As demonstrated by this work, there is a rich structural chemistry of sodium lanthanide selenites which is readily accessible using hydrothermal synthetic techniques. The stereochemically active lone pair on the selenium atom, in conjunction with high, often irregular, coordination around lanthanide atoms, may be an excellent combination in the search for novel asymmetric structures. Such materials could have useful non-linear properties with potential applications in electro-optical devices.

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Structure of Lithium Gallium Sulfide, LiGaS$_2$

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Abstract. LiGaS$_2$, $M_r = 140.787$, orthorhombic, $Pna2_1$, $a = 6.519$ (6), $b = 7.872$ (7), $c = 6.238$ (4) Å, $V = 320.1$ Å^3, $Z = 4$, $D_m = 2.98$, $D_x = 2.92$ g cm^{-3}, $F(000) = 264$, Mo $K\alpha$ ($\lambda = 0.71069$ Å), $\mu = 98.88$ cm^{-1}, room temperature, final $R = 0.049$ for 356 unique observed reflexions. The structure is based on a hexagonal closest-packed array of S atoms with the metal atoms in tetrahedral holes. It is derived from the zincite structure and related to the structure of enargite. The title compound is isostructural with NaFeO$_2$ and with LiGaO$_2$.

Introduction. LiGaS$_2$ was investigated by Ivanov-Emin & Rabovik (1947), who prepared a series of MGaS$_2$ compounds which they formulated as M_2[Ga$_2$S$_4$], but they made no X-ray studies.

Experimental. The title compound was prepared (Melibary, 1967) by heating an equimolar mixture of gallium oxide and lithium carbonate in a stream of purified dry hydrogen sulfide gas for 2 h at 1073 K, and then 4 h at 1173 K. After slow cooling under the

gas stream the brown mass was broken up and yielded suitable crystals. Analysis: Found: S 45.78, Li 4.81; calculated for LiGaS$_2$: S 45.55, Li 4.93; S gravimetrically and Li by flame photometry.

The bulk product gave an X-ray powder pattern which was indexed on the basis of the unit cell above. The structure analysis was first carried out from visually measured photographic films (Melibrary, 1967) with refinement converging at $R = 0.11$. We have now re-examined the same material using diffractometer data.

X-ray reflexion data from a small (approximately $0.13 \times 0.08 \times 0.15$ mm) brown-red crystal were collected on a Stoe Stadi-2 two-circle diffractometer operating in the $\theta/2\theta$-scan mode and using Mo $K\alpha$ radiation (graphite monochromator, $\lambda = 0.71069$ Å). The unit-cell parameters were determined by least squares from the ω measurements of 43 well centred and well distributed reflexions. The measured density is that reported by Ivanov-Emin & Rabovik (1947). Reflexions in the range $6.5 < 2\theta < 60°$ and having $0 \le h \le 9$, $0 \le k \le 11$ and $0 \le l \le 8$ were measured. A check reflexion was monitored every 50 reflexions and showed no evidence of decay. Measurements were made of 501 unique reflexions, of which 356 were accepted as observed [$I > 3\sigma(I)$]. The data were

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Table 1. *Final atomic positional parameters* ($\times 10^4$) *with e.s.d.'s in parentheses*

	x	y	z
Li	4178 (47)	1445 (54)	1255 (161)
Ga	736 (3)	1271 (4)	6135
S(1)	951 (6)	6351 (12)	65 (8)
S(2)	659 (7)	1153 (11)	9879 (10)

Table 2. *Bond lengths* (Å) *and angles* (°)

Ga—S(1)	2·260 (7)	Li—S(1)	2·41 (7)
Ga—S(1')	2·269 (7)	Li—S(1')	2·59 (7)
Ga—S(2)	2·252 (7)	Li—S(2)	2·46 (7)
Ga—S(2')	2·364 (7)	Li—S(2')	2·29 (7)

