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# Preparation and Electrical Properties of Some Thiospinels[1]

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*Received November 16, 1964*

A number of ternary transition metal sulfides of the type $AB_2S_4$ with the spinel structure have been prepared by allowing the metals to react with sulfur or by allowing the oxides to react with $H_2S$. Electrical resistivity measurements as a function of temperature and Seebeck voltages were also measured. Four of the materials are semiconductors and the rest are metallic. The conclusion is made that in the thiochromites, except for copper thiochromite, the $t_{2g}$ electrons associated with the B site chromium ions are localized and give rise to magnetic moments equivalent to those obtained from the spin-only moments of the paramagnetic ions. However, the activation energy necessary for conduction in these compounds will depend upon the influence of the A site ions. For copper thiochromite and the other metallic-like ternary sulfides, the conductivity results from the formation of unfilled $\sigma^*$ bands between the metal and sulfur orbitals.

## Introduction

A number of thiospinels of the type $AB_2S_4$, where A and B are transition metals, have been reported in the literature.[2-5] The magnetic properties of a number of the thiochromites were reported by Lotgering,[2,3,6] but only $FeCr_2S_4$ was studied as to its electrical properties. This appears to be the only work that attempts to correlate the electrical properties of these compounds with the type of bonding that may be present. The thiochromites of the type $ACr_2S_4$ are particularly attractive because they are all probably normal; *i.e.*, only divalent ions on tetrahedral sites and only trivalent ions on octahedral sites. This is a result of the decided preference of trivalent chromium for octahedral coordination and has been definitely established for $FeCr_2S_4$[7] and $MnCr_2S_4$[8] by neutron diffraction studies. X-Ray work[9] indicates that $ZnCr_2S_4$ is also normal. It is therefore possible to study the effect of different A site cations on the electrical properties of these compounds. By reducing the size of the A site cation, the unit cell size is reduced, and the $Cr^{+3}$ ions are brought closer together. This increases the possibility of electrical conduction by direct overlap of the $Cr^{+3}$ wave functions below some critical separation $R_c$. If this type of direct overlap is present in the sulfides, it will be observed only for compounds having cations which are at the beginning of the transition series; *i.e.*, where the nuclear charge is relatively low and the d orbitals extend further out in space. A study[10] of normal vanadium spinels of the type $MV_2O_4$ showed that as the size of the A site ion decreased the resistance decreased markedly, indicating increased overlap of $V^{+3}$ ions. In going from $V^{+3}$ to $Cr^{+3}$ and from an oxygen to sulfur lattice, the chances of any direct overlap are decreased. However, it is thought that the critical distance for overlap increases for a more polarizable lattice.[11] Since only $CuV_2S_4$ and $CuTi_2S_4$ form stable vanadium and titanium thiospinels, the chromium thiospinels represent the only spinel series that could afford an experimental test of the value of $R_c$ in sulfides.

The $Cr^{+3}$–$Cr^{+3}$ interactions in $MnCr_2S_4$ and $CoCr_2S_4$ are ferromagnetic,[2,8] which suggests that $R > R_c$ for the following reasons. Direct $Cr^{+3}$–$Cr^{+3}$ interactions are antiferromagnetic, whereas the indirect 90° $Cr^{+3}$–anion–$Cr^{+3}$ interactions are ferromagnetic. In oxides, the net interaction is antiferromagnetic, which points to a strong direct $Cr^{+3}$–$Cr^{+3}$ interaction. The ferromagnetic $Cr^{+3}$–$Cr^{+3}$ interactions in $MnCr_2S_4$ and $CoCr_2S_4$ indicate that the 90° $Cr^{+3}$–S–$Cr^{+3}$ interactions are much stronger, relative to the direct interactions, in sulfides than in oxides. This implies that for $Cr^{+3}$, $R_c$ (sulfides) $< 3.51$ Å.

In addition to the thiochromites, several thiocobaltites have been prepared. Lotgering[3] has shown that, based on ionic $S^{-2}$ close packing, the cell edge of a thiospinel should be $\geq 9.85$ Å., and the cell edges of the thiochromites are consistent with this value, from which he concludes that these compounds are ionic. The cell sizes of the thiocobaltites are about 9.4 Å., which is considerably smaller than that anticipated for purely ionic structures. Since a smaller sulfur–sulfur distance than that necessary for $S^{-2}$ contact is an indication of appreciable covalency, the simple ionic model does not hold for the thiocobaltites. Lotgering has demonstrated that from the cell sizes alone, it is possible to conclude that there must be considerably more covalent character in the cobalt–sulfur bonds. Low susceptibility values indicate that the atomic moments are considerably lower than the spin-only values, and the Curie constants agree with those calculated for covalent structures. For cobalt oxide spinels it has been shown[12] that the cobalt is in the low-spin state and appreciable covalency in the thiocobaltites is con-

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[1] This work has been supported by A.R.P.A. and Grant No. AF 19-(628)-3837.

