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MAGNETIC INTERACTIONS IN CHEVREL PHASE TERNARY COMPOUNDS

by

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Prepared for
International Conference on Magnetism
Munich, Germany
September 3-7, 1979

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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

**Operated under Contract W-31-109-Eng-38 for the
U. S. DEPARTMENT OF ENERGY**

Magnetic Interactions in Chevrel Phase Ternary Compounds

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Abstract

We report detailed results of ab-initio self-consistent LMTO energy band studies of several Chevrel phase ternaries, EuMo_6S_8 and SnMo_6S_8 . In these unique calculations, all electrons of the full 15 atoms/unit cell are treated explicitly with a self-consistent Hedin-Lundqvist exchange and correlation potential in the relativistic Dirac equation but without spin-orbit coupling. As in our earlier work on the rare-earth ternary borides, the total and separate (by atom) ℓ -decomposed contributions to the density of states (which show the Eu atoms to be magnetically isolated) are used to discuss their magnetic and superconducting properties.

The discovery that the ternary compounds of the rhodium borides, MRh_4B_4 , and the Chevrel phase molybdenum chalcogenides, MMo_6S_8 (or Se_8), [where M is a rare-earth metal or Sn, Pb, Cu, Ag, etc. in the second case] exhibit (i) superconductivity and/or magnetism including (ii) the co-existence of the two and (iii) re-entrant magnetism in several important systems has generated great interest in the origin of these phenomena both experimentally and theoretically. Experiments on these systems have far outstripped theoretical understanding and have generated numerous unsolved questions.

In the case of the rare-earth ternary rhodium borides, our self-consistent LMTO energy band studies have provided a qualitative understanding of the underlying electronic structure and some of the basic phenomena observed [1]. All 18 atoms/unit cell were included and total and partial (by atom type and by orbital angular momentum) densities of states (DOS) were used to discuss qualitatively the origin of magnetism in the first part of the series (M=Gd, Tb, Dy, Ho), superconductivity in the second part (M=Er, Tm, Lu) and the re-entrant state of magnetism at low temperature in ErRh_4B_4 . These results were also used to predict [1,2] a possible mixed state in ErRh_4B_4 at temperatures above the re-entrant magnetism temperature - a state which may have been seen in the magnetization vs. magnetic field measurements of Ott, et al. [3].

The complexity of the crystal structure of the Chevrel phase ternaries have made difficult even non-self-consistent energy band studies. Instead, early studies were carried out with approximate molecular cluster - tight binding [4] and (limited basis set) localized orbital methods [5]. We here report results of ab initio self-consistent LMTO energy band studies of several of the MMo_6X_8 compounds (M=Eu and Sn) which include all electrons and all 15 atoms in the unit cell. These results, mostly in the form of total and partial (by atom type and orbital angular momentum) DOS which show the Eu atoms to be magnetically isolated, are used to interpret a number of experiments involving the magnetic interactions and superconductivity in these materials [6].

The band calculations have been performed by use of the Linear Muffin Tin Orbital (LMTO) method [7] which combines high accuracy with moderate computing costs. The scheme of calculation is essentially the same as has been used for calculations on Al₅ compounds [8] and ternary borides [1]. The full LMTO formalism was used to obtain self-consistent band structures for the first compound (SnMo_6S_8), while for the others, canonical band calculations were used in the initial stage of self-consistency to reduce

the number of required LMTO iterations. In the iterations, 10 k-points were used, while the final converged bands were determined at 35 k-points of the irreducible Brillouin-zone. The degree of convergence is about 5 mRy for states below the Fermi level.

The crystal structure data of Marezio *et al.* [9] on PbMo_6S_8 has been used in all our Chevrel phase calculations, but without distortion of the Mo-octahedron and with a rhombohedral angle of 90° . With these approximations, the structure coefficients in the LMTO calculations need only be determined once for this undistorted but characteristic Chevrel structure and can be used for all compounds independent of a uniform scaling of the lattice. Further, if one considers spherical symmetric potentials around each site, this leaves only 4 types of atoms in the structure, whereas including the distortion would make most of the 15 atoms per cell inequivalent. In this simplified structure there is one Sn site, six equivalent Mo sites, but two types of S-sites. The S atoms along the diagonal (around which the smaller Mo_6S_8 cube is tilted in the unit cell cube) have different surroundings (and potential) than the other six S atoms. The Mo_6S_8 cluster itself is close packed, but around the Sn sites and along the unit cell cube edges, there is considerable open space, so touching spheres fill only about 42 percent of the total volume. This problem is partly reduced by using many plane waves in the construction of the correction matrix to the overlapping spheres.

