

substance: chalcogenides of Cr, Mo, W

property: crystal structure, chemical bond, general characterization

Of the several phases in the Cr – S system only CrS and Cr₂S₃ are semiconducting; the others are metallic, but retain spontaneous atomic moments and order magnetically at low temperatures.

Above about 550 K, stoichiometric CrS has the hexagonal B8 structure of NiAs. At lower temperatures the crystal symmetry is lowered to monoclinic [57J] by a cooperative Jahn-Teller distortion of the octahedral sites, which signals the presence of a high-spin d⁴ configuration at the Cr²⁺ ions occupying these sites. The Cr²⁺-ion atomic moments order antiferromagnetically below $T_N = 450$ K [69P]. The electrical conductivity increases sharply with temperature above T_N , particularly on passing through the monoclinic – hexagonal phase transition (550 K). The compounds tend to be Cr-deficient and p-type. Since the Cr²⁺:3d⁴ configuration should have an energy in the gap between the filled S²⁻:3p⁶ bands and the empty Cr:4s band, the electrical conductivity should be due to electronic transport in the narrow, σ^* (σ -antibonding) d bands of e_g parentage. The twofold orbital degeneracy is removed by the Jahn-Teller distortion below $T_{tr} \approx 550$ K, and intraatomic-exchange correlation splits the up-spin and down-spin energies at a given ionic position. However, the high conductivity in the hexagonal phase suggests that any correlation splitting of the σ^* band is only comparable to the band width. Indeed, stoichiometric CrSe does not exhibit the cooperative Jahn-Teller distortion, and it is metallic above T_N ; it is a small-gap semiconductor only below T_N [77J]. The reported T_N and semiconductor-metal transition varies sensitively with composition from $T_N = 575$ K down to $T_N \approx 300$ K [62M]. Below T_N , the magnetic order has the peculiar "umbrella" configuration [61C]. A semiconductor-metal transition occurs at room temperature under hydrostatic pressure [77J]. The critical pressure for CrS is $p_{crit} \approx 24$ kbar, for CrSe it is $p_{crit} \approx 4$ kbar. All these data are consistent with high-spin configurations at the Cr²⁺ ions having three localized t_{2g} electrons and a single electron in orbitals of e_g parentage that are sufficiently localized in CrS to produce a cooperative Jahn-Teller distortion, but not in CrSe. Ferromagnetic CrTe is most probably metallic and mostly low-spin. The decrease in Curie temperature with increasing hydrostatic pressure indicates itinerant-electron ferromagnetism. The spontaneous ferromagnetism disappears at pressures $p > p_{crit} \approx 28$ kbar [78L].

The two polymorphs of Cr₂S₃ consist of the hexagonal B8 structure with two-thirds of the octahedral sites vacant and ordered on every other layer. The ordering in rhombohedral Cr₂S₃ makes $c = 3c_0$, where c_0 is the c axis of the B8 unit cell, and in trigonal Cr_{2+x}S₃ makes $c = 2c_0$ [57J]. Trigonal Cr_{2+x}S₃ is metallic [73B]. Rhombohedral Cr₂S₃ contains localized ⁴A_{2g} (t_{2g}³) d-electron configurations at each octahedral Cr³⁺ ion, and below a ferrimagnetic Curie temperature $T_C (= 120$ K) the spontaneous magnetization has a maximum at about 85 K, indicative of a noncollinear spin configuration at lowest temperatures. The n-type resistivity exhibits a maximum at T_C due to spin-disorder scattering and a broad maximum at 85 K. Lack of any significant field dependence of the Hall coefficient both above and below T_C indicates that it represents a normal Hall effect. The transverse magnetoresistance $\Delta\rho/\rho_0$, where $\Delta\rho$ is the change in resistivity with applied magnetic field relative to its value ρ_0 in zero applied field, has the form $-\Delta\rho/\rho_0 = \text{const} \cdot H^p$ with $1 < p \leq 2$ for $T \geq T_C$ and $0 < p < 1$ for $T < T_C$; the negative magnetoresistance exhibits a dramatic maximum between 85 K and $T_C = 120$ K which may be attributed to spin-flip scattering. A maximum in μ_H at 85 K, where the spontaneous magnetism – and hence the spin splitting of the conduction band – has a maximum is also consistent with this interpretation.

Rhombohedral Cr₂Se₃ has been prepared at 3 kbar and at atmospheric pressure [67I, 73Y]. The former sample was an n-type semiconductor with a thermal energy gap at ≈ 300 K of 0.05 eV. The sample prepared at atmospheric pressure was metallic, but exhibited an apparent transition between two metallic states in the interval $70 < T < 225$ K. Trigonal Cr_{2.04}Se₃ prepared at atmospheric pressure was reported to be semiconducting with a thermal energy gap of 0.15 eV [73B]. The magnetic data are consistent with a localized Cr³⁺:d³ configuration, which should have its energy below the top of the Se²⁻:4p⁶ valence band.

Whereas Cr₃S₄ is reported to be metallic, isostructural Cr₃Se₄ is reported to be semiconducting. Semiconducting behaviour for this mixed-valent compound requires an ordering of Cr²⁺ in the half-occupied cation basal planes and Cr³⁺ in the totally occupied cation basal planes.

MoS₂ is found in the 2H and 3R polytypes. The valence band consists of overlapping S:3p⁶ and Mo:d_{z²} bands where the z axis is the crystallographic c axis; the conduction bands are the Mo:d_{xy}⁰d_{x²-y²}⁰, and $\sigma_{\perp}/\sigma_{\parallel} \approx 200$. MoSe₂ is analogous. MoTe_{2-x}, on the other hand, exhibits a semiconductor-metal transition at $T_{tr} = 820...880^\circ\text{C}$ going from the 2H (α -phase) to a distorted 1T (β -phase) polytype with increasing temperature [70V]. The

distortion consists of Mo-atom antiferroelectric displacements parallel to the c axis [66B]. The 1T polytype can be quenched to room temperature; this metastable phase is stable to nearly 750 K.

$\text{Mo}_{2.06}\text{S}_3$ exhibits two phase transitions, which makes its physical properties complex [70D]. The 3R and 2H polytypes of WS_2 and WSe_2 are similar to the molybdenum analogues. Orthorhombic WTe_2 is a layer structure differing from the 1T polytype by (1) hc stacking rather than hh stacking of the anion layers and (2) W displacement within the layers giving rise to zig-zag W chains having W – W separations of 2.861 Å [66B]. These displacements are not strong enough to split the 5d bands, so the compound is semimetallic with a band overlap of 0.05 eV and a conduction-band edge 0.075 eV above a broad Te:5p^6 band [66K, 72A].

References:

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