

BAND STRUCTURE OF THE PSEUDO-ONE-DIMENSIONAL COMPOUNDS OF TYPE $TlMo_3Se_3$

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We have calculated the band structures of several pseudo-one-dimensional compounds of type $TlMo_3Se_3$. The prominent feature of the transition metal *d*-bands is a bonding-antibonding gap which, in the Mo-compounds is crossed by a broad, nearly one-dimensional, singly degenerate band winding along the chain. The Fermi surface comprises a sheet from this band plus two small three-dimensional electron pockets which stabilize the structure against Peierls and anti-ferromagnetic symmetry breakings. This is consistent with the observed superconducting properties of the Mo-compounds. The Fe-compound $TlFe_3Te_3$ is predicted to be ferromagnetic.

Several ternary Mo-chalcogenides with the chemical composition MMo_3X_3 ($M = In, Tl, Na, K, Rb, Cs; X = S, Se, Te$) have been found (Hönle et al 1980, Potel et al 1980). In contrast to the related Chevrel phases they are always found to be stoichiometric. The crystal structure of these compounds is hexagonal and the projection onto the (001) plane is shown in Fig. 1. The structure is characterized by one dimensional $(Mo_3X_3)_\infty$ chains parallel to the hexagonal *c*-axis separated by parallel chains of *M* atoms. An isolated Mo chain is shown in Fig. 1 and may be regarded as being formed from slightly distorted Mo_6 octahedra condensed across a face (Simon 1981). The Mo_6X_8 cluster is the basic building block of the Chevrel phase compounds. The shortest intra-chain Mo-Mo distance of 5.0 a.u. is very close to the value in bcc Mo metal and much smaller than the shortest Mo-Mo interchain distance of 12 a.u. The direct Mo-Mo interchain coupling is negligible and one expects the indirect coupling via two chalcogen atoms to be weak. This is consistent with the large anisotropy in the physical properties.

Armici et al (1980) found $TlMo_3Se_3$ to be superconducting with $T_c \approx 3$ K. They observed an anisotropy in the upper critical field $H_{c2}^{\parallel}/H_{c2}^{\perp} \equiv \epsilon \sim 26$, and in the resistivity $\rho_{\parallel}/\rho_{\perp} \sim 10^3 = \epsilon^2$. Measurements on other compounds have not been published.

We have used (Kelly and Andersen 1982, Nohl et al 1982) the linear muffin tin orbital (LMTO) method in the atomic sphere approximation (ASA) (Andersen 1975) to investigate the band structures of the In and Tl containing compounds. These are the only compounds for which the atomic positions are accurately known. The crystal potential was determined by the standard procedure of overlapping neutral atom charge densities and using $\alpha = 1.0$ for exchange and correlation.

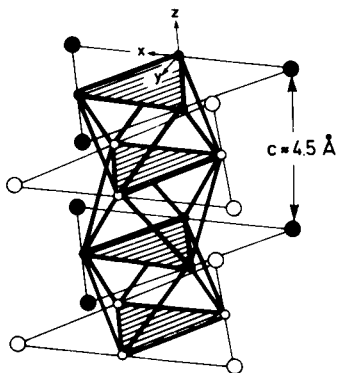
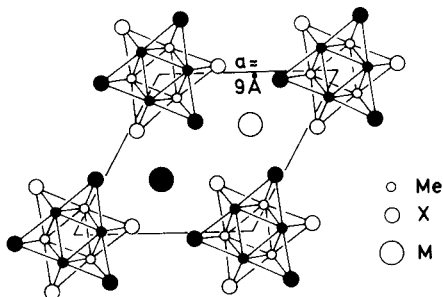


Fig.1 Hexagonal crystal structure of the MMe_3X_3 chain compounds. Black and white-coloured atoms lie in different planes separated by $c/2$ perpendicular to the *c*-axis ($=z$ -axis)

a lefthand and a righthand helix. As seen in Fig. 2a the Fermi level crosses the helix band and lies close to the top of the intrinsic d gap so that a small pocket of the doubly degenerate band there is occupied. This band has equal amounts of $3z^2-r^2$ and x^2-y^2 character and we call it an "octahedron" band because it is one of the bands derived from directed orbitals pointing towards the centre of the Mo octahedra which make up the chain.

The band calculation thus shows that the Fermi surface comprises 3 parts: an extremely one-dimensional sheet at $k_F = \pm(\pi/c-\delta)$ arising from the helix band and two small electron pockets from the octahedron band. This agrees with the magneto resistance measurements which show that there may be open orbits perpendicular to the c-axis but not along it.