The potential used the Hedin-Lundqvist treatment of exchange and correlation. The charge densities from the core states as well as from partly occupied f-states were recalculated in each iteration by using the actual MT-potential. The basis set included s, p, and d states for all atoms, while in the three-centre terms in the LMTO matrices $l_{\text{max}} \leq 3$. This results in an eigenvalue problem of dimension 135×135 . The sharp structure in the total

DOS shown in Figure 1 for EuMo_6S_8 arises from the very flat nature of the energy band structure. Very similar results were also found for SnMo_6S_8 which is a superconductor. These flat bands yield high electron velocities at E_F and appear to explain the unusually high upper critical fields, H_{c2} , found in these superconductors. We see that there is considerable structure in the total DOS, particularly around E_F , which arises from the Mo-4d electrons. From a partial DOS calculation c.f., Table 1, we find that there is a high 4d DOS at E_F which is favorable for superconductivity. There is a distinct gap in the DOS just above E_F which falls in the middle of the Mo-d bands and a smaller band gap between the Mo-d and S-p states as was also inferred or seen in the earlier calculations [4,5]. As for most other high T_c compounds, the Fermi level falls just 2 electrons below the middle of the bonding-antibonding "gap" of the metal d-states. (This explains why the ternaries $\text{Mo}_2\text{Re}_4\text{S}_8$, which have 2 more electrons per cluster, are semiconductors.) Usually for Mo compounds, the d bands are occupied up to the "gap" region where the DOS is low, but in the Chevrel compounds a large charge transfer from Mo to S (about 1 electron per Mo atom) was found to occur. In agreement with experiment, the DOS per atom at the Fermi level is 50-60 percent of that for the best superconducting AlS compounds.

Since the conditions for fairly high T_c values are present for both compounds studied here, an explanation of the fact that stoichiometric EuMo_6S_8 is not superconducting cannot be found directly from the DOS, but has to take the magnetic moments of the Eu atoms into account. The coupling of the Eu 4f electrons to the conduction electrons is found to be very weak and this makes for only very weak RKKY interactions; probably the dominant magnetic interaction is the dipole-dipole interaction. There is a large charge transfer to the cluster and Eu has essentially

no occupied conduction bands; the Eu 6s band falls high above E_F . These results agree with Mössbauer measurements of Dunlap *et al.* [9][10] which show that the product of the exchange coupling and density of states, $|J N(E_F)|$, is roughly one order of magnitude smaller than that measured in binary superconductors like Eu in LaAl_2 and an isomer shift result which is typical for Eu^{2+} in an ionic compound without conduction electron contributions.

We are grateful to B. Dunlap for helpful discussions, encouragement and support and to F.Y. Fradin, D.D. Koelling, W. Pickett and G. Shenoy for helpful discussions. Work was supported by the AFOSR (grant No. 76-2948), the NSF (grant Nos. DMR 77-23776 and DMR 77-22646 and through the Northwestern University Materials Research Center, NSF grant No. 76-80847), and the DOE.

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Table 1. Partial and total density-of-states of the Fermi energy for
EuMo₆S₈ (in states per Ryd-cell).

	s	p	d	total
Eu	0.10	0.8	1.0	1.9
Mo ₆	1.0	6.0	128	135
S ₆	1.3	14.9	13.1	29.3
S ₂	0.5	6.6	2.4	9.45
total				176.

Figure Caption

Figure 1. Total DOS in units of states per cell, Ry and spin, for EuMo_6S_8 obtained from a k-space integration routine using 35 first principle points of the irreducible Brillouin zone. The DOS includes a ~ 7 mRy Gaussian broadening function. The Fermi energy falls on the peak of 0.405 Ry.