 (n)</td>
<td>-1.4</td>
<td>[40]</td>
<td>Co^2+Co^3+O_4</td>
<td>40 (n)</td>
<td>-4</td>
<td>[37]</td>
</tr>
<tr>
<td>Fe^2+Al^3+O_4 (*)</td>
<td>8</td>
<td>-0.5</td>
<td>[37]</td>
<td>Co^2+Rh^3+O_4</td>
<td>400 (n)</td>
<td>-40</td>
<td>[39, 14]</td>
</tr>
<tr>
<td>Ni^2+Rh^3+O_4</td>
<td>18</td>
<td>-3</td>
<td>[38]</td>
<td>Mn^2+Cr^3+O_4</td>
<td>-</td>
<td>1.7 (**))</td>
<td>[14]</td>
</tr>
<tr>
<td>Fe^2+Cu^+Rh^3+O_4</td>
<td>T_N = 140 °K and θ = -420 °K gives J(AXX):/k = J(XXXXA):/k = -4 °K (**))</td>
<td>[41]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(*) 5 to 15 % invers spinels.
(**) See text for method of estimation.
(n) Simple two-lattice ordering observed using neutron diffraction.

In the oxyspinels just mentioned the AB and BB interactions dominate and are of the same order of magnitude. This gives ferrimagnetic ground states with canted B spins. The simplest assumption is the three-sublattice model of Yafet and Kittel [6]. However, calculations of Lyons, Kaplan, Dwight and Menyuk [7, 8] based exclusively on AB and BB exchange of the Heisenberg type show that the Yafet-Kittel configuration is always unstable with respect to the more complicated ferrimagnetic spiral. In both models the spin configuration is determined (apart from the easy direction) by one parameter, the ratio J_{AB}/J_{BB}. This ratio can therefore be determined from the observed ferrimagnetic moment M_0 at T = 0. Using the observed asymptotic Curie temperature θ, one can then find J_{AB} and J_{BB} without any statistical approximations.

The theory has been nicely confirmed experimentally by the observation of ferrimagnetic spirals in several oxyspinels using neutron diffraction. However, the observation never agrees in details with the theoretical spiral corresponding to M_0 (e. g. in MnCr_2O_4 [9]), or the Yafet-Kittel configuration occurs (e. g. in MnV_2O_4 [10, 11]) instead of a spiral. This may be caused by the presence of other types of energies in addition to the AB and BB Heisenberg-type superexchange considered so far, and which may be anisotropy [10, 12], exchange striction [11], AA interaction [13], next-nearest neighbour BB [13] or AB interaction, or biquadratic exchange (1). The deviation from the theoretically expected configuration introduces an unknown error into the determination of J_{AB}/J_{BB} from M_0.

If the A spins are canted, one expects a simple Yafet-Kittel configuration (introduction). This does not occur in oxyspinels in which the AA interaction is mostly very weak (section IV), but it has been observed in two sulphospinels [14]. Mn^2+Cr^3+S_4 [14] shows a nearly (but not completely [15]) ideal behaviour in accord with the Yafet-Kittel model for a system of ions with a g factor near to 2, so that this case...
seems suitable for a reliable determination of the interaction parameters. $J_{AA}$, $J_{BB}$ and $J_{AB}$ were obtained from $M_0(\delta M/\delta H) < T_\sigma$ and $\theta$. (Interaction strengths between canted spins from $\delta M/\delta H$ were first determined by Jacobs [16].)

In all cases, in which we obtained the interaction parameters from magnetic data at $T \to 0$ and $\theta$, a calculation of $T_N$ from these parameters and using the molecular-field approximation yielded values of 2 to 3 times the observed values. This points to strong short-range effects and shows that it is dubious to determine interaction in ferrimagnetic spinels using $T_c$ as experimental data.

III. BB interactions. — Normal spinels with the magnetic ions exclusively on B sites are: $\text{Ge}^{4+} \text{M}^2_2 \text{O}_4$ [18], (M = Fe, Co, Ni), $\text{M}^2_2 \text{V}^3_2 \text{O}_4$ [5], $\text{M}^2_2 \text{Fe}^{3+} \text{V}^2_2 \text{O}_4$ [19, 20], $\text{Fe}^{3+} \text{Cr}^{2+} \text{O}_4$ [2, 18, 19] and $\text{M}^2_2 \text{Mn}^{2+} \text{O}_4$ [4] with Me = Mg or Zn, and $\text{M}^2_2 \text{Cr}^{2+} \text{X}_4$ (M = Zn [3, 21], Cd or Hg [22, 23, 24] and X = S, Se).

