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Electronic Structure and Properties of NbS_3 and Nb_3S_4

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Electronic structure calculations for NbS_3 and Nb_3S_4 are reported. The NbS_3 structure is closely related to that of $ZrSe_3$. In the undistorted $ZrSe_3$ atomic arrangement, NbS_3 would be a metal; it is shown that the observed distortion, a pairing of Nb atoms along the *b*-axis relative to $ZrSe_3$, stabilizes the NbS_3 crystal by inducing a 0.5-eV semiconducting gap. Nb_3S_4 is found to be a metal with the Fermi level lying near a deep minimum in the density of electron states.

Introduction

This paper presents the continuation of a study (*1*, *2*) of transition metal trichalcogenides MX_3 (*M*: Ti, Zr, Hf, Nb, Ta; *X*: S, Se, Te). The structural feature characteristic of this class of compounds is the bicapped trigonal prismatic coordination of chalcogens around each metal atom. Successive trigonal prisms share their triangular faces, leading to infinite chains along the *b*-axis. Chalcogens on neighboring chains cap two of the rectangular faces of each prism to provide a weak bonding between chains. Two of the chalcogen atoms in the base of each trigonal prism are closely bonded.

However, transport properties within this family vary widely. In Refs. (*1*) and (*2*) it was shown that apparently small differences in the arrangement of the prismatic chains in different selenides lead to radically different energy bands which account for the observed properties. In particular, $ZrSe_3$ was shown to be a semiconductor with a gap of 1.5 eV between occupied and unoccupied states, whereas $NbSe_3$ and $TaSe_3$ were predicted to be highly anisotropic metals. Additionally, the charge-density wave transitions which have been observed experimentally in $NbSe_3$ (*3–6*) were revealed as a consequence of the pseudo-one-dimensional Fermi surface; no such one-dimensional behavior occurs in the $TaSe_3$ energy bands (*2*) and no charge-density waves have been observed in this compound.

Crystal Structure of NbS_3

The crystal structure of NbS_3 has been fully determined very recently by Rijnsdorp and Jellinek (*7*), following preliminary studies by Kadijk and Jellinek (*8*), and by Grigoryan and Novoselova (*9*). The unit cell is similar to that of $ZrSe_3$ (*10*), but with a doubling of the *b*-axis (Fig. 1). The main deviation from a $ZrSe_3$-type structure is a displacement of the metal atoms by 0.16 Å from the centers of the coordination polyhedra to form Nb–Nb pairs along the *b*-axis. Without this distortion, it is clear from our investigation of $ZrSe_3$ (*2*) that NbS_3 would be metallic. The extra electrons introduced by changing from a group IV to a group V transition element would have to be

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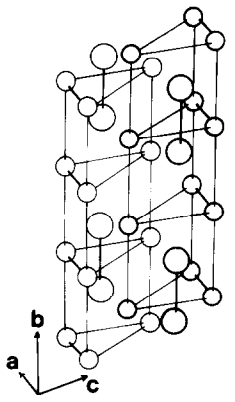

FIG. 1. Schematic picture of the NbS_3 structure. Eight S atoms (small circles) form a bicapped trigonal prism around Nb atoms (large circles). Metal–metal bonds occur parallel to the *b*-axis.

accommodated in the conduction band. In fact NbS_3 forms as black needles and displays the properties of a diamagnetic semiconductor (*7–9*). It is interesting to see how the pairing of Nb atoms leads to these effects in an electronic structure calculation.

Electronic Structure of NbS_3

The computational method was the same as that of Refs. (*1*) and (*2*). Electron states were calculated by an atomic orbital method, using a basis of chalcogen *s*- and *p*-orbitals and *s*-, *p*-, and *d*-orbitals on the metal atoms. The dimension of the secular matrix was then (84×84). There are no empirical parameters in the method. The two-centered matrix elements between undistorted atomic orbitals were evaluated explicitly in a crystal potential obtained from overlapping atomic charge densities. All three-centered effects were neglected. The same method has been very successful in describing the properties of the layered dichalcogenides (*11*).

The energy levels calculated for the isolated S and Nb atoms are shown in Table I. The position of the *d*-level of a transition element atom depends quite sensitively on the configuration of the other electrons; the *d*-occupation adopted here for the Nb atom was found to be consistent with the *d*-component of the ground state charge density in the dichalcogenide calculations (*11*).

TABLE I

ENERGY LEVELS OF ISOLATED ATOMS (eV)

	Nb ($s^{0.7}p^{0.5}d^{3.8}$)	S (s^2p^4)
s	−5.3	−17.8
p	−3.0	−8.0
d	−4.4	

The resulting density of states as a function of energy for electrons in NbS_3 is displayed in Fig. 2. Many features are reminiscent of $ZrSe_3$ (*2*). In each case the energy spectrum separates broadly into three parts, which we may loosely label (in order of decreasing binding energy) as chalcogen *s*-, chalcogen *p*-, and metal *d*-bands, respectively. These labels denote only the major component of the eigenstates in a particular band. The bonding in these compounds is provided by strong hybridization between *p*- and *d*-states, and the statement that most "*p*-states" are filled while all "*d*-states" are empty does not imply that there is a large transfer of electrons from transition metal atoms to chalcogens.

