

**substance: chalcogenides of V, Nb, Ta**

**property: crystal structure, chemical bond, general characterization**

Of the known binary vanadium chalcogenides, all are metallic with the probable exception of diamagnetic VS<sub>4</sub>, which contains only dimeric anions and V – V pairing (2.83 vs. 3.22 Å) along the monoclinic *c*-axis [65H]. NbS<sub>3</sub> crystallizes in a structure similar to the ZrSe<sub>3</sub> structure, but distorted by the formation of *c*-axis Nb – Nb dimers [78R]; TaS<sub>3</sub> has an analogous structure. With formal valences Nb<sup>4+</sup> and Ta<sup>4+</sup>, the compounds are semiconducting because there are two crystallographically distinguishable cations within a chain, which splits the occupied d band in two. On the other hand, NbSe<sub>3</sub>, which is isostructural with NbS<sub>3</sub>, remains metallic at all temperatures although exhibiting phase transitions at 142 K and 58 K due to the formation of incommensurate charge-density waves in the linear chains. A conductivity strongly non-linear with temperature below these transition temperatures appears to reflect a contribution from sliding charge-density waves [77T, 75F, 80F].

TaS<sub>2</sub>, like several other dichalcogenides, crystallizes in a variety of polytypes [69H]. Each consists of different stackings of X – M – X layers. Both octahedral and trigonal-prismatic coordination of the metal ions are found, and metallic behaviour is more common with trigonal-prismatic coordination. Of the several TaS<sub>2</sub> phases (1T, 2H, 3R and 4H), only 1T-TaS<sub>2</sub> (CdI<sub>2</sub> structure) becomes semiconducting at low temperatures, ( $T < T_d \approx 350$  K). The 1T-TaS<sub>2</sub> phase is stable at high temperatures, but it can be retained at low temperatures by quenching from above 1050 K. Three low-temperature phases are identified [74W, 75S, 76W2]: 1T<sub>1</sub> stable in the interval  $T_d \approx 350\text{K} < T \leq 450$  K, (a transformation to the 2H structure is reported at about 450 K) contains incommensurate periodic distortions ( $\mathbf{q} = 0.283 \mathbf{a}^*$ ) arising from softened LA modes (ICDW = incommensurate charge-density wave) and partially softened phonons in selected TA<sub>||</sub> modes; 1T<sub>2</sub> stable in the interval  $T_d = 190 \text{ K} < T < T_d'$ , with the ICDW having its  $\mathbf{q}$  rotated through the transition by about 11.5° and continuing to rotate with decreasing temperature towards its commensurate position  $\mathbf{q} = 0.231 \mathbf{a}^* + 0.077 \mathbf{c}^*$  in the low-temperature phase 1T<sub>3</sub> stable below  $T_d$ . The commensurate charge-density wave (CCDW) has a superlattice edge  $13^{1/2}a$  in the basal plane and a repeat every 13 layers in the *c*-direction [80S]. At lowest temperatures, the CCDW amplitude, as measured by X-ray photoelectron spectroscopy, approaches one electron per atom, and the atomic displacements at room temperature are as large as 0.25 Å [76W1]. Band-structure calculations [73M, 77W] are consistent with the opening of a band gap at the Fermi surface due to CDW formation. Although 1T-TaSe<sub>2</sub> shows analogous structural changes at low temperature [75W], it remains metallic. The ICDW sets in below the onset temperature  $T_0 \approx 600$  K, and the first-order CCDW to ICDW transition occurs at  $T_d = 473$  K. Calculation of the Fermi surface is consistent with a CCDW having the measured  $\mathbf{q} = 0.28 \mathbf{a}^* + \mathbf{c}^*/3$ , where  $\mathbf{a}^*$  and  $\mathbf{c}^*$  are the reciprocal-lattice vectors.

## References:

- 65H Haase, D. J., Steinfink, H., Weiss, E. J.: Rare Earth Research 3 (1965) 335; New York: Gordon and Breach, 1965.
- 69H Huisman, R., Jellinek, F.: J. Less-Common Met. 17 (1969) 111.
- 73M Mattheis, L. F.: Phys. Rev. B8 (1973) 3719.
- 74W Williams, P. M., Parry, G. S., Scruby, C. B.: Philos. Mag. 29 (1974) 695.
- 75F Furuseth, S., Brattas, L., Kjekshus, A.: Acta Chem. Scand. 29A (1975) 623.
- 75S Scruby, C. B., Williams, P. M., Parry, G. S.: Philos. Mag. 31 (1975) 255.
- 75W Wilson, J. A., Di Salvo, F. J., Mahajan, S.: Adv. Phys. 24 (1975) 117.
- 76W1 Wertheim, G. K., Di Salvo, F. J., Chiang, S.: Phys. Rev. B13 (1976) 5476.
- 76W2 Williams, P. M. in "Crystallography and Crystal Chemistry of Materials with Layered Structures", F. Levy (ed.) Dordrecht: Reidel, 1976, 51.
- 77T Tsutsumi, K., Takazaki, T., Yamamoto, M., Shiozaki, Y., Ido, M., Sambongi, T., Yamaya, K., Abe, Y.: Phys. Rev. Lett. 39 (1977) 1675.
- 77W Woolley, A. M., Wexler, G.: J. Phys. C 10 (1977) 2601.
- 78R Rijnsdorp, J., Jellinek, F.: J. Solid State Chem. 25 (1978) 325.
- 80F Fung, K. K., Steeds, J. W.: Phys. Rev. Lett. 45 (1980) 1696.
- 80S Sezermann, O., Simpson, A. M., Jericho, M. H.: Solid State Commun. 36 (1980) 737.