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[11] J. B. Goodenough, "Magnetism and the Chemical Bond," Interscience Publishers, New York, N. Y., 1963, p. 279.

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sistent with low-spin state $Co^{+3}$ being present in these compounds.

Goodenough has offered an alternative model[13] in which the $e_g$ levels of the B site chromium ions are broadened into a band by covalent mixing with the anion. The magnetic properties and cell sizes of the thiochromites would be the same as in Lotgering's model, since both models assume that the $t_{2g}$ electrons of the B site cations are localized. For the thiocobaltites, the Goodenough model indicates low-spin $Co^{+3}$ and therefore empty $\sigma^*$ bands in this case also. Any metallic conductivity is due to partially filled $\sigma^*$ bands associated with the A site transition metal cations. (The $\sigma^*$ bands for B site cations have $e_g$ symmetry, those for A site cations have $t_{2g}$ symmetry.) In the thiocobaltites, the observed cell sizes should be reduced because of the covalent interaction of the electrons with those of the anion. Goodenough also predicts that the nature of the conductivity in these compounds will be affected by the A site ion. The experimental measurements presented in this paper will serve to substantiate these ideas.

## Experimental

**Preparation.**—The thiospinels can be prepared by a high-temperature combination of the metals with sulfur. Only high-purity (99.99+%), freshly-reduced metals are used and the reactions are carried out in evacuated silica tubes. Several firings are necessary with grinding under dry nitrogen (about 1 hr. in a mechanical mortar grinder) between firings to achieve homogeneity.

We found that some of the thiochromites can also be prepared by reaction of the corresponding oxide spinels with $H_2S$ at elevated temperatures according to the general reaction $AB_2O_4 + 4H_2S \rightarrow AB_2S_4 + 4H_2O$. The pure oxides are prepared by the method of Whipple and Wold.[14]

For electrical resistivity and Seebeck measurements, the samples are pressed at about 30,000 p.s.i. into bars approximately 0.8 × 0.15 × 0.15 in. and fired in evacuated silica tubes. However, some materials do not sinter below their decomposition temperatures, *e.g.*, $Co_3S_4$. They must be pressed into bars in a "hot-press" apparatus where a temperature of 300–400° and a pressure of 100,000 p.s.i. are simultaneously maintained for about 4 hr.

**Analyses.**—Analysis of the final products for sulfur is done by a weight-loss procedure. If the metals in the spinel have stable stoichiometric oxides (either the parent oxides, $A_xO_y$ and $B_xO_y$, or the spinel oxides $AB_2O_4$), the weight loss on oxidation can be related to the amount of sulfur present. The oxidation is carried out until constant weight is obtained, at 700° under oxygen except when the product is volatile, *e.g.*, $V_2O_5$, and then 500° is the temperature used. If the products of oxidation are not stoichiometric, they must be reduced to the metals under hydrogen (see Table II). In this case the weight loss is just equal to the weight of sulfur present. A precision of better than 0.1% is obtained by this method. For $CuV_2S_4$, total vanadium was analyzed and corresponded to that expected for the compound. The final phases from the oxidation or reduction procedures were corroborated by X-ray analysis. For the thiochromites, total chromium and A site ion were analyzed by standard techniques.

**Physical Measurements.**—Electrical resistivity as a function of temperature was determined on the bars previously described over a temperature range from −180 to +150° at 10–20° intervals. For resistance measurements a Keithley Model 610A electrometer was used for high resistances (>500 ohms) and a Keithley Model 503 milliohmmeter at lower resistances. The two-probe technique was used for resistances greater than 3 ohms, while four probes were used at lower resistances to eliminate contact resistance. Resistivities for several of the high resistance compounds were measured by both two- and four-probe techniques; both methods gave identical results. For the semiconductors, these measurements were correlated by means of the equation $\rho = \rho_0 \exp(q/kT)$ where $\rho$ is resistivity, $\rho_0$ and $k$ are constants, and $q$ is the activation energy for conduction. It can be seen that a plot of log $\rho$ *vs.* $1/T$ gives $q$ as the slope. In most cases breaks occurred in these plots, and a low-temperature $q$ and a high-temperature $q$ are reported. The $q$ values are reproducible from sample to sample within fairly narrow limits, but this is not the case, in general, for the resistivity values, since they depend on the density of the bar and grain boundary phenomena. For this reason, experimentally measured resistivities are of only relative significance.

