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$Li_{0.7}NbS_2$: structural effects of increased alkali metal content

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Crystals of lithium niobium disulfide [Li_yNbS_2; y = 0.70 (9)] have been prepared by separated reactants metathesis (SRM) at 1073 K. Single-crystal data collected at reduced temperature [150 (2) K] indicate that the compound is isostructural with $Li_{0.63}NbS_2$ [Salyer, Barker, Blake, Gregory & Wilson (2003). *Acta Cryst.* C**59**, i4–i6], crystallizing in the hexagonal space group *P*6$_3$/*mmc* (No. 194). $Li_{0.7}NbS_2$ shows an expansion of both the *a* and *c* lattice parameters when compared with previously reported results on Li_yNbS_2 intercalation compounds with $y < 0.70$. This provides the first single-crystal structural evidence of unit cell expansion with increasing lithium content in Li_yNbS_2, where $y > 0.5$.

Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(Nb–S) = 0.001 Å
Disorder in solvent or counterion
R factor = 0.016
wR factor = 0.047
Data-to-parameter ratio = 9.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Intercalation compounds of the layered transition metal dichalcogenides (*e.g.* TaS_2, NbS_2) are composed of *M*–*X* slabs separated by wide interlayer voids. These can act as hosts to accommodate a variety of (and varying amounts of) guest intercalants. These versatile materials are known to exhibit a range of physical properties and phenomena such as superconductivity, ionic/electronic conductivity, and charge density waves. As a subgroup, the alkali metal intercalated niobium disulfides (A_yNbS_2; *A* = Li, Na, K) have been reported as both ionic/electronic conductors and superconductors, highly dependent upon alkali metal content (Kanzaki *et al.*, 1981; McEwen & Sienko, 1982*a*; McEwen *et al.*, 1985). Theoretical

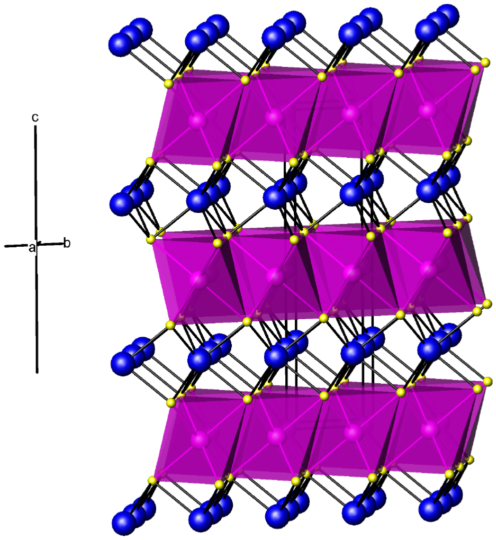

Figure 1
The structure of $Li_{0.7}NbS_2$, illustrating the location of Li^+ ions in layers of edge-sharing LiS_6 octahedra in the *ab* plane. Li-centred octahedra stack along the *c* axis and alternate with layers of NbS_2. Nb ions are denoted as blue spheres.

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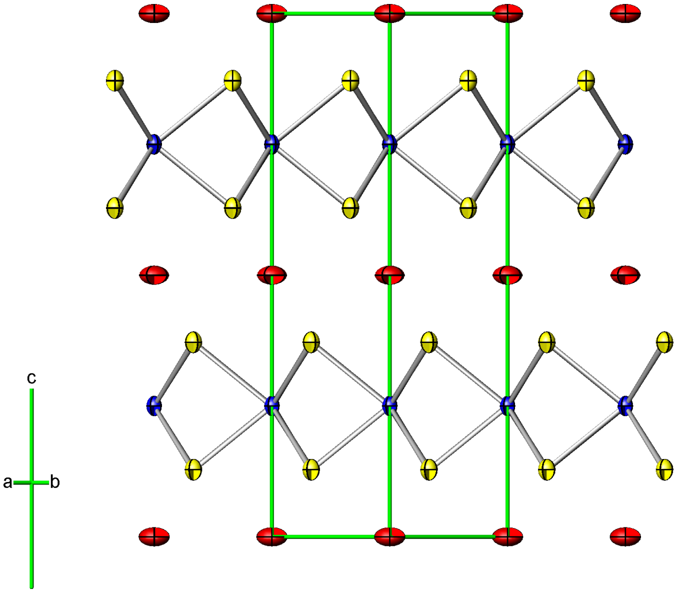