Anderson [25] has drawn attention to the essential part played by the next-nearest neighbour interactions (of type BXXB) in antiferromagnetic ordering of the B ions. The B lattice is built up from units of four nearest neighbours situated on the corners of a tetrahedron, and such a B tetrahedron shares one B site with an adjacent B tetrahedron. For negative BXB interactions, the ground state is determined by the condition that the spins in each tetrahedron cancel, but the long-range ordering is not fixed. (The degeneracy of the ground state can be verified easily for a collinear model. In a given tetrahedron two spins are up and two spins are down. For an adjacent tetrahedron only the spin of the common B ion is fixed and there are three configurations with two spins up and two spins down, that have equal energy.) The interactions between B sites in different tetrahedrons are of the type BXXB and can give antiferromagnetic long-range ordering, and the Néel temperature $T_N$ will depend on these interactions in a complicated (and unknown) way. This may explain the great difference between $\theta$ and $T_N$ in $\text{MgCr}_2\text{O}_4$ ($T_N = 15\text{ K}$ and $\theta = -350\text{ K}$): the high $\theta$ arises from strongly negative BXB interactions, whereas $T_N$ is determined mainly by the much weaker negative BXXB interactions.

This picture is supported by the neutron-diffraction results. One finds complicated patterns which are difficult to interpret (ZnFe$_2$O$_4$ [26], ZnCr$_2$O$_4$ [27], GeFe$_2$O$_4$ [28]) or antiferromagnetic structures that show spin compensation within each tetrahedron (GeCo$_2$O$_4$ [29], MgCr$_2$O$_4$ [30] (2), MgV$_2$O$_4$ [31]). An antiferromagnetic structure pointing to positive BXB interaction has been reported [32] only for GeNi$_2$O$_4$ as here a B tetrahedron contains three parallel spins and one spin uncorrelated (the deviating behaviour of Ni$^{2+}$ can be understood from the theory of superexchange: exclusively for Ni$^{2+}$ the theory predicts unambiguously positive interaction for a MXM angle of 90 degrees).

Since the long-range ordering is difficult to establish one might expect strong short-range ordering above $T_N$. The $\chi^{-1} - T$ curves, as far as published [18], do in fact show a deviation from a Curie-Weiss law at temperatures up to $\approx 10\ T_N$. Any estimation of interaction strength from $T_N$ therefore seems difficult. Moreover $\theta$ gives no reliable information in many cases because the $\chi^{-1} - T$ curve may deviate from a straight line as a consequence of (a) crystalfield splitting and spin-orbit coupling or (b) small deviations from the normal spinel structure. Figure 1 gives an example of both cases. Curve (a) [33] is calculated for a system of Co$^{2+}$ ions without interaction and occupying ideal cubic octahedral sites in an oxide, and (b) for $\text{Zn}^{2+}_{0.9}\text{Fe}^{3+}_{0.1}\text{Fe}^{3+}_{0.1}$ with 3% inversion and assuming no BB interaction (here the curvature arises from AB interaction in clusters consisting of an Fe$^{3+}$ ion on an A site with its 12 Fe$^{3+}$ neighbours on B sites). In both cases the curvature is such that, at sufficiently high temperatures, the $\chi^{-1} - T$ curve is difficult to distinguish from a Curie-Weiss law with $\theta \approx 60$ or 80 K, though the BB interaction is assumed to be zero. Only in the cases of Cr$^{3+}$ on B sites it is quite sure that these effects play no part, because the observed Curie constants are in good agreement with the spin-only value.