For the purpose of this investigation, if the resistivity of a particular compound has a positive temperature dependence, it is classified simply as metallic. The above qualification on the experimental values of resistivity holds also for metallic materials, but again, the shape of the log $\rho$ *vs.* $1/T$ curve is reproducible.

Seebeck measurements were taken at temperature difference intervals $\Delta T$ of about 20 to about 100°, using an ice bath for the constant cold-junction temperature. For the Seebeck measurements, contacts to the sample, as well as the lead wires, were made of pure copper, and the thermal e.m.f. of the lead wires was considered to be +3.1 $\mu$v./deg. at room temperature. The values reported are those at room temperature and are corrected for this lead wire e.m.f.

Crystallographic parameters were determined with a Norelco diffractometer. In most cases, nickel-filtered copper K$\alpha$ radiation was used, but for several compounds manganese-filtered iron K$\alpha$ radiation was necessary.

## Results

Table I includes the materials prepared, the methods used, and the firing conditions. Although almost all of the materials have been previously prepared, we include our firing conditions because the reported procedures often had to be varied to obtain the pure spinel phase, as determined by X-ray diffraction. Also the purity of the materials previously prepared was questionable in most cases because chemical analyses were lacking. Some of the materials had impurities in concentrations high enough to be noticed by X-ray diffraction, *e.g.*, $CuCo_2S_4$ had a small amount of unknown phase.[3]

TABLE I

MINIMUM NECESSARY FIRING CONDITIONS

| Compound | Previous preparation | Method | Firing I | Firing II | Firing III |
|---|---|---|---|---|---|
| $MnCr_2S_4$ | | *a* | 24 hr., 1100° | 24 hr., 1100° | 24 hr., 600° |
| $CoCr_2S_4$ | | *a* | 24 hr., 1100° | 24 hr., 1100° | 24 hr., 600° |
| $CoCr_2S_4$ | 1 | *b* | 48 hr., 600° | 24 hr., 900° | 48 hr., 900° |
| $FeCr_2S_4$ | | *a* | 24 hr., 1100° | 24 hr., 1100° | 24 hr., 600° |
| $FeCr_2S_4$ | 1 | *b* | 12 hr., 900° | 60 hr., 900° | |
| $ZnCr_2S_4$ | 1 | *b* | 48 hr., 850° | 24 hr., 800° | 48 hr., 800° |
| $CuCr_2S_4$ | 3 | *b, c* | 48 hr., 600° | 48 hr., 600° | 48 hr., 600° |
| $CoNi_2S_4$ | | *b, c* | 24 hr., 500° | 148 hr., 500° | 24 hr., 500° |
| $NiCo_2S_4$ | 2 | *b* | 24 hr., 500° | 4 hr., 1000° | 48 hr., 500° |
| $CuCo_2S_4$ | 2 | *b, d* | 24 hr., 500° | 72 hr., 500° | 24 hr., 600° |
| $Co_3S_4$ | 2 | *b* | 24 hr., 600° | 70 hr., 700° | |
| $CuV_2S_4$ | 3 | *b, e* | 48 hr., 800° | 48 hr., 800° | 48 hr., 800° |
| $CuTi_2S_4$ | 4 | *b* | 72 hr., 350° | 48 hr., 350° | 48 hr., 1000° |

[a] Oxide + $H_2S$. [b] Metals + sulfur. [c] 2% S added, extracted after firing with $CS_2$. [d] Done under $H_2S$. [e] 5% S added, extracted after firing with $CS_2$.