Figure 2
The structure of $Li_{0.7}NbS_2$, viewed in the [110] direction, illustrating layers of NbS_6 trigonal prisms interspersed with layers of Li^+ ions (red ellipsoids) along the *c* axis. Displacement ellipsoids are drawn at the 97% probability level.

predictions for the limits of alkali metal intercalation into these layered materials range between $y = 0 < y < 1$. In practice, the maximum levels of intercalation that have thus far been achieved in powdered A_yMS_2 compounds (A = Li, Na, K; M = Nb, Ta) are actually closer to y = 0.5–0.75, depending upon the method of intercalation (Whittingham, 1978; McEwen & Sienko, 1982*b*; McKinnon & Dahn, 1983; Dahn & McKinnon, 1984*a*,*b*; Butz *et al.*, 1984; Barker & Gareh, 1994; Gareh, Barker & Begley, 1995; Gareh, Barker, Begley & Batsanov, 1995; Salyer, Barker, Blake, Gregory & Wilson,, 2003). Part of the difficulty in fully characterizing these compounds lies with the accurate determination of alkali metal content, particularly lithium when surrounded by heavy metal atoms such as Nb or Ta.

Of interest here are the compounds of lithium niobium disulfide which have thus far been characterized primarily by X-ray powder diffraction. Lithium stoichiometries have therefore been either estimated or simply not determined. Extraction of a reliable lithium occupancy from powder X-ray diffraction data is a significant challenge. One alternative lies in the growth of high quality single crystals. This study provides the third single-crystal structure of a lithium niobium disulfide and only the second with a fully refined lithium occupancy (Gareh, Barker & Begley, 1995; Gareh, Barker, Begley & Batsanov, 1995; Salyer, Barker, Blake, Gregory & Wilson, 2003). Thus, together with previous studies, we can begin to elucidate the structural changes which occur with increasing lithium content in crystalline Li_yNbS_2, particularly within the ill-defined phase region with $y > 0.5$.

The growth of single crystals of composition Li_yNbS_2 [y = 0.70 (9)] has been accomplished. Additional structural data collected for recently reported Li_yNbS_2 [y = 0.63 (6)] (Salyer, Barker, Blake, Gregory & Wilson, 2003) also corroborate our findings here. Collectively, these data indicate that the Li_yNbS_2 lattice expands with increasing alkali metal content, as predicted by Omloo & Jellinek (1970) and Whittingham (1978), and as observed in powder samples with nominal lithium content y, by McEwen *et al.* (1985).

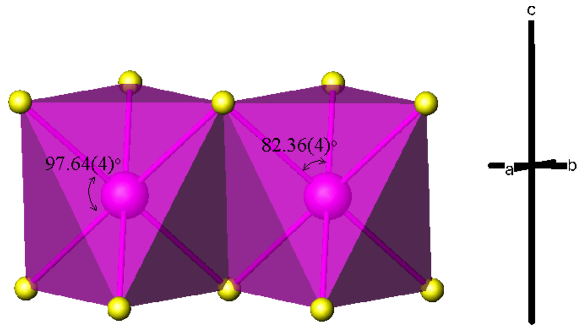

Figure 3
An Li-centred polyhedral representation of LiS_6 distorted octahedra, as evidenced by S—Li—S bond angles.