\begin{figure}
\centering
\includegraphics{fig1}
\caption{Crosses: reciprocal susceptibilities per gram-ion Co$^{2+}$ or Fe$^{3+}$ calculated as a function of temperature for (a) Co$^{2+}$ ions without exchange interactions, occupying ideal octahedral sites in an oxide, and (b) for $\text{Zn}^{2+}_{0.9}\text{Fe}^{3+}_{0.1}\text{Fe}^{3+}_{0.1}$ taking into account exclusively AB interaction between the Fe$^{3+}$ ions. Straight lines: «Curie-Weiss law» adjusted to the calculated points.}
\end{figure}
For MCr\textsubscript{2}X\textsubscript{4} (X = S, Se) the BXB interaction is positive, as appears from a positive \( \theta \) and the ferromagnetic behaviour \([12, 23, 24]\) of CdCr\textsubscript{2}S\textsubscript{4}, CdCr\textsubscript{2}Se\textsubscript{4} and HgCr\textsubscript{2}Se\textsubscript{4}. Although \( \theta \) is positive for ZnCr\textsubscript{2}Se\textsubscript{4}, the material is not ferromagnetic but antiferromagnetic, which can be explained as being due to a combination of positive BXB and negative BXXB interactions \([21]\). The antiferromagnetic ordering is that of a simple spiral \([35]\), which consists of ferromagnetic (001) sheets with a spin direction that turns by propagation in the [001] direction. There are four types of BXXB interactions and a mean value of the ratio \( J(BXXB)/J(BBX) \) can be estimated roughly from the turning angle of the spiral \([35, 14]\). An extensive analysis \([36]\) shows that the spiral is only stable if J(BXB) is positive, J(BXXB) is negative for three types of these interactions and positive for one type, and if one type of interaction at a larger distance exists. However, the ferromagnetic and helical configurations seem to be the stable states for this kind of compounds if the positive interaction is not too weak (only in ZnCr\textsubscript{2}S\textsubscript{4} with \( \theta = 18 \)\(^\circ\) another configuration occurs). It seems therefore questionable whether the spiral is indeed stabilized by such a rather specific combination of interactions and it may be that small energies of a different type (mentioned above) play a part.

For the ferromagnetic compounds MCr\textsubscript{2}X\textsubscript{4}, \( \theta \) is found to be considerably higher than \( T_c \) (by a factor 1.6 to 1.9), i.e. considerable short-range order exists above \( T_c \). Values for J(BXB) and J(BXXB) have been obtained \([23]\) from the two temperatures.

IV. AA interactions. Normal spinels with the magnetic ions exclusively on A sites are : Co\textsuperscript{2+}Co\textsuperscript{3+}O\textsubscript{4} \([37]\), M\textsuperscript{2+}Rh\textsuperscript{3+}O\textsubscript{4} \([38]\), (M = Mn, Co, Ni) and Co\textsuperscript{2+}Rh\textsuperscript{3+}S\textsubscript{4} \([39]\), whereas M\textsuperscript{2+}Al\textsuperscript{3+}O\textsubscript{4} \([37]\), (M = Mn, Fe, Co) and MnGa\textsubscript{2}S\textsubscript{4} \([40]\) are mainly normal (5 to 15 \( \% \) inversion), Co\textsuperscript{2+} and Rh\textsuperscript{3+} occupying the B sites are in the non-magnetic, low spin \( t_{2g} \) state.

Since two A sites do not share a nearest-neighbour \( X^{-} \) ion, the shortest superexchange path is AXA. All substances are antiferromagnetic according to the simple two-lattice model mentioned in section I, which shows that a negative AXA interaction between nearest A neighbours dominates. Here an estimation of the interactions from \( T_N \) seems justified as there are no indications of short-range ordering above \( T_N \). For all normal spinels \([38, 39]\) a Curie-Weiss law is found that holds at temperatures down to \( T_N \) in contrast to the behaviour of the spinels with magnetic B ions (section III).

\( \theta \) gives no reliable information about the interaction in most cases for reasons mentioned in section III. Only for MnRh\textsubscript{2}O\textsubscript{4} is the observed Curie constant in agreement with the spin-only value, so that \( \theta \) can be used, and a value of 0.3 is found for the ratio of the next-nearest and nearest neighbour interactions (both of type AXA) from \( \theta = -25 \)\(^\circ\)K and \( T_N = 15 \)\(^\circ\)K.

In Fe\textsuperscript{3+}Cu\textsuperscript{2+} \([41]\) the Fe\textsuperscript{3+} and Cu\textsuperscript{2+} ions are ordered in accordance with the two-sublattice model mentioned in the introduction, i.e. the Fe\textsuperscript{3+} ions occupy one of the f. c. c. Bravais lattices from which the spinel lattice is built up. The Fe\textsuperscript{3+} ions are exclusively magnetic, and the nearest-neighbour interaction is of type AXXA, whereas the next-nearest neighbour interaction takes place between Fe\textsuperscript{3+} ions at a distance equal to the cell edge (\( \sim 10 \)\( \AA \)) and is of type AXXAXX. From the observation of MnS type of antiferromagnetic ordering of the f. c. c. lattice it appears that the latter interaction is decisive, and the two interactions can be obtained from \( \theta = -420 \)\(^\circ\)K and \( T_N = 140 \)\(^\circ\)K. Interactions at such a long distance, which may occur also in other sulphospinels, can be detected in this special case as a consequence of the ionic ordering on the A sites.

