

The Crystal Structure of Niobium Trisulfide, NbS₃

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The crystal structure of NbS₃ was determined from single-crystal diffractometer data obtained with MoK α radiation. The compound is triclinic, space group $P\bar{1}$, with: $a = 4.963(2)$ Å; $b = 6.730(2)$ Å; $c = 9.144(4)$ Å; $\alpha = 90^\circ$; $\beta = 97.17(1)^\circ$; $\gamma = 90^\circ$. The structure is closely related to the ZrSe₃ structure type; it shows that the compound can be formulated as Nb⁴⁺(S₂)²⁻S²⁻, in agreement with XPS spectra. The main difference with ZrSe₃ is that the Nb atoms are shifted from the mirror planes of the surrounding bicapped trigonal prisms of sulfur atoms to form Nb-Nb pairs (Nb-Nb = 3.04 Å); this causes a doubling of the b axis relative to ZrSe₃, and a decrease of the symmetry to triclinic.

Introduction

The compound NbS₃ is a diamagnetic semiconductor (1, 2). Kadijk and Jellinek (1) undertook a preliminary study of the structure of NbS₃; they found a unit cell similar to that of ZrSe₃ (3), but with a doubling of the b axis. On analogy with ZrSe₃, it was assumed that NbS₃ could be formulated as Nb⁴⁺(S₂)²⁻S²⁻, containing both disulfide groups (S₂)²⁻ and isolated sulfide ions S²⁻. The physical properties were explained by assuming the presence of Nb-Nb pairs, which would also cause the doubling of the b axis.

Our XPS study of NbS₃ (4) indeed indicates the presence of both disulfide ions (S₂)²⁻ and isolated sulfide ions S²⁻, just as had been found for ZrS₃ and ZrSe₃ (5). The XPS spectra also confirm the 4d¹ configuration of Nb; however, no indication for the presence of Nb-Nb pairs was observed in the spectra.

We had found NbS₃ among the products of thermal decomposition of NbS₂Cl₂ and NbS₂Br₂. NbS₂Cl₂ (NbS₂Br₂) was heated for 2 days in evacuated sealed quartz tubes in a temperature gradient of 588 to 570°C and

then slowly cooled. Mixtures of black platelets and a variety of needle-shaped crystals were obtained; among the latter were black needles which were identified as NbS₃. Since NbS₃ obtained in this way was in the form of good, untwinned single crystals, a detailed study of its crystal structure was considered worthwhile.

Structure Determination

Accurate unit-cell dimensions of NbS₃ were determined from Weissenberg photographs (CuK α radiation) calibrated with NaCl as internal standard. Calculations by least squares gave the values (standard deviations in units of the last decimal):

$$\begin{aligned} a &= 4.963(2) \text{ \AA}; & b &= 6.730(2) \text{ \AA}; \\ c &= 9.144(4) \text{ \AA}; \\ \alpha &= 90^\circ; & \beta &= 97.17(1)^\circ; & \gamma &= 90^\circ; \end{aligned}$$

in agreement with Kadijk and Jellinek (1). With a unit-cell content of Nb₄S₁₂ the density is calculated as 4.143 g cm⁻³, which is a reasonable value.

TABLE I

POSITIONAL AND THERMAL (IN 10^{-2} Å²) PARAMETERS OF NbS₃^a

	Nb(1)	Nb(2)	S(1)	S(2)	S(3)	S(4)	S(5)	S(6)
x	0.7156(3)	0.7154(3)	0.7632(7)	0.7636(7)	0.8747(8)	0.8830(7)	0.4631(8)	0.4708(8)
y	0.8526(3)	0.4013(3)	0.6163(4)	0.1327(4)	0.6288(4)	0.1248(4)	0.6274(5)	0.1224(4)
z	0.3509(1)	0.3464(1)	0.5618(4)	0.5453(3)	0.1552(4)	0.1837(4)	0.1610(4)	0.1873(4)
U ₁₁	0.22(6)	0.49(7)	0.40(16)	0.21(15)	1.36(18)	0.99(16)	1.39(18)	1.08(17)
U ₂₂	0.14(6)	0.43(7)	0.66(12)	0.34(11)	0.56(12)	0.16(11)	0.72(13)	0.37(12)
U ₃₃	0.15(5)	0.40(5)	0.37(13)	0.22(12)	0.61(14)	0.50(14)	1.00(15)	0.44(13)
U ₁₂	0.07(4)	0.06(4)	-0.09(10)	0.14(9)	0.02(10)	0.28(9)	0.21(11)	-0.11(10)
U ₁₃	-0.03(4)	-0.02(4)	-0.07(10)	0.18(10)	-0.07(11)	-0.02(11)	-0.14(12)	0.03(11)
U ₂₃	0.10(3)	-0.07(4)	0.09(9)	0.26(9)	-0.02(10)	0.06(9)	-0.06(11)	0.07(9)

^aStandard deviations in units of the last decimal are given in brackets.

The intensities of the X-ray reflections were measured with an Enraf-Nonius automatic three-circle diffractometer using Zr-filtered MoK α radiation. The dimensions of the crystal were $0.51 \times 0.12 \times 0.11$ mm³. Reliable intensities [$I > 3\sigma(I)$] of 1590 independent reflections with $\sin \theta/\lambda < 0.71$ Å⁻¹ were measured by the θ - 2θ scan method. The intensities were corrected for Lorentz and polarization factors and for absorption [$\mu(\text{Mo}) = 55$ cm⁻¹]. It was found that $I(0kl) \neq I(0\bar{k}l)$; therefore, the true symmetry of the structure is triclinic and the space group is $P\bar{1}$ or $P1$.

