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Structure refinement on NbS_2.* By B. MOROSIN, *Sandia Laboratories, Albuquerque, New Mexico* 87115, *U.S.A.*

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Parameters on the structure of NbS_2 have been refined by the least-squares method using 271 Mo $K\alpha$ intensity data. In space group $R3m$ with $a=3{\cdot}3303$ and $c=17{\cdot}918$ Å, the environment about the niobium atom consists of a trigonal prism with Nb–S separations of 2·473 and 2·476 Å.

Introduction

A large new class of superconductors has been discovered over the past few years in which various organic molecules have been shown to penetrate between the crystalline layers (lamina) of a number of transition metal dichalcogenides (Gamble, DiSalvo, Klemm & Geballe, 1970), stimulating many studies on the transport properties and tunneling characteristics. In some of our previous studies (Jones, Shanks, Finnemore & Morosin, 1972), pressure was used as a variable on the superconducting compounds $NbSe_2$ and NbS_2 in order to test the tunneling hypothesis without the complication of additional atoms between the lamina. Since structural data on NbS_2 are sparse (Wyckoff, 1965; Jellinek, Brauer & Muller, 1960), our refinement of the crystal structure parameters is reported in this note.

Experimental details and results

Lattice constants [$a_o=3{\cdot}3303$ (3) and $c_0=17{\cdot}918$ (2) Å] were determined by least-squares fit to 10 reflections in the range 130–160° 2θ (λ for Cu $K\alpha_1=1{\cdot}54050$ Å) measured on a Picker diffractometer. A thin diamond-shaped single-crystal specimen ($\sim 0{\cdot}031\times0{\cdot}031\times0{\cdot}0013$ cm) was examined by photographic methods, verifying the probable space group $R3m$, and selected for intensity measurement. The θ–2θ scan technique and a scintillation detector employing pulse-height discrimination were used to measure a complete hemisphere (to 100° 2θ; both $\pm l$'s) of Mo $K\alpha$ intensity data. Initially, a unique set of 524 reflections, containing both + and − l's, was obtained by averaging the symmetry-related absorption-corrected ($\mu=64{\cdot}0$ cm^{-1}) values provided the differences were less than $3\sigma_{\rm ave}/\sqrt{n}$, where $\sigma_{\rm ave}$ is the average σ for n measurements with the usual definition of $\sigma=(N_{SC}+K^2N_B)^{1/2}$, where N_{SC}, N_B, and K ($\simeq$4–5) are the total scan count, background counts (20 s on each side of scan), and time ratio of the scan to background, respectively. In the few instances where one did not know which intensity to discard, the values of the Friedel-related reflections prejudiced our choice. In space group $R3m$ with the choice of hexagonal axes, $Z=3$ and the niobium and two different sulfur ions are located on special threefold sites of $3m$ symmetry at $(0,0,z)$ from the equivalent lattice positions $(0,0,0;\frac{1}{3},\frac{2}{3},\frac{2}{3};\frac{2}{3},\frac{1}{3},\frac{1}{3})$; the niobium ion was fixed at $z=0{\cdot}0$ in our least-squares refinement procedure. Initial parameters were taken from Wyckoff (1965) and the intensity data subjected to least-squares refinement. The function $w(F_o-F_c)^2$ was minimized with $w=n/\sigma^2_{\rm ave}$ and with structure factors calculated using S^{2-} and Nb^{4+}[Nb–Δ(Zr–Zr^{4+})] scattering factors taken from Tables 3·3·1A and 3·3·1B and dispersion corrections from Table 3·3·2C of *International Tables for X-ray Crystallography* (1962). The residuals $R=|\sum|F_o|-|F_c||/\sum|F_o|$ were nearly identical for both configurations, probably because of the rather small value of the imaginary part of the scattering factors ($\Delta f''$) involved and of small errors resulting from the absorption corrections (ranged from 2·63 to 1·08). Hamilton's (1965) R-ratio criterion ($\mathcal{R}=1{\cdot}0002$) does not allow the selection of the proper configuration with any confidence; furthermore, the absolute values of the sulfur z parameters for the two configurations differ by less than one standard deviation.

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Table 1. *Positional and thermal parameters for* NbS_2

Atomic positions are all $(0,0,z)$; the Nb atom was fixed at 0·0 in our least-squares refinement; $U_{13}=U_{23}=0$ and $U_{11}=U_{22}=2U_{12}$ required by symmetry: U_{ij} of the form

$$\exp\left(-2\pi^2\sum\sum U_{ij}h_ih_ja_i^*a_j^*\right).$$

	z	$U_{11}(\times10^{-2}$Å$^2)$	$U_{33}(\times10^{-2}$Å$^2)$
Nb	0·0	0·58 (2)	1·28 (2)
S(1)	0·2464 (1)	0·89 (4)	1·15 (5)
S(2)	0·4201 (1)	1·17 (4)	1·07 (5)

Table 2. *Bond lengths and angles for* NbS_2

Nb–S(1)	2·476 (1) Å	S(1)–Nb–S(1)	84·54 (4)°
Nb–S(2)	2·473 (1)	S(1)–Nb–S(2)	78·00 (6)
S(1)–S(1)	3·3303*	S(2)–Nb–S(2)	84·67 (5)
S(2)–S(2)	3·3303*	S(1)–Nb–S(2)	134·27 (2)
S(1)–S(2)	3·114 (3) interlamina		
S(1)–S(2)	3·445 (3) intralamina		

* Unit-cell translation.