S(1)—Ga—S(1')	110·5 (2)	S(1)—Li—S(1')	106 (3)
S(1)—Ga—S(2)	107·6 (2)	S(1)—Li—S(2)	108 (3)
S(1)—Ga—S(2')	108·7 (2)	S(1)—Li—S(2')	115 (3)
S(1')—Ga—S(2)	113·3 (2)	S(1')—Li—S(2)	104 (2)
S(1')—Ga—S(2')	108·6 (2)	S(1')—Li—S(2')	114 (3)
S(2)—Ga—S(2')	108·1 (2)	S(2)—Li—S(2')	110 (3)

originally collected in the setting $Pbn2_1$ but have been transformed to the standard setting. The Patterson map indicated the choice of the non-centrosymmetric space group ($Pna2_1$ rather than $Pnam$) and this choice was confirmed by subsequent successful refinement. The structure was solved by Patterson and difference Fourier methods and refined by a combination of block-diagonal and full-matrix least squares [function minimized $\Sigma(|F_o - F_c|^2)$] with unit weights, to a final R of 0·049 (31 refined parameters). The z coordinate of the Ga atom was held fixed. Anisotropic thermal parameters were used for the Ga and S atoms only.

The shifts on the final cycle of refinement were all less than 0·04 of the corresponding e.s.d.'s; the maximum and minimum heights on the final difference Fourier map were 0·2 and $-0·1$ e Å^{-3}, respectively; the map showed no peak which could be interpreted as an atom. Analysis of variance against $\sin\theta$ and against $|F|$ showed no unusual features. Atomic scattering factors, linear absorption coefficients and f' and f'' values were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The Sheffield crystallographic programs were used throughout on a ICL 1906S computer.

The atomic parameters are listed in Table 1 and principal bond lengths and angles are in Table 2.* The structure is illustrated in Figs. 1 and 2.

Discussion. The S-atom lattice is very nearly perfectly hexagonal closest packed. (The axial ratios are within

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* Lists of structure factors and thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53037 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

2% of those of the orthorhombic cell of a hexagonal closest-packed lattice with doubling of the b dimension.) The metal atoms occupy one half of the tetrahedral interstices, *viz* all those tetrahedra which point in the $+z$ direction (as in the zincite structure), but are ordered on these sites so that the Li and the Ga atoms populate alternate puckered (220) sheets. The tetrahedra containing gallium are somewhat smaller than those containing lithium (mean S⋯S distances 3·733 and 3·973 Å respectively). The Ga atom is displaced from the centre of its tetrahedron towards the base by about 0·08 (1) Å, giving rise to the long Ga—S(2') bond. The lithium appears to have a similar but larger displacement but its larger e.s.d. makes it uncertain whether this effect is real.

The present structure may be related to that of the mineral enargite (the orthorhombic form of Cu_3AsS_4), which has closely similar cell dimensions but with interchange of the a and b dimensions and with the space group $Pmn2_1$. In both structures the tetrahedrally coordinated cations may be regarded as occurring in strings parallel to [010] (and also to [210] and [2̄10]). In LiGaS$_2$ each [010] string consists of alternate Li and Ga atoms; the other strings
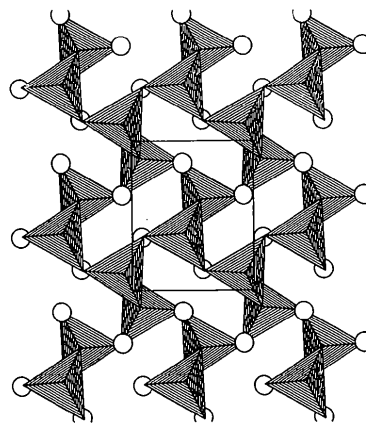

Fig. 1. View of the structure projected on (001). To avoid confusion, the gallium–sulfur tetrahedra are shown as shaded solids; the lithium ions are represented by circles.
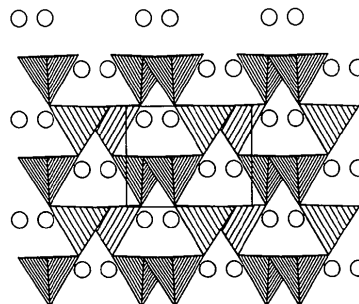

Fig. 2. View of the structure projected on (100).

contain pairs of Li atoms alternating with pairs of Ga atoms. The puckered (220) sheets govern the registration between the strings. In Cu_3AsS_4 the [010] strings are of two kinds, all copper and alternating copper and arsenic; the [210] and [$2\bar{1}0$] strings are all of the same kind and have the sequence three coppers and one arsenic.

