

The Crystal Structure of 3-*R* Nb_{1.06}S₂

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The X-ray single crystal structure of 3-*R* Nb_{1.06}S₂ has been determined. The material crystallizes in the space group R_{3m} with $a = 3.3285(4)$ and $c = 17.910(4)$ Å when indexed on a hexagonal lattice. The structure was refined by full matrix least squares procedures to a final residual of $R = 0.026$ based on 79 observed ($I > 3\sigma_I$) reflections. The sulfurs form closest-packed layers with the majority of the metal in sheets of trigonal prismatic sites. A small portion of niobium was found to occupy octahedral sites, between the van der Waals gaps of the sulfur lattice. Niobium in the van der Waals region is trigonally distorted from octahedral symmetry, with niobium-sulfur distances of 2.234(8) and 2.577(11) Å, because of repulsion from niobium in adjacent trigonal prismatic layers.

Introduction

Interest in transition metal chalcogenides has been recently sparked by the use of these materials as cathodes in secondary batteries (1, 2). Cell reactions include the intercalation of Li⁺ ions into the van der Waals layers of these materials. However, the intercalation reaction is inhibited by the presence of parent metal ions in these layers (1). In order to acquire a better structural understanding of such systems, a single crystal X-ray structure determination of 3-*R* Nb_{1+x}S₂ was undertaken. Although Morosin (3) has reported the single crystal structure of 3-*R* NbS₂, only powder studies have been reported on the structure of the metal-rich 3-*R* Nb_{1+x}S₂ ($4a-c$). Fisher and Sienko (4c) have recently given a detailed discussion of changes in the powder pattern vs stoichiometry.

Experimental

A sample of the title compound was

kindly supplied by Dr. H. Shanks. A plate-shaped crystal (0.02 × 0.04 × 0.01 mm) was aligned and indexed (5) on a four-circle diffractometer designed and built in this laboratory. Lattice constants, $a = 3.3285(4)$, $c = 17.910(4)$ Å, were determined from a least-squares fit (6) to 13 strong, independent reflections measured at $\pm 2\theta(2\theta > 25^\circ)$ using graphite-monochromated MoK_α radiation, $\lambda = 0.70954$ Å. Reflections not meeting the condition $-h + k + l = 3n$ were the only systematic absences. This extinction condition is consistent with the space group R_{3m} . Neither axial oscillation photographs nor incremental step scans taken out the $\langle 10l \rangle$, $\langle 11l \rangle$, $\langle h10 \rangle$, and $\langle hh0 \rangle$ lines showed any diffuse rings or supercell spots as reported by Boswell *et al.* (7).

Diffraction data were collected at room temperature using graphite monochromated MoK_α radiation and the instrument described by Rohrbaugh and Jacobson (8). A total of 371 reflections were measured in the hkl , $hk\bar{l}$, $h\bar{k}l$, $h\bar{k}\bar{l}$ octants within a 2θ

TABLE I
FINAL STRUCTURAL PARAMETERS^a

	<i>g</i>	<i>z</i>	β_{11}	β_{33}
Nb1	0.97(1)	0.0	0.030(2)	0.00156(4)
S1	1.0	0.2463(2)	0.030(3)	0.00129(10)
S2	1.0	0.4201(2)	0.030(3)	0.00140(11)
Nb2	0.09(1)	0.8171(9)	0.051(15)	0.0013(4)

^a In this and in Table II the values in parentheses denote the estimated standard deviations in the last digits. The parameters without standard deviations were not refined. Anisotropic thermal factors are of the form $\exp(-\beta_{11}(h^2 + k^2 + hk) - \beta_{33}l^2)$. The temperature factor for Nb2 was only refined isotropically.

sphere of 60° using an ω -stepscan technique. Three reflections were periodically remeasured during the course of data collection, but they showed no significant decrease in intensity. The data were corrected for absorption ($\mu = 63.0 \text{ cm}^{-1}$), Lorentz, and polarization effects. The estimated variance in each intensity was calculated by

$$\sigma_I^2 + C_T + k_i C_B + (0.03 C_T)^2 + (0.03 C_B)^2 + (0.03 C_N/A)^2$$

where C_T , C_B , C_N , k_i , and A are the total count, the background count, the net count, a counting time constant, and an absorption factor, respectively, and the factor 0.03 represents the estimate of non-statistical errors. The estimated standard

deviation in each structure factor was calculated by the finite difference method (9). The observed data ($F > 3\sigma_F$) were averaged yielding 79 independent reflections.