As expected, Li_yNbS_2 [y = 0.70 (9)] indexes as a hexagonal cell in space group $P6_3/mmc$ (No. 194). The displacement parameters for all atoms were refined anisotropically, without constraints, and gave physically meaningful values. As with compounds of lower lithium content (Salyer, Barker, Blake, Gregory & Wilson, 2003), Li^+ ions are situated in edge-sharing octahedral sites between NbS_2 layers (Figs. 1 and 2). The displacement parameters for Li^+ are relatively anisotropic in the *ab* plane compared to Nb and S and this is also observed in the y = 0.63 disulfide (Salyer, Barker, Blake, Gregory & Wilson, 2003). Octahedra are distorted by an elongation in the *c* direction, as indicated by the S—Li—S angles 82.36 (4)° (for S atoms in the same layer) and 97.64 (4)° (S atoms in adjacent layers) (Fig. 3). Nb ions are trigonal-prismatically coordinated, forming edge-sharing NbS_2 layers. Observed Nb—S and S—Li bond distances of 2.4954 (9) and 2.5495 (9) Å, respectively, are in keeping with the lattice expansion model when compared with those reported for '$Li_{0.5}NbS_2$' [Nb—S = 2.475 (2) Å; S—Li = 2.541 (2) Å; Gareh, Barker, Begley & Batsanov, 1995] and $Li_{0.63}NbS_2$ [Nb—S = 2.4886 (9) Å and S—Li = 2.5420 (9) Å; Salyer, Barker, Blake, Gregory & Wilson, 2003], and with the parent NbS_2 structure [Nb—S = 2.476 (1) and 2.473 (1) Å; Morosin, 1974].

The *c* lattice parameter of 12.912 (3) Å is in good agreement with the lattice parameter limits determined by Omloo & Jellinek (1970) for samples of 'maximum' alkali metal content [*i.e.* c = 12.90 (1) Å for a nominal y value of 0.75] at room temperature. The a parameter of 3.3572 (5) Å exceeds that predicted by Omloo & Jellinek (1970) [a = 3.331 (1) Å]. Both the a and c lattice parameters for the current compound are also significantly larger than those reported for $Li_{0.5}NbS_{2.06}$ (Gareh, Barker & Begley, 1995), *viz.* a = 3.348 (1) Å and c = 12.894 (1) Å (reported only with an estimated Li content) and for $Li_{0.63}NbS_2$ (Salyer, Barker, Blake, Gregory & Wilson, 2003), *viz.* a = 3.3477 (8) Å and c = 12.875 (4) Å.

In keeping with the prediction of lattice expansion with increasing alkali metal content, the current findings indicate

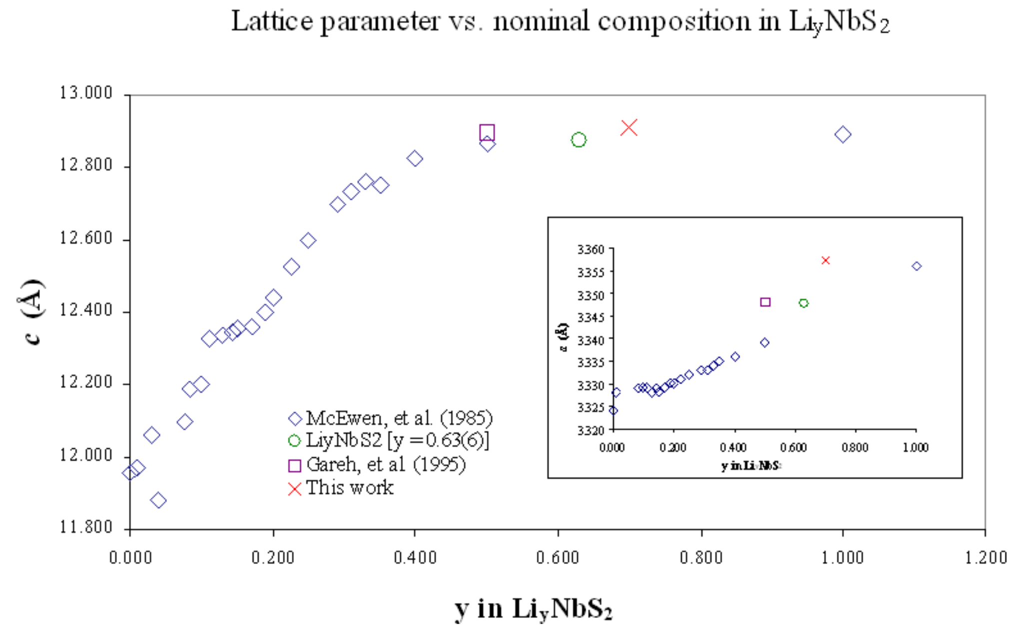

Figure 4
Variation in *a* (inset) and *c* lattice parameters with nominal composition in the powder Li_yNbS_2 compounds compiled by McEwen *et al.* (1985), compared with those of reported Li_yNbS_2 single crystals. [The Gareh reference is Gareh, Barker & Begley (1995).]

