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J. B. Goodenough

Tetrahedral-Site Copper in Chalcogenide Spinels

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Group 83

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ABSTRACT

The ferromagnetism and metallic conductivity of the compounds $Cu[Cr_2]X_4$, where X = S, Se, or Te, have been interpreted in terms of collective "d" electrons of t_{2g} symmetry from Cu^{2+} ions and localized d electrons of t_{2g} symmetry at Cr^{3+} ions. Lotgering and van Stapele have studied the compounds $CuCrRhSe_4$, $CuCrTiS_4$, and $M_{1-x}Cu[Cr_2]Se_4$, where M = Zn, Cd, or Hg. They have asserted that their results disprove this hypothesis and strongly support the existence of Cr^{4+} ions in the presence of Cu^+ ions. It is shown that these assertions are incorrect.

Accepted for the Air Force
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TETRAHEDRAL-SITE COPPER IN CHALCOGENIDE SPINELS

Lotgering and van Stapele[1] have recently published data that they claim disprove my hypothesis[2] that tetrahedral-site copper in $Cu[Cr_2]X_4$, where X = S, Se, or Te, has collective d electrons of t_{2g} symmetry. The purpose of this note is to point out that, contrary to this assertion, all of their data are compatible with my model and that they do not establish the existence of Cr^{4+} ions in chalcogenide spinels.

I have previously pointed out that there appear to be two thermodynamic states for the outer d electrons in transition-metal compounds: a localized-electron state that is well described by crystal-field theory and a collective-electron state that is reasonably well described by a band model, provided correlations among the collective electrons can be handled.[3] Further, I have shown that the conditions for localized d electrons may break down as a result of either cation-cation interactions or cation-anion-cation interactions.[3,4] Finally, I have argued that the σ-bond cation-anion-cation interactions for tetrahedral-site "Cu^{2+}" ions in a sulfur sublattice are strong enough to break down the localized-electron state.[2] (Jahn-Teller distortions may stabilize localized electrons at octahedral-site Cu^{2+}.) This means that the copper "d" electrons of t_{2g} symmetry in $Cu[Cr_2]X_4$ should be described by a band model rather than by crystal-field theory. Since it is difficult to imagine stable Cr^{4+} ions in a chalcogenide sublattice, especially in the presence of Cu^+ ions, I concluded[2] that the metallic ferromagnetics $Cu[Cr_2]X_2$ contain collective t_{2g}^{A*} electrons at tetrahedral-site "Cu^{2+}" ions and localized t_{2g}^{B*} electrons at octahedral-site "Cr^{3+}" ions. (Superscripts A and B refer to tetrahedral-site and octahedral-site sublattices and an asterisk to the fact that the orbitals are antibonding with respect to the chalcogenide ions.) The formal charges on the ions signify one hole per molecule in the t_{2g}^{A*} band and a $^4A_{2g}$ ground state for the localized electrons at each chromium atom. The nearest-neighbor Cr^{3+}-Cr^{3+} superexchange interactions contain two components: ferromagnetic 90° cation-anion-cation interactions and antiferromagnetic cation-cation interactions.[5] The ferromagnetic interactions are enhanced by indirect interactions via the conducting t_{2g}^{A*} electrons. Whereas the indirect interactions between localized 4f electrons in a rare-earth metal via conducting s-p electrons induce a net parallel-spin polarization of the band electrons, in $Cu[Cr_2]S_4$ a net antiparallel-spin polarization is anticipated. This is because A-B superexchange in spinels having localized d electrons is always found to be negative, which means that the molecular exchange field at the collective t_{2g}^{A*} electrons from the localized t_{2g}^{B*} electrons is negative. Thus, the model envisages ferromagnetically coupled chromium atomic moments $\mu_{Cr} = 3\mu_B$ and an antiparallel spin density distributed over the copper-chalcogenide array having a net moment of $-1\,\mu_B$/molecule. (The charge density would be more localized at the copper atoms, but the spin density induced by the localized $3\,\mu_B$ at each Cr^{3+} ion would be quite spread out.) Thus, conventional neutron diffraction experiments would reveal unambiguously only the localized moments at the chromium atoms ($6\,\mu_B$/molecule), whereas magnetization measurements would give the $5\,\mu_B$/molecule that have been observed.[6]

In order to distinguish between my model and Lotgering's hypothesis[6] of strong double exchange via chromium-chromium interactions, which requires the chemical formula $Cu^+[Cr^{3+}Cr^{4+}]X_4$, Lotgering and van Stapele performed the following experiments:

1. The compounds $M^{2+}[Cr_2]Se_4$, with M = Zn, Cd, or Hg, are semiconductors. They investigated $M_{1-x}Cu_xCr_2Se_4$ compounds and found they become p-type conductors (ρ reduced by $\sim 10^4$) for $x \approx 0.002$. From this they conclude that the copper must substitute as Cu^+.

This conclusion is not justified, since the particular M atoms chosen all have filled outer d shells. This means that the compounds MCr_2Se_4 all have filled, narrow t_{2g}^{A*} bands that are separated from the broad conduction bands by a finite energy gap. Some excited Cr^{2+}-ion states lie in this gap, but they serve as relatively deep acceptor levels. However, substitution of an M^{2+} ion by a Cu^{2+} ion creates shallow t_{2g}^{A*} acceptor levels to produce a p-type conductor, as found experimentally. Robbins[7] has performed similar experiments and shown that antiferromagnetic $ZnCr_2Se_4$ becomes ferromagnetic with T_c above room temperature for $x \approx 0.02$ which demonstrates the enhancement of ferromagnetic near-neighbor interactions via indirect coupling with the conducting electrons. On the other hand, substitution of twice as much silver leaves the compound antiferromagnetic, semiconducting, and with Se vacancies. Apparently silver substitutes as Ag^+, leaving the t_{2g}^{A*} orbitals filled, and Se vacancies are formed in preference to Cr^{4+}.