The symmetry of the space group R_{3m} with $Z = 3$ required that the atoms be located at sites of $3m$ symmetry with coordinates of the form $(0, 0, z)$. The principal niobium (Nb1) was fixed at $z = 0.0$, and the sulfurs were initially input with the positions of Morosin (3). The sulfur positions, and all thermal parameters were refined by full matrix least-squares (10) to a conventional crystallographic residual of $R = 0.052$. A difference map (11) indicated the presence of additional electron density between the van der Waals layers. Niobium (Nb2) was placed at this interstitial site with an occupancy factor of 0.1 and an isotropic thermal parameter identical to that of Nb1. All variables including the occupancy factors of both niobium atoms were refined by full matrix least squares (10) to a final conventional residual $R = 0.026$ and weighted residual $R_w = 0.031$. The function minimized was $\sum \omega |F_o| - |F_c|^2$ where $\omega = 1/\sigma_F^2$. Refinement using the inverse structure model yielded nearly identical results. The scattering factors used were those for Nb⁴⁺ from Thomas and Umeda (12) and S²⁻ from Tomiie and Stam (13) modified for anomalous dispersion effects (14). Unit occupancy of the sulfur atom sites was as-

TABLE II
BOND DISTANCES (Å) AND ANGLES (°)

Nb1-S1	2.474(2)	Nb2-S1	2.577(11)
Nb1-S2	2.471(2)	Nb2-S2	2.234(8)
Nb1-Nb2	3.276(16)	S1-S2(same lamina)	3.311(5)
Nb-Nb ^a	3.3285(4)	S1-S2(interlamina)	3.443(4)
S1-Nb1-S1	84.53(6)	S1-Nb2-S1	80.4(4)
S2-Nb1-S2	84.65(6)	S2-Nb2-S2	96.3(5)
S1-Nb1-S2	78.00(9)	S1-Nb2-S2	91.1(1)
S1-Nb1-S2	134.27(3)	S1-Nb2-S2	168.9(7)
Nb1-S1-Nb2	81.0(3)		

^a Unit cell translation.

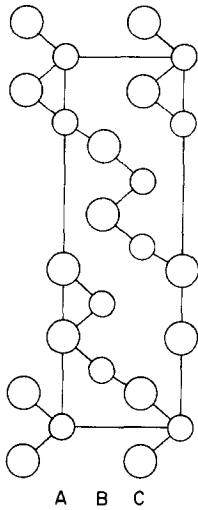


FIG. 1. View of 3-R Nb_{1.06}S₂ projected onto the (11 $\bar{2}$ 0) plane with the *c* axis vertical. The small and large circles represent niobium and sulfur atoms, respectively. The letters A, B, and C denote atoms with coordinates (0, 0, *z*), ($\frac{1}{3}$, $\frac{1}{3}$, *z*), and ($\frac{2}{3}$, $\frac{2}{3}$, *z*), respectively.

sumed. Refinement using neutral atom scattering factors (15) produced nearly identical structural parameters and a larger residual $R = 0.030$. Final structural parameters are listed in Table I. A final difference map (11) revealed no peaks greater than $0.2 e^-/\text{Å}^3$. Selected bond distances and angles are listed in Table II. A view of the cell is presented in Fig. 1. The observed and calculated structure factors are listed in Table III.

Discussion

The distances and angles involving Nb1 and the sulfurs are in good agreement with those reported by Morosin (3). The S-S distances (3.311–3.443 Å) indicate that the structure is made up of successive layers of closest-packed anions. The sulfurs form a trigonal prism around Nb1. In contrast, the sulfurs in the coordination environment of the van der Waals niobium, Nb2, comprise a distorted octahedron.