The positional and thermal parameters ($R=0{\cdot}055$) and the interatomic separations are given in Tables 1 and 2.*

The structure consists of lamina or 'sandwiches' which are stacked upon each other, with three such lamina in a repeat unit; each 'sandwich' consists of hexagonal-close-packed atoms, formed by a layer of niobium between two layers of sulfur atoms. The sulfur–sulfur separation between 'sandwiches' is 3·445 Å. The environment about the sixfold-coordinated niobium atom consists of a trigonal prism with the S–S separation along the ends or within the sulfur layer (3·3303 Å) slightly longer than along the sides or between sulfur layers within one 'sandwich' (3·114 Å); the niobium is located (within the errors of this determination) at the center of the prism (not required by space group). The an-

* A list of observed and calculated structure factors may be obtained from the author, and has also been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30280 (6 pp.). Copies may be obtained through The Executive Secretary, IUCr, 13 White Friars, Chester CH1 1NZ, England.

isotropy in the niobium thermal parameters may partly result from the laminar structure of this compound; however, that for the sulfur atoms should not be considered significant.

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The absolute configuration of lycopodine: a warning.

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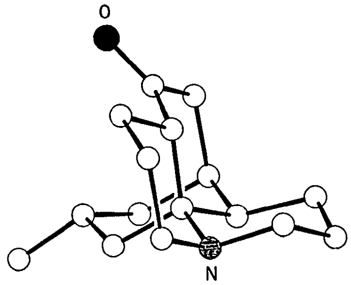
Attention is drawn to the inability of the *FC* link in X-RAY 63 and 70 to allow correctly for dispersion. In one instance, lycopodine, use of these programs gave a significantly strong bias in favour of the wrong chirality. The chirality (I) is confirmed.



(I)

Lycopodine, one of numerous alkaloidal constituents of *Lycopodium lucidulum* Michx, has been assigned the structure and chirality (I) on the basis of extensive chemical work and a positive Cotton effect (Manske & Marion, 1946; Harrison & MacLean, 1960; Anet, 1960; Wiesner, Francis, Findlay & Valente, 1961; Burnell & Taylor, 1961). Recently, Ayer, Altenkirk, Burnell & Moinas (1969) have reexamined the o.r.d. evidence for several members of this group of alkaloids, their salts, and derivatives. They found that lycopodine salts, epilycopodine and its salts, and the alkaloid L23 all have negative Cotton effects and that the structure of the o.r.d. curves is more complex than was realized when Wiesner *et al.* (1961) first assigned the chirality of annotinine and lycopodine. As the octant diagrams are not altered by protonation and are generally similar for all these compounds, they concluded that it was not safe to apply octant rules for carbonyl groups in this context until the large and obviously different contributions of N: and N^+ were properly understood, and they specifically queried whether (I) correctly depicted lycopodine. They adduced other items of indirect evidence and concluded, but with less confidence than before, that (I) was probably correct after all.

We have recently completed the determination of the crystal structure of lycopodine hydrochloride (which will be reported elsewhere), and as a byproduct have confirmed that (I) is correct. But because of a flaw in a well-known computer program, we initially came to the opposite conclusion. The circumstances seem to us serious enough to justify a warning to crystallographers.

Lycopodine hydrochloride ($C_{16}H_{26}NOCl$) is orthorhombic, $P2_12_12_1$, with $a=7{\cdot}606$, $b=9{\cdot}540$, $c=21{\cdot}371$ Å, $Z=4$. Of 1716 reflexions measured with Cu $K\alpha$ radiation on a Siemens diffractometer to $\theta=70°$, 1695 were observed, corrected for absorption, and, apart from eight zonal reflexions affected by extinction, were used to refine the structure to $R\sim0{\cdot}05$. Allowance for anomalous dispersion for the chloride ion was applied initially to all these reflexions for both possible molecular chiralities. $R(+)$, corresponding to configuration (I) was 0·0586, while $R(-)$, from its enantiomorph, was 0·0559. Application of Hamilton's (1965) significance test shows that these figures are *strongly in favour of the enantiomorph of* (I) (at a confidence level $\geqslant 99{\cdot}5\%$).

This conclusion led us to check every step, which revealed that a fault lay in the computer program used for calculating structure factors. This was the *FC* link in X-RAY 70 (Stewart, Kundell & Baldwin, 1963–1972). Subsequent tests have shown that both the X-RAY 63 and 70 versions of *FC* calculate structure factors correctly when the atomic scattering factors are real, but fail to allow correctly for the imaginary dispersion component. They give in fact $A(+)+iB(-)$ for $\Delta f''$ positive, and $A(-)+iB(+)$ for $\Delta f''$ negative. The X-RAY 72 version of *FC*, however, works correctly.