2. Polycrystalline $CuCrRhSe_4$ was prepared and found to be ferromagnetic ($T_c = 255°K$) with a saturation molecular moment $\mu = 2.1_5\,\mu_B$ between 80° and 300°K. At high temperatures a Curie-Weiss law holds with $C = 1.1_5$ and $\Theta = 255°K$. From these measurements Lotgering and van Stapele conclude that this compound corresponds to $Cu^+[Cr^{4+}Rh^{3+}]Se_4$ rather than to $Cu^{2+}[Cr^{3+}Rh^{3+}]Se_4$ and that therefore they have provided strong supporting evidence for Cr^{4+} in all the chalcogenide spinels $Cu[Cr_2]X_4$.

Although we agree that the rhodium ions are diamagnetic, low-spin $Rh^{3+}(t_{2g}{}^6e_g{}^0)$ ions and that the conductivity and large T_c demonstrates against Lotgering's original double-exchange hypothesis, we disagree on the origin of the low resistivity (presumably metallic conduction in single crystals) and of the reduced molecular moment μ and Curie-Weiss constant C. They point out that a spin-only value for $Cu^+[Cr^{4+}Rh^{3+}]Se_4$ would give $\mu = 2.0\,\mu_B$ and $C = 1.0$; metallic conductivity then requires formation of a Cr^{4+}-Cr^{4+} t_{2g}^{B*} band (i.e., breakdown of electron localization via cation-cation interactions). According to my model, $Cu^{2+}[Cr^{3+}Rh^{3+}]Se_4$ contains a partially filled t_{2g}^{A*} band that gives the high conductivity and the enhanced ferromagnetic coupling between Cr^{3+} ions. Although Cr^{3+} ions alone would give a spin-only $3\,\mu_B$/mole and a $C = 1.875$, antiparallel polarization of the t_{2g}^{A*} band below T_c reduces the molecular moment toward $\mu \approx 2.0\,\mu_B$. Above T_c, each localized Cr^{3+} ion continues to polarize antiparallel the narrow-band t_{2g}^{A*} electrons in its immediate neighborhood, and this decreases C toward 1.0. Thus, the experimental results are quite compatible with my hypothesis and do not necessarily support their requirement of a stable Cr^{4+} ion. In fact, Robbins[7] has investigated the entire system $Cu[Cr_{2-y}Rh_y]Se_4$ and found ferromagnetism still persists at $y > 1.8$, suggesting long-range coupling between Cr^{3+} ions via conducting t_{2g}^{A*} electrons.

3. Polycrystalline $CuCrTiS_4$ was found to obey a Curie-Weiss law with $C = 1.97$ and $\Theta = 0°$ or 25°K for two different samples. The compound also exhibited a low (5×10^{-3} ohm-cm), temperature-independent resistivity between 80° and 300°K.

My model accepts the configuration $Cu^{+}[Cr^{3+}Ti^{4+}]S_4$, since there is no reason to argue against a Ti^{4+} ion, and the t_{2g}^{A*} band is filled. However, the Ti^{4+} ions would provide shallow acceptor levels for this band, as also would small deviations from stoichiometry, thus introducing a low resistance and an enhancement of the ferromagnetic component of the coupling. The variation from $\Theta = 0°K$ to $\Theta = 25°K$ in the two samples investigated suggests the expected sensitivity to stoichiometry.

4. The fact that NMR measurements on $CuCr_2Se_4$ can be interpreted by the assumption of a simple ferromagnet[8] is also quite compatible with my model. Copper-core polarization would be minimal if induced by collective t_{2g}^{A*} electrons having a spin density distributed out over the selenium atoms. Further, the fact that the t_{2g}^{A*} conducting electrons have an induced magnetization antiparallel to the chromium-ion spins is not to be confused with localized-electron ferrimagnetism.

More direct evidence in support of my model as opposed to the alternative model proposed by Lotgering and van Stapele comes from neutron-diffraction studies.[9,10] These indicate a localized $\mu_{Cr} = 3\,\mu_B$ and an apparent $\mu_{Cu} \approx 0\,\mu_B$, suggesting a $\mu_o = 6\,\mu_B$/molecule, whereas magnetization measurements always give a spontaneous magnetization $\mu_o \leqslant 5\,\mu_B$. This not only demonstrates the presence of Cr^{3+} ions, but strongly implies a distributed spin density not identified by neutron diffraction and corresponding to $-1\,\mu_B$/molecule.

It is concluded that the experimental data are compatible with my model for the $Cu[Cr_2]X_4$ compounds. Assertions to the contrary are based on a misunderstanding of that model. In addition, any alternative model that requires the presence of Cr^{4+} ions remains implausible.

As a final remark, it is to be emphasized that the valences used in this discussion are strictly formal. By a Cu^{2+} ion, for example, is meant two holes in the t_{2g}^{A*} orbitals, and the t_{2g}^{A*} orbitals contain considerable anionic character.

Whereas Lotgering and van Stapele assume in their new model that the copper-core d^{10} states are much more stable than the top of the valence band, my model envisages overlap of the valence and t_{2g}^{A*} bands, but the top of the bands are t_{2g}^{A*} states with primarily copper 3d character.

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