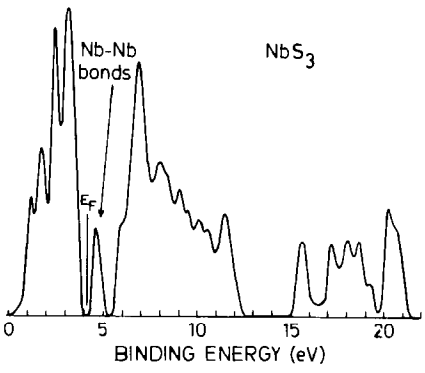

FIG. 2. Valence band density of states of NbS_3 (smoothed by a Gaussian of half-width $\sigma = 0.15$ eV).

The s-bands in $ZrSe_3$ form three subbands as a consequence of the bonding and antibonding levels of the two closely spaced Se atoms being pushed below and above the s-level of the third Se atom in the triangular base of each prism. A similar effect may be seen in the s-bands of NbS_3, though in this case, because of the lower crystal symmetry the division is less marked and the nonbonding and antibonding bands overlap.

The semiconducting gap of 1.5 eV in the calculated spectrum of $ZrSe_3$ occurs after eight "p-bands" per formula unit have been doubly occupied. The experimentally observed gap is 1.8 eV (*12*). This gap comes after eight and not nine bands because the ninth p-band would be the antibonding component of the closely bonded Se–Se pairs and lies up in the conduction band. It is in this semiconducting gap that the main distinction between the $ZrSe_3$ and NbS_3 densities of states can be seen. Nb–Nb pairing along the b-axis pulls one "metal d-band" down by splitting one of the conduction bands into bonding and antibonding subbands. Occupation of the lower subband stabilizes the structure at a Nb–Nb spacing of 3.04 Å. The nearest-neighbor interaction between d_{z^2}-orbitals (where z is the direction of the b-axis) is then −0.8 eV. The result is an energy gap of 0.5 eV above the highest occupied band. Thus the electronic structure investigation accounts naturally for the semiconducting properties and black needle-like appearance of NbS_3 crystals.

Nb_3S_4

For completeness, the electronic structure resulting from a similar investigation of Nb_3S_4 is also presented here. Nb_3S_4 may be prepared in needle-shaped crystals from the elements at 1000–1300°C, using iodine as a carrier in a vapor transport reaction (*13*). The crystal lattice is hexagonal (space group $P6_3/m$) and the atomic arrangement is isotypic with Nb_3S_4 and Nb_3Te_4 (*14*). The structure (Fig. 3) is built up from NbS_6 octahedra, linked by shared faces and edges. There are some similarities to the NbS_3 structure: each metal atom is displaced from the center of the coordinating octahedron toward one of the faces, so that zigzag Nb–Nb–Nb chains are formed running along the c-direction (which is also the needle axis). The Nb–Nb distances within these chains are again comparable to those in metallic Nb. There are no close S–S approaches.

The resulting electronic density of states of Nb_3S_4 is displayed in Fig. 4. The interpretation of bands is less simple because the geometrical structure is much more complicated than that of the trisulfide. There are two types of S environment in the unit cell: two S(1) sites each surrounded by six Nb neighbors in a trigonal prism, and six S(2) sites with very asymmetric surroundings formed by four Nb atoms. Sulfur s-states form a peak at −19 eV. Nb–S bonding states, or "p-bands," form the broad band of states at energies between −6 and −12 eV; the corresponding Nb–S antibonding states lie unoccupied at higher energies of −1 to −3.5 eV. The remaining d-orbital contributions may be loosely classified as nonbonding with respect to the octahedral directions of the coordinating S atoms, and form states of very complicated hybridization between the bonding and antibonding peaks. In parti-

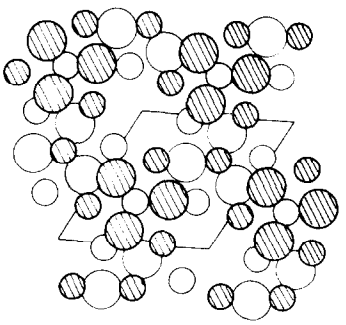

FIG. 3. The crystal structure of Nb_3S_4, projected along the c-axis. Nb atoms are denoted by large circles, S by small circles. Atoms at $z = \frac{3}{4}$ are hatched, and those at $z = \frac{1}{4}$ are open. The unit cell is outlined.

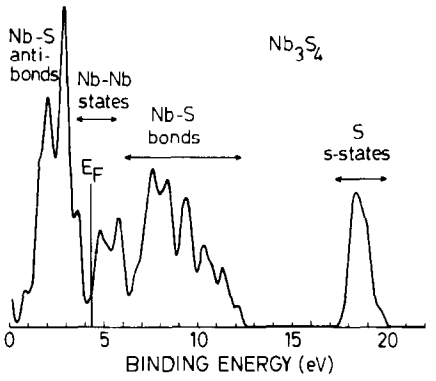

FIG. 4. Valence band density of states of Nb_3S_4.

cular, the close approaches of Nb atoms along zigzag chains parallel to the c-axis lead to three quasi-one-dimensional bands each of width ~1.5 eV in which the charge density is almost entirely located on the Nb atoms. The conduction electron number is sufficient to fill only one-third of this group of bands. Thus Nb_3S_4 has metallic properties rather akin to those of $NbSe_3$ (*2*).

We note how both the $NbSe_3$ and Nb_3S_4 structures are stabilized by adopting an atomic configuration in which the Fermi level E_F lies close to a deep minimum in the density of states. Indeed, the room temperature resistivities of Nb_3S_4 (*13*) and $NbSe_3$ (*4*) are quite similar ($\sim 10^{-4}$ ohm·cm).

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