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Lithium niobium disulfide, $Li_{0.63}NbS_2$

Pamela A. Salyer, Marten G. Barker,† Alexander J. Blake, Duncan H. Gregory* and Claire Wilson

School of Chemistry, University of Nottingham, Nottingham NG7 2RD, England
Correspondence e-mail: duncan.gregory@nottingham.ac.uk

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Lithium niobium disulfide, $Li_{0.63}NbS_2$, has been prepared by a metathesis reaction between physically separated solid reactants, *i.e.* separated reactant metathesis (SRM). Single-crystal data were collected at reduced temperature [150 (2) K], yielding a refined Li content of $y = 0.63$ (6). The Li content in the crystalline samples was also determined analytically by flame photometry. The compound crystallizes in hexagonal space group $P6_3/mmc$ (No. 194), with Li^+ ions situated in octahedral sites between NbS_2 layers.

Comment

Layered transition metal dichalcogenides and their alkali metal intercalated derivatives are of interest for both their physical properties and potential technological applications (Dahn *et al.*, 1986; Chen *et al.*, 1993; Starnberg, 2000). Li-intercalated compounds, such as Li_yNbS_2, warrant particular attention, due to their ability to serve as the basis for high performance rechargeable battery materials (Wilson & Yoffe, 1969; Jellinek, 1972; Whittingham, 1978). Accurate determination of the Li stoichiometry, the limit(s) of Li-intercalation and the effects on the crystal structure of the parent dichalcogenide are of prime importance in understanding the nature of the resulting electronic and transport properties.

Despite the importance of ascertaining Li content precisely, the inherent difficulties involved in the detection and quantification of a light ionic guest within the heavier host framework have often prevented accurate determination of occupancy. Previous reports have predicted the limits of Li intercalation in Li_yNbS_2 to lie in the range $0.5 < y < 1.0$, and lattice parameters have been found for samples (crystals and powders) in the ranges a = 3.331 (1)–3.348 (1) Å and c = 12.861 (7)–12.90 (1) Å for $y < 0.75$ (Omloo & Jellinek, 1970; Barker & Gareh, 1994; Gareh, Barker & Begley, 1995; Gareh, Barker *et al.*, 1995). To date, the lowest Li occupancy reported for an Li_yNbS_2 single crystal is $y = 0.5$ in $Li_{0.5}NbS_{2.06}$, obtained by reaction of Li_2CO_3 under a flow of CS_2–argon (Gareh, Barker & Begley, 1995). However, this Li stoichiometry was not quantitatively determined (or refined), but was estimated by comparison with powder data to be a minimum of $y = 0.5$. The earlier study (Omloo & Jellinek, 1970) proposed a model on the basis only of observed intensities in the X-ray powder pattern.

For the present work, the single-crystal structure of Li_yNbS_2 [y = 0.63 (6)] has been determined using data collected at reduced temperature [150 (2) K] in a stream of cold nitrogen gas. The compound indexed as an hexagonal cell, with lattice parameters a = 3.3477 (8) Å and c = 12.875 (4) Å, consistent with what is expected for lithium occupancies in the range $0.5 < y < 1.0$. The fractional occupancy of the Li-atom position was allowed to vary freely, converging to 0.63 (6) with physically meaningful anisotropic displacement parameters.

This refined Li occupancy is in excellent agreement with flame photometry experiments (Corning 400 flame photometer) performed on crystals of Li_yNbS_2 dissolved in dilute nitric acid solution. Analysis yielded an Li occupancy of y = 0.51 (11). Furthermore, preliminary results from refinement of powder neutron diffraction (PND) data taken at 1.8 K on the POLARIS instrument at the ISIS facility, Rutherford–Appleton Laboratory, Oxfordshire, for a bulk sample of Li_yNbS_2 from the same reaction vessel, yielded an occupancy for Li of y = 0.58 (1). Details of PND investigations of intercalated dichalcogenides will be published elsewhere.

The coordination and structural environments of Li, Nb and S in $Li_{0.63}NbS_2$ are illustrated in Figs. 1 and 2. $Li_{0.63}NbS_2$ has a layered structure, consisting of Li^+ ions situated in octahedral sites between NbS_2 layers. The coordination sphere of the Li

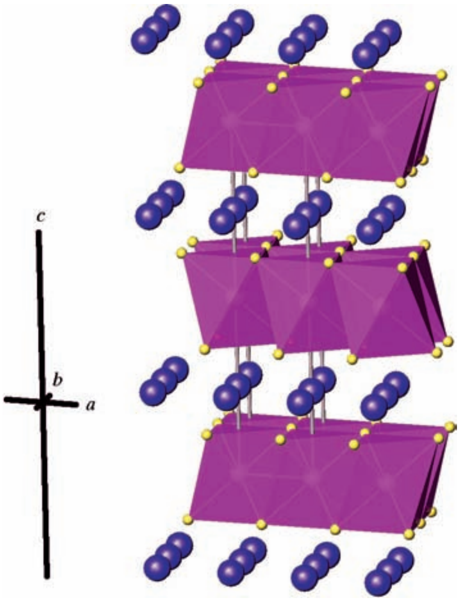

Figure 1
An Li-centred polyhedral representation of $Li_{0.63}NbS_2$, depicting layers of edge-sharing LiS_6 octahedra which stack along the c axis. Nb atoms (large grey spheres) are surrounded by a hexagonal close-packed array of S ions.