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TABLE II

X-RAY DATA AND ANALYSES

| Compound | $a_0$, Å. (ours) | $a_0$, Å. (lit.) | Ref. | % S Calcd. | % S Found |
|---|---|---|---|---|---|
| $CuCo_2S_4$ | 9.461 ± 0.002 | 9.482 | 3 | 41.41 | 41.11 |
| $CuTi_2S_4$ | 9.994 ± 0.002 | 9.88 ± 0.008[a] | 5 | 44.59 | 44.28 |
| $ZnCr_2S_4$ | 9.986 ± 0.002 | 9.983 | 2 | 43.09 | 42.78 |
| $CuV_2S_4$ | 9.808 ± 0.002 | 9.824 ± 0.008[a] | 4 | 43.67 | 43.77 |
| $FeCr_2S_4$ | 9.995 ± 0.002 | 9.998 | 2 | 44.51 | 43.97 |
| $CuCr_2S_4$ | 9.814 ± 0.002 | 9.63 ± 0.006[a] | 4 | 43.36 | 43.20 |
| $CoNi_2S_4$ | 9.418 ± 0.002 | ... | ... | 42.11 | 41.88[b] |
| $NiCo_2S_4$ | 9.384 ± 0.002 | 9.392 | 3 | 42.08 | 42.21 |
| $Co_3S_4$ | 9.399 ± 0.002 | 9.416 | 3 | 42.04 | 42.12[b] |
| $MnCr_2S_4$ | 10.110 ± 0.002 | 10.129 | 2 | 44.67 | 44.36 |
| $CoCr_2S_4$ | 9 3 ± 0.002 | 9.934 | 2 | 44.04 | 43.93 |

[a] Converted kX. units. [b] Reduction to the metals necessary.

In general, when a thiochromite can be synthesized by both methods, it is slightly more crystalline, as shown by its X-ray pattern, when made by the combination of elements. However, the two methods give very similar products electrically ($FeCr_2S_4$ prepared by elements gives, in e.v., $q_{ht} = 0.03$ and $q_{lt} = 0.02$, while $FeCr_2S_4$ prepared with $H_2S$ gives $q_{ht} = 0.04$ and $q_{lt} = 0.02$).

The X-ray data and analyses are presented in Table II. Of all the compounds examined electrically, only four were found to be semiconducting and these are all thiochromites. Their electrical parameters are given in Table III. A plot of log $\rho$ (resistivity in ohm cm.) *vs.* $10^3/T$ for these materials is illustrated in Figure 1.

TABLE III

ELECTRICAL PARAMETERS

| Compounds | Room temp. resistivity, ohm cm. | $q_{ht}$, e.v. | $T_{trans}$, °K. | $q_{lt}$, e.v. | Seebeck coeff. at 25°, μv./deg. |
|---|---|---|---|---|---|
| $CoCr_2S_4$ | $5 \times 10^3$ | 0.32 ± 0.01 | 235 | 0.012 ± 0.003 | +852 |
| $MnCr_2S_4$ | $4 \times 10^9$ | 0.30 ± 0.02 | 260 | 0.091 ± 0.005 | *b* |
| $ZnCr_2S_4$ | $5 \times 10^{10}$ | 0.59 ± 0.03 | ... | *a* | *b* |
| $FeCr_2S_4$ | 20 | 0.038 ± 0.005 | 200 | 0.018 ± 0.002 | +388 |
| $CuCr_2S_4$ | $9 \times 10^{-4}$ | Metallic | | | +16.0 |
| $CuV_2S_4$ | $6 \times 10^{-4}$ | Metallic | | | +5.2 |
| $CuTi_2S_4$ | $4 \times 10^{-4}$ | Metallic | | | −11.8 |
| $CuCo_2S_4$ | $4 \times 10^{-4}$ | Metallic | | | +12.7 |
| $NiCo_2S_4$ | $8 \times 10^{-4}$ | Metallic | | | −17.7 |
| $CoNi_2S_4$ | $4 \times 10^{-4}$ | Metallic | | | −1.8 |
| $Co_3S_4$ | $3 \times 10^{-4}$ | Metallic | | | +4.8 |

[a] Even at fairly high temperatures, $ZnCr_2S_4$ has a resistivity approaching $10^{11}$ ohms. This is experimentally the limit of our measurement, and it is probably better to consider $ZnCr_2S_4$ an insulator for all practical purposes. [b] Resistances are too great to yield Seebeck voltages using our technique.

It should be noted (Table III) that the resistivity values decrease in the order $ZnCr_2S_4 > MnCr_2S_4 >> CoCr_2S_4 > FeCr_2S_4$. All of the other materials have metallic properties, *i.e.*, their resistivities increase with increasing temperature, and their Seebeck voltages are very low, as can be seen from Table III. A plot of log $\rho$ *vs.* $10^3/T$ is illustrated in Figure 2 for the metallic materials.

