

substance: chalcogenides of Ni, Pd, Pt

property: crystal structure, chemical bond, general characterization

The millerite forms of NiS and NiSe are metallic. However, the high-temperature B8 phase of NiS may be stabilized to low temperatures by rapid quenching to room temperature [63S, 70T] or by direct synthesis [35L]. This phase is metallic with temperature-independent (Pauli) paramagnetism for $T > T_N = 265$ K [68S]. The Ni_{1-x}S phase is stable only over a narrow range of x ; and T_N decreases with increasing x , vanishing near $x \approx 0.03$. The magnetic transition is characterized by a first-order dilatation of the structure, and the magnetically ordered state is suppressed by the application of hydrostatic pressure. The resistivity changes by more than one order of magnitude at T_N and the Hall coefficient changes by over two orders of magnitude. The magnetic moment of the nickel ions decreases sensitively with decreasing lattice parameter, and hence with x , changing from $1.5 \mu_B$ at $T = 0$ K for $x = 0$ to $1.0 \mu_B$ for $x = 0.03$ [74C]. Below the transition the half-filled bands of e_g parentage at the octahedral-site Ni^{2+} ions are split in two by strong correlations, but it is not clear whether the correlation splitting is large enough to create a semiconducting state; the low-temperature phase is semimetallic [72M].

Single-crystal NiS_2 with pyrite structure has been prepared by chlorine transport of powder samples obtained at 600°C in sealed tubes [68B1] and by direct synthesis from elemental nickel and sulfur at 65 kbar [68B2]. Samples prepared at high pressure were sulfur-rich. It appears that the sulfur-rich samples with smaller lattice parameter can be distinguished from the nickel-rich samples. This conclusion is reinforced by their magnetic and electric properties [68B1, 73G]. The sulfur-rich samples are good conductors with low activation energy. The nickel-rich samples exhibit a larger activation energy and hence a much smaller conductivity at low temperatures [68B1]. Measurements of conductivity vs. pressure reveal a semiconductor-metal transition near 30 kbar at room temperature; the magnitude of $\Delta\rho$ across the transition decreases with increasing temperature and with increasing S/Ni ratio x . The semiconductor-metal phase boundary represents a maximum in the resistivity as a function of temperature for a fixed pressure. It can be seen that the magnetic susceptibility has a maximum at the same temperature in the sulfur-rich compounds. The nickel-rich compounds, on the other hand, exhibit no such maximum in the resistivity; they are semiconductors at all temperatures, and extrapolation of the temperature-dependent optical band gap of $\text{NiS}_{1.99}$, the gap would vanish at 650°C , a temperature above the onset of decomposition at about 400°C . Moreover, the nickel-rich compounds are antiferromagnetic with a Néel temperature $50 < T_N < 70$ K below which the nickel atomic moments order. Below $T_C \approx 30$ K, the more complex magnetic order is found; it has a weak ferromagnetic component that decreases with increasing sulfur content. The proposed density-of-states model for nickel-rich $\text{NiS}_{1.99}$ contains a correlation splitting of half-filled 3d bands of e_g parentage at the nickel ions with impurity states presumably associated with anion vacancies.

The semiconducting PdX and PtX compounds with $X = \text{S}$ or Se contain low-spin Pd(II) or Pt(II) in square-coplanar coordination. The tetragonal B17 structure of PtS may be derived from the hexagonal NiAs structure by diffusionless displacement of the atoms [57J]; the tetragonal B34 structure of PdS is more complex. In these compounds, the conduction bands are derived from the σ -bonding $d_{x^2-y^2}$ orbitals of the metal atoms; the valence bands are derived from the anionic p^6 configurations. The semiconducting PdX_2 compounds, $X = \text{S}$ or Se , similarly contain low-spin Pd(II) in square-coplanar coordination; the orthorhombic Pbca structure can be derived by diffusionless displacements of the atoms from the cubic pyrite structure [65H]. The conduction and valence bands are similar to those in PdX and PtX compounds, the antibonding σ^* orbitals of a polyanion pair lying above the conduction-band edge. The $\text{Pt}_{1-x}\text{S}_2$ and PtSe_2 compounds, on the other hand, contain low-spin Pt(IV) in octahedral coordination, and the anions are monomeric. This makes the parentage of the conduction bands the metal d orbitals of e_g symmetry.

References:

- 35L Levi, G. R., Baroni, A.: Z. Kristallogr. 92 (1935) 210.
- 57J Jellinek, F.: Acta Crystallogr. 10 (1957) 620.
- 63S Sparks, J. T., Komoto, T.: J. Appl. Phys. 34 (1963) 1191.
- 65H Haase, D. J., Steinfink, H., Weiss, E. J.: Rare Earth Research 3 (1965) 335; New York: Gordon and Breach, 1965.
- 68B1 Bouchard, R. J.: J. Cryst. Growth 2 (1968) 40.
- 68B2 Bither, T. A., Bouchard, R. J., Cloud, W. H., Donohue, P. C., Siemons, W. J.: Inorg. Chem. 7 (1968) 2208.
- 68S Sparks, J. T., Komoto, T.: J. Appl. Phys. 39 (1968) 715.
- 70T Trahan, J., Goodrich, R. G., Watkins, S. F.: Phys. Rev. B2 (1970) 2859.
- 72M McWhan, D. B., Marezio, M., Remeika, J. P., Dernier, P. D.: Phys. Rev. B5 (1972) 2552.
- 73G Gautier, F., Krill, G., Lapierre, M. F., Robert, C.: J. Phys. C 6 (1973), L320.
- 74C Coey, J. M. D., Brusetti, R., Kallel, A., Schweizer, J., Fuess, H.: Phys. Rev. Lett. 32 (1974) 1257.