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† Deceased.

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atoms is octahedral, forming edge-sharing layers in the *ab* plane (Fig. 1). S—Li—S bond angles of 82.37 and 97.63° (for coordination of Li to S ions in the *ab* plane and along *c*, respectively) indicate that the Li octahedra are distorted by an elongation along one of the threefold axes in the *c* direction. Nb ions are trigonal-prismatically coordinated to S and are edge-sharing (Fig. 2) along the *a* and *b* directions. The Nb—S bond distance of 2.4886 (9) Å in $Li_{0.63}NbS_2$ is in good agreement with those in the NbS_2 structure [2.476 (1) and 2.473 (1) Å; Morosin, 1974]. S ions are arranged in slabs, surrounding Nb in an hexagonal close-packed array. Each S ion is coordinated to three Nb and three Li ions.

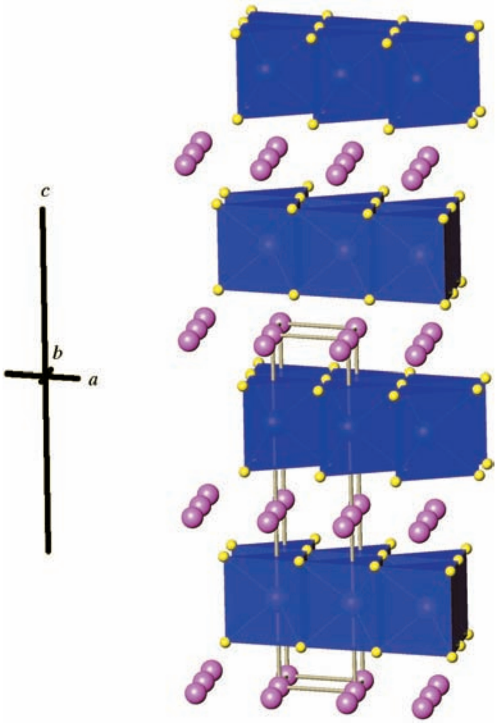

Figure 2
An Nb-centred polyhedral representation of $Li_{0.63}NbS_2$, depicting layers of edge-sharing NbS_6 trigonal prisms which stack along the *c* axis. Li ions (mid-grey spheres) are situated in octahedral holes between NbS_2 layers.

Experimental

Single crystals of $Li_{0.63}NbS_2$ were prepared by the separated reactant metathesis reaction between an oxide precursor ($LiNbO_3$) and excess chalcogen source material (Y_2S_3). The reactants were weighed out in an approximate 1:2 ($LiNbO_3$:Y_2S_3) ratio and placed into separate alumina crucibles inside a silica ampoule, which was then evacuated to approximately 10^{-5} Torr (1 Torr = 133.322 Pa) and sealed. The silica ampoule was reacted inside a muffle furnace at 1073 K for 7 d, then cooled slowly to room temperature at a rate of 10 K h^{-1}. Metallic grey platelets of $Li_{0.63}NbS_2$ were found growing within the inner crucible, which originally contained $LiNbO_3$. Opening of the ampoule and all manipulations of the crystals were carried out under a nitrogen atmosphere in a nitrogen-filled dry glove-box. Single crystals were extracted by hand and placed under moisture-free perfluoropolyether oil (RS3000; Riedel de Hahn) for protection from the atmosphere during analysis.

Crystal data

$Li_{0.63}NbS_2$
$M_r = 161.40$
Hexagonal, $P6_3/mmc$
$a = 3.3477$ (8) Å
$c = 12.875$ (4) Å
$V = 124.96$ (6) Å^3
$Z = 2$
$D_x = 4.290$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 294 reflections
$\theta = 3.2$–27.4°
$\mu = 6.08$ mm^{-1}
$T = 150$ (2) K
Tablet, metallic grey
0.09 × 0.07 × 0.03 mm

Data collection

Bruker SMART1000 CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SHELXTL*; Bruker, 2001)
$T_{min} = 0.762$, $T_{max} = 0.832$
383 measured reflections
79 independent reflections
76 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 27.4°$
$h = -4 \rightarrow 4$
$k = -2 \rightarrow 3$
$l = -16 \rightarrow 4$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.044$
$S = 1.42$
79 reflections
9 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0215P)^2 + 0.2484P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.68$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Nb—S	2.4886 (9)	S—Li	2.5420 (9)
S^{i}—Nb—S	84.54 (4)	S^{iv}—Li—S	180.00 (4)
S^{ii}—Nb—S	134.299 (17)	S—Li—S^{i}	82.37 (4)
S^{iii}—Nb—S	78.09 (5)	S—Li—S^{v}	97.63 (4)

Symmetry codes: (i) $x-1, y-1, z$; (ii) $x, y-1, \frac{1}{2}-z$; (iii) $x, y, \frac{1}{2}-z$; (iv) $-x, -y, -z$; (v) $-x, 1-y, -z$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT* and *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1998) and *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2002).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1001). Services for accessing these data are described at the back of the journal.

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