that the lithium content of the title compound is likely greater than that of either '$Li_{0.5}NbS_2$' (Gareh, Barker & Begley, 1995) or $Li_{0.63}NbS_2$. Although the lithium content determined in $Li_{0.63}NbS_2$ and the title compound are within one standard uncertainty (s.u.) of one another [y = 0.63 (6) and 0.70 (9), respectively], the observed cell expansion in the title compound is consistent with an increased Li content. Further evidence is provided by comparison with the lattice parameter trends and changes in superconducting T_c compiled by McEwen *et al.* (1985) for Li_yNbS_2 powder compounds, where $y < 0.5$. The *a* and *c* lattice parameters for $Li_{0.7}NbS_2$ fit well with their lattice expansion model, which extrapolates the lattice parameters for Li_yNbS_2 compounds of $y > 0.5$. According to their model, a Li_yNbS_2 compound with $y = 0.7$ should have *a* and *c* lattice parameters of approximately $a = 3.35$ Å and $c = 12.9$ Å at room temperature, in good agreement with the findings here at 150 (2) K (Fig. 4). Furthermore, as reported by McEwen & Sienko (1982*b*) and by McEwen *et al.* (1985), the superconductivity of Li_yNbS_2 is expected to disappear above $y = 0.4$. We observe weak temperature-independent susceptibility and no superconducting transition for $Li_{0.7}NbS_2$. The disappearance of superconductivity with increased alkali metal content has also been observed in isostructural Li_yNbSe_2 (McEwen & Sienko, 1982*a*).

Definitive reasons for the lattice expansion observed in Li_yNbS_2 with increasing lithium content have been the subject of some debate in the absence of reliable structural data. The related disulfides Li_yTiS_2, crystallize with the 1*T* structure and the *c* parameter increases steeply and almost linearly with increasing *y* for $y < 0.5$ (Whittingham, 1978). The magnitude of the lattice expansion in Li_yTiS_2 gradually decreases at higher lithium content ($0.5 < y < 1$). Importantly, NMR data support a structural model of Li_yTiS_2 in which lithium is substantially ionized (Silbernagel & Whiitingham, 1976). Similar trends are observed in the 2*H* structures of Li_yTaS_2 and Li_yNbSe_2, compounds isostructural with Li_yNbS_2 (Whittingham, 1978; Dahn & McKinnon, 1984*a*,*b*; Dahn & Haering, 1982; Kanzaki *et al.*, 1981). Assuming substantial electron transfer from the Li to the NbS_2 layers as in Li_yTiS_2, the expansion of the *c* parameter with *y* in the Li–Nb–S system can be rationalized in terms of the reduction of the NbS_2 layers (towards $[NbS_2]^-$) and concomitant lengthening of the Nb–S bonds – as nominally Nb^{IV} is reduced towards $Nb^{III}(LiNbS_2)$. This reduction also has an effect on the expansion of *a*. In the host materials, MX_2, the *a* parameter serves as an effective measure of electron transfer from *M* to *X* (Hibma, 1982). In the intercalates, however, this measure is less reliable and *a* is also correlated to the coulombic attraction between A^+ and the negatively charged layers and to the intralayer repulsion between intercalated A^+, effects which should become more pronounced as *y* increases.

As in other lithium intercalates of the disulfides, Li occupies octahedral interstices, minimizing repulsion between sulfur layers. Increasing *y* also has an effect on the expansion of the interlayer region, with Li—S bond lengths (more accurately Li/vacancy—S bond lengths) expanding 0.3% from $y = 0.63$ to $y = 0.7$ at 150 K. Hence the effective Li—S bond length increases from 2.5420 (9) Å in $Li_{0.63}NbS_2$ (Salyer, Barker, Blake, Gregory & Wilson, 2003) to 2.5495 (9) Å in $Li_{0.7}NbS_2$ and compares with 2.572 Å in fully intercalated 1*T* $LiTiS_2$, for example (Dahn *et al.*, 1980). A further indication of the effect of *y* on *c*-axis expansion can be gleaned by consideration of the thickness of the $[NbS_2]$ and $[Li_y]$ slabs and the S—S separations. Both slabs increase from $y = 0.63$ (3.131 and 3.306 Å, respectively) to $y = 0.7$ (3.142 and 3.313 Å, respectively) and compared to 3*R* NbS_2 (3.112 and 2.860 Å for $y = 0$, respectively) (Morosin, 1974). There are similar increases in the S—S distances between $[NbS_2]$ slabs (*e.g.* 3.839 Å in