The helix band sheet has a slight wobble proportional to the dispersion perpendicular to the chain. Near the Fermi energy the helix band may be parameterized by the first few terms of a Fourier series. This expression represents the computed bands very well and allows an analytical evaluation of the anisotropy parameter ϵ . For the sheet we find values of ϵ between 18 and 50. The reason for this spread comes from the sensitivity of the dispersion perpendicular to the chains ($\sim 1mRyd$) to the details of the band calculation. The density of states from the sheet at the Fermi level, N_s , is about 0.6 states / Ry. Mo at.spin. Even allowing for phonon enhancement, this value is too low in comparison with the experimental specific heat value of 3.0.

Turning our attention now to the electron pockets we find that their volume is also very sensitive to the details of the calculation. We find that the helix band at π/c and the octahedron band at A have an overlap of $\lesssim 10mRyd$. This fixes the occupancy of the pockets at $\lesssim 0.1$ electron per $TlMo_3Se_3$ unit. With the maximum overlap and corresponding occupancy the pockets would dominate the anisotropy and the density of states, such that $\epsilon \gtrsim 7$ and $N \lesssim 3.7$ states / Ry. Mo at. spin. By taking a slightly smaller overlap we can obtain agreement for both the anisotropy ($\epsilon_{exp} = 26$) and density of states ($N_{exp} = 3.0$).

There is another reason for believing that the 3-dimensional pockets in the octahedron band at A are occupied. If they were not, then the structure would be unstable against any distortion which would destroy the twofold screw axis and open up a gap at π/c . The atomic rearrangement necessary to do this need not be a simple dimerization but could be more subtle such as a relative twist of the alternating Se triangles. The band structure may also explain why the chain compounds are found to be stoichiometric. To accommodate more than 13 electrons would mean populating anti-bonding levels with high state density. This is energetically unfavourable and the system would choose a more stable structure. If there are less than 13 electrons and the Fermi level cuts only the singly degenerate band then - for an ideal one-dimensional band, at least - a distortion with wave vector $2k_F$ will always reduce the energy of the system. In this case the columns would break up as the result of the Peierls distortion and phases containing chain fragments like bioctahedra, trioctahedra, etc. would be more stable. Such phases have indeed been found.

Also antiferromagnetism could, in principle, create a gap at the Fermi level. The unenhanced susceptibility $\chi(2\pi/c)$ is dominated by the helix band and an upper bound on the size of the gap Δ may therefore be obtained if we assume that the helix band is purely one-dimensional and that $k_F = \pi/c$, i.e. that there is no overlap with the octahedron bands. With the value $I = 40mRy$ for Mo (Glötzel et al 1983, Mackintosh and Andersen 1980) we thus obtain

$$\Delta \lesssim \left[3N_s \sinh(1/I N_s) \right]^{-1} \approx 10^{-18} \text{ Ry} !$$

Of all the Mo chain compounds which have been investigated so far, only $TlMo_3Se_3$ has been found to be superconducting. We saw that the electron pockets