Finally we should like to mention some experimental information concerning the interaction mechanism for larger distances, taking the interaction of Co\textsuperscript{2+} ions on A sites as an example. Blasse \([38]\) has introduced interactions of type Co—O—B—O—Co in spinels with non-magnetic B ions: the non-magnetic O\textsuperscript{2—}→ B\textsuperscript{3+}—O\textsuperscript{2—} group plays the role of the intermediate X ion in MXM superexchange. The value \( T_N = 4, 27 \) and 40\( \circ\)K for B\textsuperscript{3+} —Al\textsuperscript{3+}, Rh\textsuperscript{3+} and Co\textsuperscript{2+} (table III) show a strong dependency of the AA interaction on the type of the B ion, which can be attributed \([38]\) to increasing covalency of the B\textsuperscript{3+}—O\textsuperscript{2—} bond in the sequence B = Al, Rh, Co. This interpretation has been supported by NMR results \([42]\).

However, the mechanism seems to be not generally valid. The mixed crystals Co\textsubscript{1—x}Rh\textsubscript{x} \textsubscript{2} \textsubscript{S} \textsubscript{4} \([14]\) are ferrimagnetic and the Yafet-Kittel configuration occurs for \( 0 < x < 1.65 \). From the observation of a linear increase of the saturation with \( x \) it follows that the ratio of the AA and BB interaction is constant \( J_{CoCo} = 1.03 J_{CoB} \). The high values of the critical temperatures \( T_{C}(x = 0) = 400 \)\(^\circ\)K and \( T_{C}(x = 2) = 240 \)\(^\circ\)K show that the CoCo interaction in the whole series of mixed crystals is an order of magnitude larger than in CoRh\textsubscript{2}O\textsubscript{4} and Co\textsubscript{3}O\textsubscript{4}. The anomalously strong interaction cannot be attributed to Co—S—Rh—O exchange because the interaction remains anomalously strong if Rh\textsuperscript{3+} is replaced by Cr\textsuperscript{3+} ions. The observation that the CoCo interaction is weak in CoRh\textsubscript{2}O\textsubscript{4} and strong in CoRh\textsubscript{2}S\textsubscript{4} and in CoCr\textsubscript{2}S\textsubscript{4} shows that the presence of Rh\textsuperscript{3+} is not the decisive factor, but that the difference must be sought in the replacement of oxygen by sulphur. The much stronger interaction in the sulphides may be attributed to a more covalent Co-X bond and (or) stronger XX overlap in sulphides than in oxides (the S-S distance in CoRh\textsubscript{2}S\textsubscript{4} is \( \approx \) smaller, the O-O distance in CoRh\textsubscript{2}O\textsubscript{4} is 14\% larger than the sum of the Goldschmidt radii).

V. Conclusions. 1. The interaction parameters of even the simple spinel systems mentioned in this paper can be determined only in rough approximation and in a limited number of cases.

2. In addition to the AXB and BXB interactions, interactions of type AXAX and BXXB (and possibly AXBX) may influence the configuration (ferromagnetic spiral) or play an essential part (MnCr\textsubscript{2}S\textsubscript{4} ; antiferromagnetic ordering on B sites).

3. Tables I, II and III give estimates of interaction parameters \( J \), defined using the relation \( E_{exc} = -2J_{1}S_{1}S_{1} \). The superexchange of type AXAX and BXXB \( (J/k = 0.5 \text{ to } 5 \)\(^\circ\)K) is an order of magni-
tude smaller than the AXB and BXB superexchange (\(J/k = 5\) to 50 K).

4. Anomalously strong long-distance interactions occur in \(\text{CoRh}_2\text{S}_4\) (\(J/k \approx -40\) K for the \(\text{Co}^{2+}\text{SSCo}^{2+}\) interaction) and in \(\text{Fe}_9\text{Cu}_6\text{Rh}_2\text{S}_4\) (\(J/k \approx -4\) K for the \(\text{Fe}^{2+}\text{SSSSFe}^{2+}\) interaction).

5. The BXB interaction for a given B ion is practically independent of the kind of A ion in the series \(\text{M}_{\text{C}}\text{R}_3\text{S}_4\), \(\text{M}_{\text{C}}\text{R}_3\text{Se}_4\) and \(\text{M}_3\text{S}_4\), whereas this interaction changes by about a factor of 2 in the series \(\text{M}_{\text{C}}\text{R}_3\text{O}_4\). A great difference for the \(\text{V}^{2+}\text{OV}^{2+}\) interaction in \(\text{M}_{\text{N}}\text{V}_4\text{O}_4\) and \(\text{CoV}_3\text{O}_4\) is found. However, the absolute values are very uncertain in the latter case (table I).

References

[17] Plumier (R.), Lotgering (F. K.) and Van Stapele (R. P.), this Conference.