

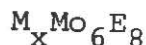
Chevrel Phases

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First synthesized [1] by Chevrel in 1971 [2], the Chevrel phases are a series of solid solution compounds characterized by the general formula



where M is a metallic element and E the chalcogenides. The fundamental structural unit is the cluster $Mo_6 E_8$ [3]. This building block has the same geometry and stoichiometry as the $M_6 X_8^{n+}$ unit in a number of early transition metal halides [4] (Figure 1).

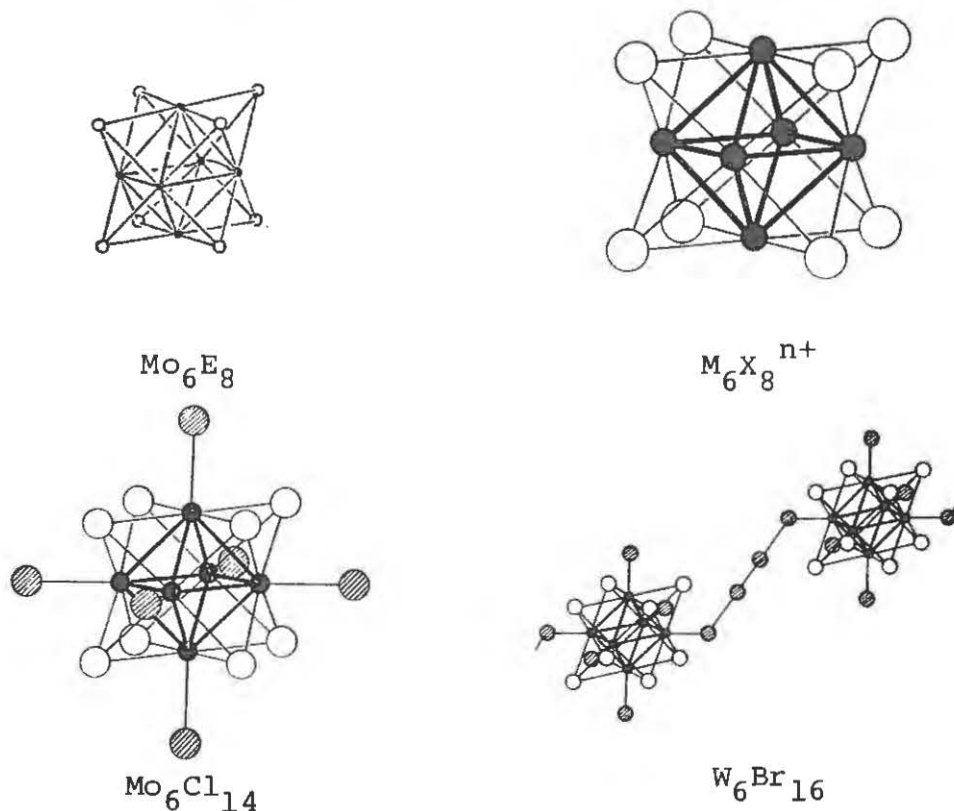


Figure 1

The halogenides can occur as discrete molecules, $MoCl_2$, or separated by additional ligands, W_6Br_{16} . However, the chalcogenides consist of $Mo_6 E_8$ clusters contacted through intercluster Mo-Mo and Mo-E interactions [3,5,6]. The compounds, $M_x Mo_6 E_8$ crystallize in a rhombohedral-hexagonal structure having a rhombohedral unit cell with $\alpha \sim 90^\circ$.

This arrangement of the $Mo_6 E_8$ units results in cavities in the chalcogenide network. These cavities are filled by the element M and consist of two types. The first, generally occupied by large elements, is located at the origin with an approximately cubic environment of chalcogenides. The second type is circularly delocalized about the origin in 12 pseudo-tetrahedral sites (Figure 2).



Figure 2

Generally, these compounds are prepared directly [2,7,8,9] from the elements at temperatures in excess of 1000°C, or from the metal chalcogenide. The binary phases, Mo_6Se_8 and Mo_6Te_8 , can be prepared by direct syntheses. The Mo_6S_8 phase has been found too thermally unstable to be prepared directly but indirect methods were found successful.

To better understand the structural and superconducting properties of these phases, a number of molecular orbital and band structure calculations have been performed [10]. There is general agreement on the overall distribution of the energy levels: there is rough separation of the chalcogen-p states and the Mo d states; an energy gap exists between 12 Mo d states from the remaining Mo d states; and the Fermi level lies within the first, narrow, set of 12 Mo d states. The states of the conduction band correspond to partially filled Mo $d_{x^2-y^2}$ orbitals.

The Chevrel phases are characterized by their unusual superconducting properties. These properties include high critical temperatures (T_c) [11], high upper magnetic field (H_{c2}) [12], and, apparently, the coexistence of magnetism and superconductivity [13]. For the Chevrel phases [14],

$$T_c = 10 f_1 f_2 \exp\left(\frac{-1.04(1+\lambda)}{1.9-0.062\lambda}\right).$$

The quantities f_1 and f_2 are correction factors and λ is the electron-phonon interaction.

The high critical fields, up to 600 kG for PbMo_6S_8 are due to the particular structural and electronic features of the phases. For a "dirty" superconductor, BCS theory gives [15],

$$H_{c2}^* \sim \frac{T_c}{\xi v_F} \sim \rho N_{BS}(0) T_c \quad \text{or} \quad \left(\frac{dH_{c2}^*}{dT}\right)_{T_c} = 4.4 \times 10^4 \rho \gamma$$

where ℓ is the mean free path, ρ is the normal state resistivity and v_F is the Fermi velocity ($= \frac{1}{\hbar} \frac{dE}{dk}$). The last expression predicts a linear relationship between $(\frac{dH}{dT})_{T_c}$ and the specific heat coefficient, γ .

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