Relation between Electronic Structure and T_c in Binary and Ternary Molybdenum Chalcogenides

D. W. Bullett
Cavendish Laboratory, Madingley Road, Cambridge CB3 OHE, England

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Localized orbital calculations are presented for the electronic structure of Chevrel-phase molybdenum chalcogenides. Densities of states at the Fermi energy, $N(E_F)$, are found to depend sensitively on the modification of intercluster interactions because of lattice distortions introduced by the ternary component. Calculated $N(E_F)$ values in Mo_6S_8, $PbMo_6S_8$, Mo_6Se_8, and $PbMo_6Se_8$ are 0.5, 1.7, 1.1, and 0.9 states/(spin Mo-atom eV), respectively, and show a strong correlation with T_c. States near to E_F are strongly confined within Mo_6 octahedra.

The unusual superconducting properties[1,2] of the ternary molybdenum chalcogenides have generated considerable interest in their electronic structure. These compounds, first synthesized by Chevrel, Sergent, and Pringent,[3] have the general formula $M_m Mo_6X_{8-x}$, where X is S, Se, or Te and M may be Cu, Pb, Sn, Ag, etc., or a rare earth,[4] and they frequently occur nonstoichiometrically. They display superconducting transition temperatures as high[1] as 15 K and critical fields[2,5] up to 600 kG (for $Pb_{0.92}Mo_6S_{7.5}$). Recent experiments have detected soft vibrational modes which contribute substantially to the mass enhancement λ.[6] We report here a theoretical investigation of the electronic structure of the compounds $PbMo_6S_8$ and $PbMo_6Se_8$ together with the related binary compounds Mo_6S_8 and Mo_6Se_8. The results confirm a strong relation between T_c and the density of states at the Fermi surface $N(E_F)$, which depends rather sensitively on the small distortions caused by the addition of the third component to the lattice.

The stoichiometric structures have rhombohedral symmetry $R\bar{3}$ with the rhombohedral angle close to 90° and one formula unit per unit cell.[7] The binary compounds consist of a distorted primitive cubic network of chalcogen atoms with every eighth cube occupied by a Mo_6 octahedron. The vertices of this octahedron lie near the face centers of the chalcogen cube, which is tilted approximately 15° with respect to the rhombohedral axes. Such an arrangement leaves vacant channels running through the structure along the rhombohedral axes and it is along these channels that the Pb atoms are accommodated in the ternary compounds. An alternative way of visualizing the structure is as a distorted CsCl structure in which Pb atoms replace Cs at the origin and a cubic Mo_6X_8 cluster replaces Cl at the center. The Mo_6X_8 unit is slightly deformed from cubic symmetry and rotated 25° about a $\langle 111 \rangle$ axis.

Because of the complexity of these crystal structures (containing fourteen or fifteen atoms per unit cell), no full band-structure calculations have previously been attempted. Andersen, Klose, and Nohl[8] have presented level schemes using muffin-tin orbitals and the atomic-sphere approximation to the Korringa-Kohn-Rostoker method for Mo_6X_{14} clusters, corresponding to a basic Mo_6X_8 unit and the six nearest X atoms from neighboring clusters. Mattheiss and Fong[9] have reported a tight-binding calculation for a cubic Mo_6S_8 cluster. The interaction parameters were derived indirectly from a tight-binding fit to an augmented-plane-wave energy-band calculation for a hypothetical Mo_3S crystal in the Cu_3Au structure. Although they provide a useful discussion of a cubic Mo_6S_8 cluster, the relevance to the properties of real Chevrel-phase compounds is questionable since intercluster banding effects could not be included with any certainty.

The results presented here were obtained in a localized-orbital calculation. There were no adjustable parameters; all matrix elements in the (non-Hermitian) localized-orbital secular equation[10] were computed by direct integration of the appropriate atomic wave functions and potentials.[11] For Mo the d^5s^1 configuration was adopted and the exchange constant α in the Herman and Skillman[11] free-atom program was set equal to 0.7 throughout. The basis consisted of s and d orbitals on Mo sites, s and p chalcogen orbitals, and s and p orbitals on Pb sites (when present), giving a secular matrix of dimension 72×72 or 68×68. Interatomic interactions were neglected beyond a separation of about 8.0 a.u.; the precise range in each case was chosen so that the

TABLE I. Free-atom energy levels (in eV) used in the molecular orbital calculations.