Atomic parameters were derived from a Patterson synthesis, adopting space group $P\bar{1}$, and refined by a full-matrix least-squares calculation. The atomic scattering factors were taken from Cromer and Mann (6) and corrected for anomalous dispersion (7). To each reflection a weight

$$w = 80/|F_0| \quad \text{for } |F_0| > 80 \quad \text{or} \\ w = |F_0|/80 \quad \text{for } |F_0| < 80$$

was assigned. At the end of the (anisotropic) refinement the discrepancy factor

$$R_w \equiv [\sum w(F_o - |F_c|)^2 / \sum w F^2]^{1/2} \text{ was } 0.063.$$

Lists of observed and calculated structure factors are available from the authors on request.

The final positional and thermal parameters with their standard deviations are given in Table I. The structure was checked by a difference Fourier synthesis which showed no unusual features.

Discussion

The structure of NbS₃ is shown in Fig. 1; bonding distances and their standard deviations are listed in Table II. It is seen that the structure is closely related to that of ZrSe₃ (3). Just as in ZrSe₃ the metal atoms are surrounded by eight chalcogen atoms forming bicapped trigonal prisms; these coordination polyhedra are distorted, since two of their edges are formed by S(3)-S(5) and S(4)-S(6)

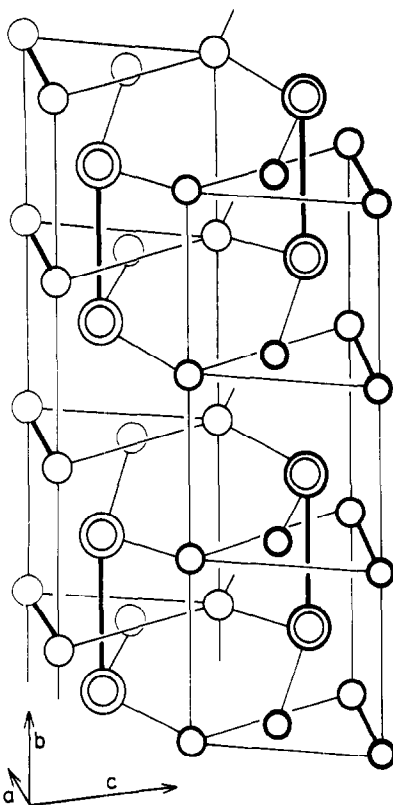


FIG. 1. The structure of NbS₃; niobium atoms are indicated by double circles, sulfur atoms by open circles. Nb-Nb and S-S bonds are shown by thick lines; the bi-capped trigonal prisms of sulfur around the niobium atoms are also shown.

TABLE II
BONDING DISTANCES IN NbS₃ (Å)^a

Nb(1)-Nb(2)	3.037(3)	S(3)-S(5)	2.050(8)
		S(4)-S(6)	2.050(8)
Nb(1)-S(1)	2.488(4)	Nb(2)-S(1)	2.432(4)
-S(3)	2.539(5)	-S(3)	2.523(5)
-S(5)	2.518(4)	-S(5)	2.500(4)
-S(2) ^b	2.642(4)	-S(1) ^b	2.619(6)
-S(2) ^b	2.670(5)	-S(1) ^b	2.621(5)
-S(2)	2.582(3)	-S(2)	2.554(3)
-S(4)	2.589(4)	-S(4)	2.584(4)
-S(6)	2.561(3)	-S(6)	2.584(3)

^a Standard deviations in units of the last decimal are given in brackets.

^b "Caps" of the trigonal prisms.

pairs, respectively. The S(3)-S(5) and S(4)-S(6) distances of 2.05 Å suggest the presence of single S-S bonds. The S(1) and S(2) atoms have no close sulfur neighbors; these atoms are surrounded by four metal atoms in a distorted tetrahedron. In this way the coordination polyhedra around the metal atoms are linked to form sheets parallel to the (*a*, *b*) plane, which explains the lath-shaped habit of the crystals.

The main deviation of NbS₃ from a ZrSe₃-type structure is a displacement of the metal atoms by 0.16 Å from the (pseudo) mirror planes of the coordination polyhedra to form Nb-Nb pairs; this leads to a doubling of the *b* axis and to a decrease of the symmetry from monoclinic to triclinic. The S(1) and S(2) atoms are slightly dragged by the neighboring Nb atoms and shifted by about 0.055 Å in the *b* direction.

The crystal structure, therefore, confirms that NbS₃ can be formulated as Nb⁴⁺(S₂)²⁻S²⁻. The metal is present as Nb-Nb pairs which causes the diamagnetism and semiconducting properties of the compound (1, 2). The Nb-Nb bonding distance of 3.04 Å is somewhat longer than in the compounds NbS₂Cl₂ (2.90 Å) (8), NbSe₂Cl₂ (2.97 Å) (4) and Nb₃Se₃Cl₇ (= 2NbSe₂Cl₂ · NbSeCl₃) (2.94 Å) (4), but a Nb-Nb bond of similar length (3.06 Å) has been found in NbCl₄ (9) and even longer Nb-Nb bonds in the oxide halides NbOCl₂, NbOBr₂, and NbOI₂ (4, 9); all of these compounds contain pairs of Nb⁴⁺ ions and are diamagnetic semiconductors. In contrast, no Nb-Nb pairs are present in the structure of NbSe₃ (10) which indeed has metallic properties (11).

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