$Li_{0.7}NbS_2$ *versus* 3.447 Å in NbS_2). Previous data have suggested a sharp increase in the *c*-parameter with *y* for $y < 0.4$ (steep slope in Fig. 4), followed by a reduction in this gradient for higher *y*, almost analogous to the 1*T* Li_yTiS_2 system (Whittingham, 1978). The change in gradient (*c*/*y*) in these systems could therefore be prescriptive of intercalant size *versus* increased coulombic attractive effects, whereas *a* continues to increase linearly with *y* due to [MX_2] reduction and Li^+–Li^+ repulsion effects. It would be informative to revisit Li_yNbS_2 compounds of lower *y* and reassess these changes on the basis of accurate structural data, particularly in light of the observed two-phase region (2*H*/3*R*) at low *y* (McEwen & Sienko, 1982*b*).

Experimental

Single crystals of $Li_{0.7}NbS_2$ were grown in evacuated, sealed silica ampoules at 1073 K by separated reactants metathesis (SRM). An oxide precursor, $LiNbO_3$, and a chalcogen source material, Y_2S_3, were weighed separately in the approximate ratio 1:2 to allow for chalcogen excess. The reactants were placed into separate, concentric alumina crucibles and sealed inside a silica ampoule at reduced pressure (approximately 10^{-5} Torr; 1Torr = 133.322 Pa). The silica ampoule was placed inside a muffle furnace and heated at 1073 K for 7 d, then cooled slowly to room temperature at a rate of 10 K h^{-1} (Salyer, Barker, Blake, Gregory, Weston & Wilson, 2003; for further details of the SRM experimental set-up and procedure). Hexagonal metallic platelets of $Li_{0.7}NbS_2$ were found growing within the crucible originally containing the oxide precursor, $LiNbO_3$. The ampoule was opened under a dry nitrogen atmosphere in a recirculating nitrogen-filled glove-box. All manipulations of the crystals were carried out in this atmosphere. Single crystals were selected and extracted by hand, then placed under moisture-free perfluoropolyether oil (*RS*3000; Riedel de Hahn) for protection from the atmosphere during analysis. Temperature-dependent magnetic susceptibility studies were carried out on a sample of $Li_{0.7}NbS_2$ crystals ground lightly and packed into a gelatine capsule. Data were collected on a Cryogenic S100 SQUID susceptometer using a scan length of 3 cm to reduce field inhomogeneity to 0.5%. Data were taken between 5 K and 85 K, cooling first to 4 K at zero field and then subsequently warming under a field of 1 Oe.

Crystal data

$Li_{0.70}NbS_2$
$M_r = 161.89$
Hexagonal, $P6_3/mmc$
$a = 3.3572$ (5) Å
$c = 12.912$ (3) Å
$V = 126.03$ (4) Å^3
$Z = 2$
$D_x = 4.260$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 778 reflections
$\theta = 3.2$–$28.9°$
$\mu = 6.02$ mm^{-1}
$T = 150$ (2) K
Hexagonal tablet, metallic gray
0.10 × 0.10 × 0.04 mm

Data collection

Bruker SMART1000 CCD area-detector diffractometer
ω scans
Absorption correction: by integration (*SHELXTL*; Bruker, 2001)
$T_{min} = 0.600$, $T_{max} = 0.789$
974 measured reflections
85 independent reflections
83 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 28.8°$
$h = -4 \rightarrow 4$
$k = -4 \rightarrow 4$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.016$
$wR(F^2) = 0.047$
$S = 1.58$
85 reflections
9 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0212P)^2 + 0.2307P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.69$ e Å^{-3}
$\Delta\rho_{min} = -0.60$ e Å^{-3}

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); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 1990, 2002).

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