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Comment on the Magnetic Properties of Several Indium Thiospinels*

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The negative Weiss constants observed in the thiospinels In[M^{2+}In]S_4, where M = Fe, Co, and Ni, are interpreted to be due to a delocalization of the electrons of e_g symmetry that makes M^{2+}–S–S–M^{2+} interactions dominate the 90° M^{2+}–S–M^{2+} interactions. Lack of antiferromagnetic ordering above 4.2°K is attributed to the peculiar character of the B-site subarray of the spinel structure.

Schlein and Wold (*1*) report paramagnetic susceptibility data for the thiospinels MIn_2S_4, where M = Mn, Fe, Co, Ni, and the selenium-substituted thiospinels $MIn_2S_{4-x}Se_x$, where M = Mn, Fe, Ni and $0 \leqslant x \leqslant 1.0$. Each compound exhibits an apparent Curie–Weiss behavior between 4.2°K and room temperature. Although there is no evidence of long-range antiferromagnetic order, the Weiss constants for the thiospinels are $\theta = -78$, –76, –134, and –144°K, respectively, for M = Mn, Fe, Co, and Ni. The authors point out that the large, negative θ for the inverse spinel In[NiIn]S_4 is anomalous, since the 90° Ni^{2+}–S–Ni^{2+} interaction is expected to be positive, according to the rules for the sign of the superexchange interaction, and the $Ni^{2+}(t_{2g})$–$Ni^{2+}(t_{2g})$ interactions are negligible because the t_{2g} orbitals are filled. It is known (*2*) that the 90° Ni^{2+}–O–Ni^{2+} interactions are ferromagnetic in the spinel Ge(Ni_2)O_4, in accordance with the superexchange rules. In $RbNiF_3$, which has the hexagonal $BaTiO_3$ structure, the 90° Ni^{2+}–F–Ni^{2+} interactions between Ni^{2+} ions sharing a common octahedral-site face are also ferromagnetic and surprisingly large (*3*). Therefore the anomalous behavior of the thiospinels is particularly intriguing.

Unlike Ni^{2+} in fluorides and most oxides, where the 3*d* electrons are clearly localized and well described by crystal-field theory, the Ni^{2+} ions in sulfides and selenides tend to have σ-bonding 3*d* electrons that are delocalized by strong covalent mixing with the anions. Where the concentration of Ni^{2+} ions is large, as in NiS or NiS_2, the σ-bonding 3*d* electrons form bands of itinerant-electron states. However, these bands are sufficiently narrow that the electrostatic correlation energy associated with the creation of polar states ($2Ni^{2+} \rightarrow Ni^{3+} + Ni^{+}$) gives rise to a splitting of the half-filled bands, a spontaneous atomic moment and antiferromagnetic ordering at lowest temperatures. The small value of the atomic moment obtained from neutron-diffraction data, the large μ_{eff} obtained from paramagnetic-susceptibility data, and the large magnitude of the Weiss constant relative to the Néel temperature show that the spontaneous magnetism cannot be interpreted with a localized-electron model. These compounds clearly exhibit itinerant-electron antiferromagnetism.

In the compound In[NiIn]S_4, the concentration of Ni^{2+} ions is more dilute. Nevertheless, strong covalent mixing of the anion orbitals will extend the 3*d* orbitals of e_g symmetry at the Ni^{2+} ions, so that they more nearly correspond to acceptor orbitals in an extrinsic semiconductor than to localized 3*d* orbitals. Although the concentration of Ni^{2+} is large enough for the formation of an impurity band, the random distribution of Ni^{2+} ions on the B sites of the spinel lattice introduces perturbations in the potential that narrow an already narrow band, so the electrostatic correlation energy associated with polar states will split any impurity bands even more than they split the narrow σ^* bands of NiS and NiS_2. Therefore, a spontaneous atomic moment at the Ni^{2+} ions must be anticipated, and a splitting of the half-filled e_g orbitals by intra-atomic exchange makes the compound semiconducting.

The significant feature of this model, in contrast to a localized-electron model, is that the dominant magnetic interactions arise from the electron

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correlations among delocalized e_g electrons in a narrow band of pseudoparticle states that is split by electron correlations from an otherwise half-filled band. This is the condition for antiferromagnetic interactions. Therefore, even though the nearest-neighbor 90° Ni^{2+}–S–Ni^{2+} interactions may be ferromagnetic, the $Ni^{2+}(e_g)$–S–S–$Ni^{2+}(e_g)$ interactions between more distant neighbors would be dominant, as is indicated by a $\theta = -144°K$.

Another indication that the interactions between more distant neighbors may play a dominant role in $In[NiIn]S_4$ is the antiferromagnetic ordering that occurs in $Ge[Ni_2]O_4$ in spite of a $\theta > 0$ due to positive nearest-neighbor interactions (*2*).

The lack of any apparent long-range magnetic ordering above 4.2°K in $In[NiIn]S_4$ is presumably due not only to the random distribution of Ni^{2+} ions on the B sites of the spinel structure, but also to the complex competition for different antiferromagnetic orderings among the B-site ions, which sharply reduces any entropy change across a magnetic-ordering transition (*4*). The spinels $Zn[Fe_2]O_4$ and $Mg[Cr_2]O_4$ both exhibit low (below 20°K) Néel temperatures and relatively large magnitudes for $\theta < 0$.

The situation in $In[CoIn]S_4$ and $In[FeIn]S_4$ would be similar, except that the e_g electrons are somewhat more localized, especially at the Fe^{2+} ions, as a result of the larger intra-atomic exchange at the ions and of the reduced stability of the 3*d*-state manifold. This is consistent with the reduced magnitudes of θ in these compounds ($\theta = -134$ and $-76°K$, respectively). Although the magnitude of $\mu_{eff} = 4.78\mu_B$ for $In[CoIn]S_4$ indicates sufficient localization of the 3*d* electrons for spin-orbit coupling similar to that at localized 3*d* electrons, the orbital angular momentum is associated with the t_{2g} electrons, not the e_g electrons. The lack of any similar orbital contribution to μ_{eff} in $In[FeIn]S_4$, where $\mu_{eff} = 4.98\mu_B$, may be attributed to the trigonal component of the B-site crystalline field.

The situation in $MnIn_2S_4$ is quite different. The fact that MnS and MnSe appear to have localized 3*d* electrons would seem to require localized 3*d* electrons in the mixed spinel $Mn_xIn_{1-x}(In_{1+x}Mn_{1-x})S_4$. However, in this compound all interactions are expected to be antiferromagnetic, so a $\theta = -78°K$ is not anomalous. Nevertheless, failure to observe any ferrimagnetism above 4.2°K is rather surprising and seems to require the presence of short-range order in random clusters.

Since Se ions bond more covalently than S ions, this explanation of the negative values of θ in the MIn_2S_4 spinels requires an increase in the magnitude of θ upon substitution of sulfur by selenium. This requirement was satisfied in all the mixed spinels studied by Schlein and Wold (*1*).

References

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