

substance: chalcogenides of Mn, Tc, Re

property: crystal structure, physical properties, general characterization

Cubic α -MnS appears to be stable above room temperature. The β - and γ -phases can be prepared at low temperatures, but they transform to the α -phase above 200°C [67S]. The α -phase is retained at all temperatures. Photoelectron spectroscopy has confirmed a $\text{Mn}^{2+}:\text{3d}^5$ valence band [78H], but holes in this band have a mobility that is not activated [78H] even though the manganese atoms carry a localized, high-spin atomic moment [56C]. Reversal of the sign of the Hall effect with temperature, Fig. 1, is attributed to a much larger electron mobility in the $\text{Mn}:\text{4s}$ conduction band than hole mobility in the valence band, (some authors assign the charge-transfer optical absorption edge to $\text{Mn}:\text{3d}^6$ rather than $\text{Mn}:\text{3d}^5\text{4s}^1$). The properties of α -MnSe are similar. MnTe, on the other hand, has the B8 structure with the top of the $\text{Te}:\text{5p}^6$ band above the $\text{Mn}^{2+}:\text{3d}^5$ band [77A], and lattice hole mobilities are about $50 \text{ cm}^2/\text{V s}$. However, drift mobilities are lowered markedly as the temperature is raised through $T_N = 310 \text{ K}$ because of a large magnon-drag contribution [64W]. This magnon-drag contribution increases the Seebeck coefficient and the resistivity as shown in Fig. 2.

Antiferromagnetic MnS_2 has the pyrite structure with dimeric anions [59H]; the σ -antibonding S – S orbitals of a dimer are empty with energies above the top of the cationic conduction band. As in MnS, photoelectron spectroscopy [59H] indicates that the valence band is the high-spin $\text{Mn}^{2+}:\text{3d}^5$ band responsible for the localized atomic moments, which order below $T_N = 48.2 \text{ K}$ [68L]. The magnetic susceptibility data suggest that holes in the $\text{Mn}^{2+}:\text{3d}^5$ valence band have non-activated mobilities, as was found for α -MnS [78H]. The transport data for isostructural MnTe_2 show evidence of a magnon drag, which should be even more pronounced in MnS_2 [79A].

The technetium and rhenium disulfides, diselenides and ditellurides are layered compounds having distorted CdCl_2 structures [71W] as a result of a metal-metal bonding that changes the translational symmetry so as to split the d bands into a filled valence band and empty conduction bands.

References:

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Fig. 1.

α -MnS. Hall coefficient vs. reciprocal temperature for a sintered bar [78H].

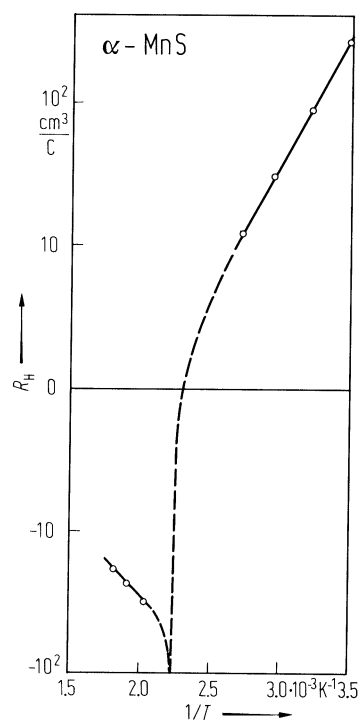


Fig. 2.

MnTe. Thermoelectric power (a) and resistivity perpendicular to the c axis (b) vs. temperature for a degenerate p-type sample [64W].