When a break occurs in the plot of log $\rho$ *vs.* $10^3/T$ for the semiconductor materials, it indicates that different mechanisms are operative in different regions of the curve. For $FeCr_2S_4$ and $CoCr_2S_4$, which are ferrimagnetic, the temperature at which the break occurs appears to be approximately coincident with the magnetic order–disorder transition at the Curie point. This has already been pointed out[2] for $FeCr_2S_4$, which has a $T_c$ of 195 ± 5°K. The experimental curve starts to deviate from linearity at about 190°K., after which it reaches a maximum, decreases, then increases again as temperature decreases. The electrical behavior is much more straightforward for $CoCr_2S_4$, which has a Curie temperature of 240 ± 5°K. It can be seen from our curve that a sharp break occurs at about 235°K.

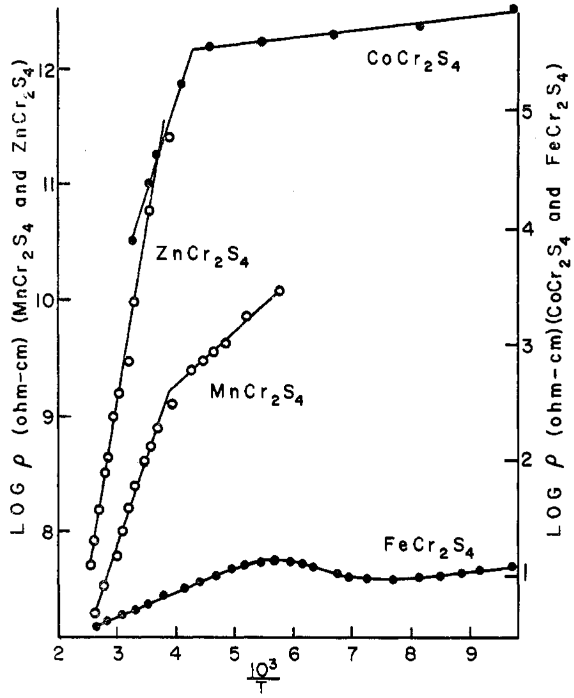

Figure 1.—Electrical resistivity measurements *vs.* temperature for semiconductors.

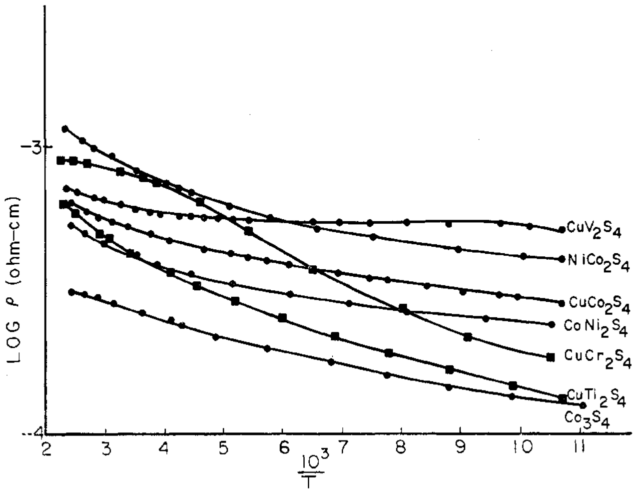

Figure 2.—Electrical resistivity measurements *vs.* temperature for metallic materials.

It can be seen from Table III that most of the Seebeck coefficients are positive. This is usually taken to mean that the material is exhibiting *p*-type behavior rather than n-type, *i.e.*, the principal carriers of electric current are holes rather than electrons. The low Seebeck voltages obtained for the metallic materials are consistent with the low resistivities measured and illustrate one of the characteristic properties of a metal.

## Discussion

It is apparent from Table III that the relative resistivities and activation energies do not show any straightforward dependence on the size of the A site cation. The magnitudes of these parameters decrease in the order $Zn^{+2} > Mn^{+2} >> Co^{+2} > Fe^{+2}$, whereas the predicted order is $Mn^{+2} > Fe^{+2} \sim Zn^{+2} > Co^{+2}$, based only on size considerations. This is an indication that the influence of the A site cation is more complicated than in the vanadium spinels mentioned earlier, where a decrease in $\rho$ and $q$ paralleled a decrease in the A site cation. These observations indicate that the transport properties of the thiochromites cannot be understood on the basis of an ionic model. Because of the high resistivity values, it seems likely that conduction probably does not occur to any significant degree through direct overlap of $Cr^{+3}$ wave functions. A simple calculation shows that the $Cr^{+3}$ ions are about 3.5 Å. apart in these materials. This is in accordance with previous considerations which placed the value of $R_c < 3.5$ Å. for chromium ions in a sulfide lattice.