	S	Se	Mo	Pb
E_d	⋯	⋯	−5.0	⋯
E_p	−8.0	−7.4	⋯	−4.5
E_s	−17.8	−17.4	−4.0	−10.6

TABLE II. Analysis of orbital character of molecular levels near E_F for the cubic Mo_6S_8 cluster.

State	Energy (eV)			Mo			
		s	d_{xy}	$d_{yz,zx}$	$d_{x^2-y^2}$	d_{z^2}	S_p
Γ_{25}	−2.98			0.51	0.39		0.10
$\Gamma_{25'}$	−3.05		0.70				0.26
Γ_1	−3.08	0.84				0.06	0.07
$\Gamma_{2'}$	−3.13		0.57				0.38
Γ_{12}	−3.40	0.02				0.91	0.05
Γ_{15}	−3.66			0.18		0.70	0.13
Γ_{12}	−4.49 (E_F)				0.78	0.01	0.20
Γ_{25}	−4.88			0.48	0.47		0.04
$\Gamma_{25'}$	−4.96		0.07	0.77			0.18
Γ_{15}	−5.50			0.62		0.25	0.14
Γ_1	−7.12	0.13				0.75	0.12
$\Gamma_{15'}$	−7.26			0.06			0.93
Γ_{15}	−7.46			0.03		0.04	0.93

same types of interaction were included in each structure to avoid possible spurious differences between calculations for different materials. The free-atom energy levels used in the calculations are shown in Table I.

The bars in Fig. 1 indicate the molecular levels of a single Mo_6S_8 cluster, both before and after applying the rhombohedral distortion characteristic of bulk Mo_6S_8. A more detailed analysis of the orbital content of levels near to E_F is given in Table II for the undistorted cubic case. The x, y, and z directions are the conventional cube axes and z points from a Mo site towards the cube center. In agreement with other calculations,[8,9] the spectrum separates roughly into a set of bonding levels weighted predominantly on chalcogen sites and a set of levels mainly derived from Mo d orbitals. The groups are about 3 and 4 eV wide, respectively, and their centers are separated by about 4.5 eV. Sulfur s states form a group of levels ~1 eV wide centered about 10 eV below the middle of the p band and have been omitted from the figure and from Table II.

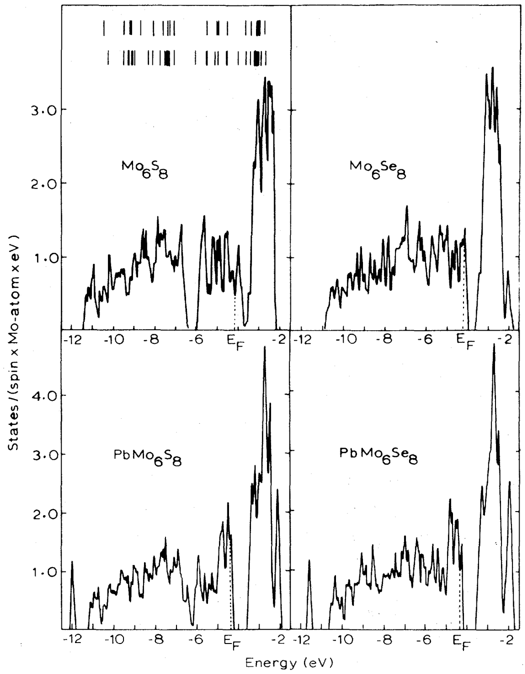

FIG. 1. Calculated electronic densities of states for Mo_6S_8, Mo_6Se_8, $PbMo_6S_8$, and $PbMo_6Se_8$. Upper and lower bars for Mo_6S_8 show the molecular energy levels of an isolated Mo_6S_8 cluster before and after applying the noncubic distortion which occurs in the solid.