The present compound is strictly isostructural with $LiGaO_2$ (Marezio, 1965) and with β-$NaFeO_2$ (Bertaut & Blum, 1954). In the former case the similarity extends to the displacement of the gallium from the centroid of the tetrahedron (only 0·016 Å in the oxide) and the deviations of bond angles from the ideal tetrahedral values.

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Structure and Phase Transition of K₃Na(CrO₄)₂

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Abstract. Tripotassium sodium chromate, $M_r = 372\cdot27$, trigonal, $P\bar{3}m1$, $a = 5\cdot8580$ (6), $c = 7\cdot523$ (2) Å, $V = 223\cdot57$ (7) Å³, $Z = 1$, $D_m = 2\cdot77$ (2), $D_x = 2\cdot77$ Mg m⁻³, $\lambda(Mo\ K\alpha) = 0\cdot7107$ Å, $\mu = 3\cdot837$ mm⁻¹, $F(000) = 180$, $T = 293$ K, $R = 0\cdot030$ for 709 unique observed reflections. A decrease in the elastic stiffness tensor component C_{44} near 239 K reveals a phase transition at this temperature. The configuration of the domain structure confirms the ferroelastic character of the low-temperature phase and the sequence of point groups $\bar{3}m$ and $2/m$.

Introduction. The $K_3Na(CrO_4)_2$ crystal belongs to a family of compounds, with the common chemical formula $A_3C(BX_4)_2$ (where A, C = Li, Na, K, Rb, Cs, NH₄; BX_4 = SO₄, SeO₄, CrO₄), which frequently exhibit ferroic phases.

In $K_3Na(CrO_4)_2$ a second-order phase transition, at 239 K, has recently been detected by thermal, elastic and dielectric measurements performed in the temperature range 100–300 K (Krajewski, Mroz, Piskunowicz & Breczewski, 1990). The phase below 239 K is ferroelastic as the above authors have confirmed by the direct observation of a domain structure, reorientable under the action of external mechanical stress.

Following the structural work carried out by Okada & Ossaka (1980) and given the structural isomorphism between this compound and the corresponding sulfate, $K_3Na(SO_4)_2$, the point symmetry $\bar{3}m$ was assumed for the room-temperature phase of $K_3Na(CrO_4)_2$ (Krajewski, Mroz, Piskunowicz & Breczewski, 1990). This point group, together with the orientation of the domain walls observed below 239 K, allowed these authors to assign the point group $2/m$ to the ferroelastic phase (Sapriel, 1975).

With the aim of confirming this suggested point-symmetry change at the transition temperature, we have determined the crystal structure of $K_3Na(CrO_4)_2$ at 293 K and performed ultrasonic measurements in the temperature range 200–300 K.

Experimental. Yellow well shaped crystals of $K_3Na(CrO_4)_2$ were grown from aqueous solutions by the steady-state method at 315 K. The reagents used for synthesis were chemically pure sodium and potassium hydroxides and chromic acid anhydride. The crystals obtained displayed a hexagonal prism shape with an edge length of about 10 mm (density measured by flotation); one of the crystals was ground to a sphere of radius 0·12 mm and mounted on an Enraf–Nonius CAD-4 diffractometer. Graphite-monochromated Mo $K\alpha$ radiation was used. Unit-cell parameters were refined using a set of 25 reflections ($10 < \theta < 50°$). Intensity data were collected by

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