TABLE III
STRUCTURE FACTORS ($\times 10$) FOR 3-R Nb_{1.06}S₂

<i>H</i> = 0				<i>H</i> = 1			
<i>K</i>	<i>L</i>	<i>F</i> _o	<i>F</i> _c	<i>K</i>	<i>L</i>	<i>F</i> _o	<i>F</i> _c
0	3	838	867	2	2	436	415
0	6	242	248	2	5	758	736
0	9	771	801	2	8	471	456
0	12	954	1023	2	11	340	349
0	15	340	334	2	14	250	253
0	18	67	69	2	17	408	406
0	21	403	382	3	1	299	295
1	2	751	755	3	4	405	410
1	5	1228	1266	3	7	422	431
1	8	724	734	3	10	251	251
1	11	543	543				
1	14	365	376				
1	17	589	585			<i>H</i> = 2	
1	20	280	273				
2	1	579	548	0	2	561	531
2	4	776	744	0	5	940	914
2	7	773	767	0	8	559	561
2	10	455	450	0	11	428	427
2	13	308	316	0	14	300	304
2	16	476	476	0	17	498	486
2	19	311	306	0	20	228	229
3	3	376	369	1	1	458	432
3	6	95	103	1	4	619	595
3	9	396	396	1	7	613	622
3	12	538	559	1	10	362	364
3	15	165	182	1	13	253	263
				1	16	388	396
				1	19	256	258
				2	0	695	670
				2	3	293	307
				2	9	333	332
				2	12	474	468
						<i>H</i> = 3	
0	1	769	788	0	0	865	808
0	4	1035	1045	0	3	372	369
0	7	1010	1019	0	6	108	103
0	10	557	581	0	9	389	396
0	13	394	390	0	12	535	559
0	16	565	577	0	15	181	182
0	19	387	365	0	18	279	282
1	0	1282	1266	1	2	483	505
1	3	594	592	1	5	314	319
1	6	220	212	1	8	230	242
1	9	605	595	1	11		
1	12	813	817				
1	15	276	265				
1	18	60	54				
1	21	327	319				

In the structure of stoichiometric NbS₂, the stacking sequence is . . . AbABcBCaC . . . where the capital letters denote the sulfur sequence and the small letters denote the niobium sequence. The additional niobium atoms, designated by primed letters, go between the layers so as to give an octahedral arrangement yielding a stacking sequence . . . b'AbAc'BcBa'CaC. . . . These additional niobium atoms apparently move closer to one set of sulfurs in order to reduce repulsion effects from the Nb1 type atom directly over it, i.e., in the . . . Ac'BcB . . . arrangement, c' is closer to the A sulfur layer increasing the c'-c distance. The Nb2-S distances are 2.234(8) and 2.577(11) Å, and the shortest Nb1-Nb2 distance is 3.276(16) Å. The niobium-niobium distance in the layer is 3.3285(4) Å.

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References

1. D. W. MURPHY AND F. A. TRUMBORE, *J. Crystal Growth* **39**, 185 (1977).
2. M. S. WHITTINGHAM, *J. Solid State Chem.* **29**, 303 (1979).
3. B. MOROSIN, *Acta Crystallogr.* **B30**, 551 (1974).
4. a. F. JELLINEK, G. BRAUER, AND H. MÜLLER, *Nature (London)* **185**, 376 (1960).
b. F. KADLIK AND F. JELLINEK, *J. Less-Common Metals* **19**, 421 (1969).
c. W. G. FISHER AND M. SIENKO, *Inorg. Chem.* **19**, 39 (1980).
5. R. A. JACOBSON, *J. Appl. Crystallogr.* **9**, 115 (1976).
6. F. TAKUSAGAWA, Iowa State University, Ames, Iowa, private communication, 1975.
7. F. W. BOSWELL, A. PRODAN, AND J. M. CORBETT, *Phys. Status Solidi (a)* **35**, 591 (1976).
8. W. J. ROHRBAUGH AND R. A. JACOBSON, *Inorg. Chem.* **13**, 2535 (1974).
9. S. L. LAWTON AND R. A. JACOBSON, *Inorg. Chem.* **1**, 2124 (1968).
10. W. R. BUSING, K. O. MARTIN, AND H. A. LEVY, "ORFLS, A Fortran Crystallographic Least-Squares Program," U.S. Atomic Energy Commission Report ORNL-TM-305, Oak Ridge, Tenn. (1962).
11. C. R. HUBBARD, C. O. QUICKSALL, AND R. A. JACOBSON, "The Fast Fourier Algorithm and the Programs ALFF, ALFFDP, ALFFPROJ, ALFFT, and FRIEDEL," U.S. Atomic Energy Commission Report IS-2625, Ames, Iowa (1971).
12. L. H. THOMAS AND K. UMEDA, *J. Chem. Phys.* **26**, 293 (1956).
13. Y. TOMIIE AND C. H. STAM, *Acta Crystallogr.* **11**, 126 (1958).
14. D. H. TEMPLETON, "International Tables for X-Ray Crystallography," Vol. III, pp. 215-216, Table 3.3.2.c. Kynoch Press, Birmingham, England (1962).
15. H. P. HANSON, F. HERMAN, J. D. LEA, AND S. SKILLMAN, *Acta Crystallogr.* **17**, 1040 (1960).
16. L. PAULING, "The Nature of the Chemical Bond," 3rd ed. Cornell University Press, Ithaca, New York (1960).
17. F. R. GAMBLE, *J. Solid State Chem.* **9**, 358 (1974).
18. M. S. WHITTINGHAM AND F. R. GAMBLE, *Matter. Res. Bull.* **10**, 363 (1975).