The valence levels of Mo_6X_8 contain a total of 84 electrons and we find that states near the Fermi level involve primarily the nonbonding $d_{x^2-y^2}$ orbitals.[8,9] The weakness of the coupling between these and the surrounding X atoms (leading to bandwidths of ~0.3 eV in the solid) is presumably responsible for the high critical fields characteristic of these materials. The next higher levels are of primarily d_{z^2} character, nonbonding with respect to intracluster X atoms but capable of strong interaction with X atoms in adjacent Mo_6X_8 units in the solid. Higher levels tend to contain considerable d_{xy} and X_p character, as expected for antibonding Mo-X states.

In the bulk crystal the basic Mo_6X_8 units distort and rotate relative to the (approximately orthogonal) rhombohedral axes, in order to optimize the formation of intracluster Mo(d_{z^2})-X bonds at a distance very close to the intracluster Mo-X bond length. Thus we must expect substantial banding effects from the intercluster interaction. Densities of states for the measured crystal structures[7] of Mo_6S_8, Mo_6Se_8, $PbMo_6S_8$, and $PbMo_6Se_8$ were calculated by diagonalizing the secular matrix at 64 regularly spaced k points in the irreducible Brillouin zone (although to the degree of detail considered here it was found that a 28-point sampling would have sufficed).

TABLE III. Comparison between calculated $N(E_F)$ [states/(spin Mo-atom eV)] and experimental T_c (K).

	Mo_6S_8	$PbMo_6S_8$	Mo_6Se_8	$PbMo_6Se_8$
$N(E_F)$	0.5	1.7	1.1	0.9
T_c	1.6	13	6.3	3.9

Results for these four materials are shown in Fig. 1. Intercluster interactions are sufficiently strong that the only gaps in the energy spectrum occur in the middle of the *d* band, separating what we might call the nonbonding and antibonding Mo-*X* states, and, for the more electronegative element, between bonding and nonbonding Mo-S states. The Fermi level lies just below the former gap. In the binary sulfide the nonbonding-antibonding gap barely exists whereas the clear gap of 0.6 eV in $PbMo_6S_8$ demonstrates the stabilizing effect of the third component in the structure. It appears that in Mo_6S_8 there is some mismatch between the demands of the intercluster Mo-S bonds and those of the weaker intercluster S-S bonds and that this strain can be relieved by a third component. In the selenide these competing intercluster demands are somewhat better optimized; the corresponding gap in Mo_6Se_8 is 0.4 eV wide (this compound is known to form more easily than Mo_6S_8) and increases to 0.7 in $PbMo_6Se_8$.

Densities of states at the Fermi energy $N(E_F)$ are compared in Table III with experimental superconducting transition temperatures T_c. The change brought about by addition of Pb to Mo_6S_8 is particularly dramatic; $N(E_F)$ increases from 0.5 to 1.7 states/(spin Mo-atom eV), and at the same time T_c jumps from 1.6 to about 13 K. It is clear that this is not simply the result of shifting the Fermi level in a rigid-band model. We can demonstrate that the function of the lead is primarily a passive one of distorting the Mo_6S_8 structure, by computing the density of states for the hypothetical $PbMo_6S_8$ structure with Pb sites left empty. The resulting spectrum of energy levels is substantially the same as for the true Pb Chevrel phase (except for the removal of the sharp features just above and below the S *p* band, both of which arise from Pb *s* states). This is consistent with the experimental observation that a wide variety of third (and fourth) components can be incorporated into Mo_6S_8 to raise T_c; the size of the added components should be more important than their chemical nature. For the selenide the change in $N(E_F)$ is much less dramatic and it is known that the ternary elements can either increase or decrease T_c.[4]

These results show that in the Chevrel phases $N(E_F)$ and T_c depend sensitively on the modification of intercluster interactions resulting from lattice distortions introduced by the ternary component (or by changes in pressure[12]). A more detailed discussion of these distortions and their effects will be presented elsewhere. Unfortunately, the present results show little reason to suppose that in this series of compounds T_c can be increased significantly beyond the value for $PbMo_6S_8$.

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