In the ionic model of Lotgering for thiochromites, conduction occurs by electron "hopping" between crystallographically equivalent ions of different valencies. In stoichiometric thiochromites having only trivalent chromium ions on the B sites, carriers, *i.e.*, $Cr^{+2}$ and/or $Cr^{+4}$ ions, must be created. The measured activation energy, $q$, is the sum of the activation energies needed for the creation of carriers and moving the electrons from ions of lower charge to those of higher charge over a potential barrier due to lattice polarization. Because the energy necessary for the creation of carriers is quite high, ionic thiochromites would be insulators or semiconductors. However, this mechanism for the conductivity in these compounds fails to explain the wide variations in the $q$ values and resistivities with different A site ions.

The thiochromites can be more adequately discussed on the basis of a band model approach that has been applied to the thiospinels in general.[13]

The fact that all the metallic materials (see Table III) have the same order of magnitude for their resistivities suggests that they all may conduct by the same mechanism. It has recently been suggested by Goodenough[15] that there are two possible mechanisms for metallic conductivity in transition metal oxides: partially filled band states are formed either as a result of cation–cation d-orbital overlap or as a result of cation–anion covalence. The latter possibility is enhanced in sulfides due to the polarizability of the sulfide ion.

For the thiospinels, cation–anion covalence can occur with both octahedral and tetrahedral ions. Because the sulfide ions have four near neighbor cations, $\sigma$-bonding is much stronger than $\pi$-bonding and the partially filled band is composed of antibonding $\sigma^*$ states.[13]

In the thiocobaltites, although the small cell sizes indicate considerable covalent character, the distance between B site metals varies from 3.31 to 3.34 Å. This is almost certainly too great for any conduction to occur *via* direct overlap of metal orbitals, because $R_c$ should be less for $Co^{+3}$ than for $Cr^{+3}$. Also, since the $Co^{+3}$ ion is probably in the low-spin state,[12] it has filled $t_{2g}$ levels and any cation $t_{2g}$ sublattice would be filled. It appears that metallic conductivity in the thiospinels may be due to partially-filled band states extending throughout the lattice of the type proposed by Goodenough.[13,15]

In the compounds $CuTi_2S_4$ and $CuV_2S_4$ there is the possibility that partially filled B site $t_{2g}$ bands are also formed, since it is estimated[13] that $R \approx R_c$. Those materials containing copper may have $Cu^+$ in tetrahedral sites because of the great instability of $Cu^{+2}$ in a sulfur lattice[16] and the well-known preference of $Cu^+$ for a four-coordinated tetrahedral arrangement. The fact that all these copper compounds are cubic is also a good indication that $Cu^{+2}$ is not present, in the conventional sense, since "normal" spinels containing $Cu^{+2}$ are almost always distorted from cubic symmetry. $CuCr_2O_4$[17] and $CuRh_2O_4$,[18] for example, have $c/a = 0.91$. X-Ray evidence indicates that $CuTi_2S_4$,[5] $CuV_2S_4$,[4] and $CuCr_2S_4$[4] are all normal. It should be noted, however, that if molecular orbitals are formed between the metal ions and the anions, the $t_{2g}$ levels of the $Cu^{+2}$ ion would no longer be localized. Since these levels are responsible for any distortion produced at the $Cu^{+2}$ on tetrahedral sites, delocalizing them would remove the driving force for the distortion, and X-ray data would no longer be a useful criterion for the presence or absence of $Cu^{+2}$. Lotgering assigns the $Cu^{I}[Cr^{III}Cr^{IV}]S_4$ formula on the basis of magnetic data,[7] X-ray diffraction techniques being unable to differentiate between $Cu^{I}[B^{III}B^{IV}]S_4$ and $Cu^{II}[B^{III}B^{III}]S_4$. The lack of a distortion from cubic symmetry also favors the former formula. Further, this ionic distribution has the same metal in different valence states on crystallographically equivalent sites. Although this is a condition that is sufficient for high conductivity, semiconductor properties with a low activation (as in $Fe^{III}[Fe^{II}Fe^{III}]O_4$)[19] are anticipated, rather than metallic properties, as observed. This is because of the lattice polarization barrier mentioned earlier. Either this barrier has disappeared because $R < R_c$, which seems improbable, or the copper $t_{2g}$ electrons form a partially-filled $\sigma^*$ band, which implies $Cu^{II}[Cr^{III}Cr^{III}]S_4$.

**Acknowledgment.**—The authors wish to thank Dr. John B. Goodenough of Lincoln Laboratory of Massachusetts Institute of Technology and Dr. Herbert Flicker of Brown University for their helpful comments and criticism.

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