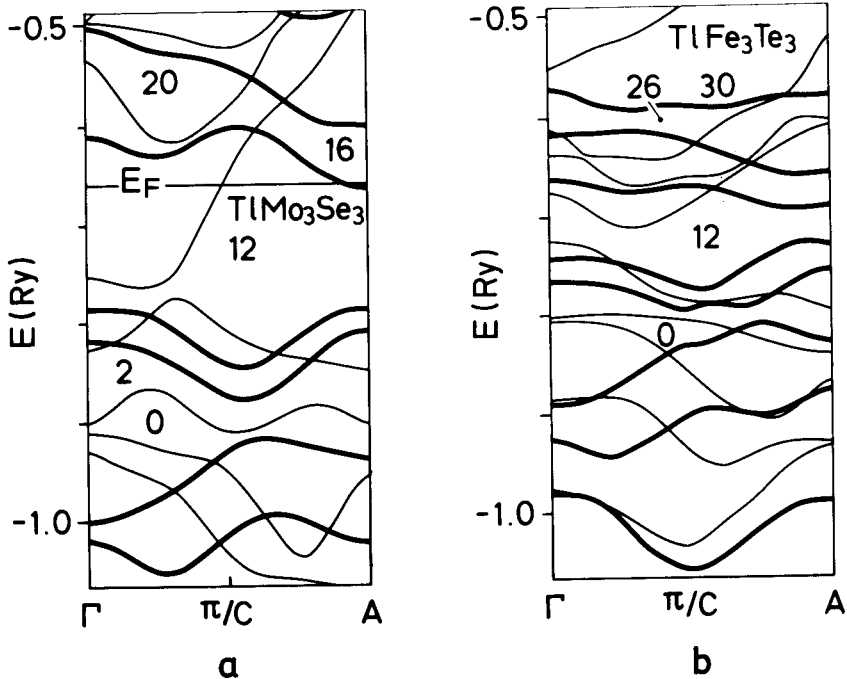


Fig. 2 a) Band structure of TlMo_3Se_3 in the double zone representation and for k along the chain. The numbers between the bands give the Mo-d electron count. Doubly degenerate and singly degenerate bands are indicated by strong and weak lines respectively. b) Band structure of TlFe_3Te_3 .

The band structure for TlMo_3Se_3 is shown in Fig. 2a for k along the direction of the chain (c -axis). The existence of a two-fold screw axis along the centre of a chain has been used to unfold the bands corresponding to a TlMo_3Se_3 unit cell. There is, in addition, a three-fold symmetry which gives rise to doubly (heavy lines) and single (light lines) degenerate representations.

The gross features of the band structure are the same as for the Chevrel phase compounds. The nine X p-like bands are centered around -1 Ry and are about 0.3 Ry wide. The fifteen Mo d-like bands are about 0.5 Ry wide and are centered around -0.7 Ry. The X p-bands are merged together with the lower part of the Mo d-like bands. The Mo sp-like bands are shifted upwards by the covalent hybridization with the X p-orbitals and lie above the Mo d-band region. Whereas the Tl 6s state forms a band at -0.9 Ry and is filled, the Tl 6p + states lie above the Mo d-states and are empty. Thus Tl is in a nominal Tl⁺ state and there are 13 electrons with which to fill the Mo d-bands. The numbers in Fig. 2a refer to this electron count. The Mo d-bands are themselves divided by a gap of 0.1 Ry at -0.7 Ry into six bonding and eight antibonding states. This gap is responsible for the stability of the chain structure. It is crossed by the remaining wide, singly degenerate band with xz character (for the definition of axes see Fig. 1). We call this band a "helix" band because it is made up of the two Bloch states which wind along the column in

which contain the superconducting electrons are very sensitive to the computational details. Our calculated band structures for the remaining Tl and In selenides and tellurides are almost identical, the differences being less than the absolute accuracy of the calculations so that no trend is found in the pocket occupancy. Noting the remark of Hönle et al (1980), that the superconductivity of $TlMo_3Se_3$ might be connected with its c/a ratio being very close to 0.5, we examined the effect of changing the c/a ratio, keeping the potential constant. We found that the occupancy of the pockets at A increased with increasing c/a ratio (going from $TlMo_3Te_3 \rightarrow InMo_3Te_3 \rightarrow TlMo_3Se_3 \rightarrow InMo_3Se_3$). At the same time the mass of the pockets decreased. Thus it is at least conceivable that there is a maximum in the pocket density of states at a value of c/a corresponding to $TlMo_3Se_3$, which favours superconductivity. While the electron pockets are occupied in the other compounds, so stabilizing them against a Peierls distortion, the density of states and T_C 's are very low. It should be possible to verify the existence of these pockets directly experimentally. If they are the reason for the superconductivity and stability of $TlMo_3Se_3$ then it should be possible to control its properties by external means e.g. by doping, applying stress etc.

The chain structure was first discovered (Klepp and Boller 1979) for $TlFe_3Te_3$. The band structure (Fig. 2b) of this compound is very similar to those considered previously when allowance is made for the fact that the Fe 3d bands are a factor of 2.5 narrower than the Mo 4d bands. However we now have 19 electrons in the d-bands so that some of the antibonding states are occupied. We find that the average density of states about the Fermi energy is sufficiently high that a ferromagnetic state with magnetic moment of $\sim 3.7 \mu_B$ /Fe atom is energetically favorable. The spin up and spin down Fermi levels ($n_{\uparrow} = 19 + 11 = 30$ and $n_{\downarrow} = 19 - 11 = 8$) then lie in regions of low state density and this accounts for the structural stability of this Fe-containing compound. For similar reasons we predict the existence of a ferromagnetic chain compound with $n_{\uparrow} = 30$ and $n_{\downarrow} = 12$, that is Co_3X_3 .

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