

TABLE III. Calculation of the parameters in the semiempirical equation of state of sodium<sup>a</sup>

Atomic volume $\Omega_0^b$	37.8
Ionization potential <sup>c</sup>	1.81
Heat of sublimation <sup>d</sup>	8.23
$-E_c$	10.04
$\Omega B_0^e$	2.74
$A$ (empirical)	2.29
$B$ (empirical)	5.46
$B$ (theoretical)	3.11
$C$ (empirical)	17.79
$C$ (theoretical)	16.6
$-\Omega dB/d \ln \Omega$ (empirical)	8.73
$-\Omega dB/d \ln \Omega$ (experimental)	8.80

<sup>a</sup> All entries except the atomic volume are in units of  $10^{-12}$  erg atom<sup>-1</sup>.  $\Omega_0$  is in units of  $10^{-24}$  cm<sup>3</sup> atom<sup>-1</sup>.

<sup>b</sup> From x-ray data corrected using S. L. Quimby and S. Siegel thermal expansion data, Phys. Rev. **54**, 76 (1938).

<sup>c</sup> F. Seitz, see reference 16.

<sup>d</sup> American Institute of Physics Handbook (McGraw-Hill Book Company Inc., New York, 1957).

<sup>e</sup>  $B_0$  at 4.2°K from C. A. Swenson, Phys. Rev. **99**, 423 (1955).

In addition, the experimental value of  $\Omega dB/d \ln \Omega$  is given to compare with the value calculated from the

equation of state. The atomic volume at 0°K is also given in Table III.

$B$  (empirical) and  $B$  (theoretical) do not agree especially well, at least in part due to the structure of the equations, a small error in the bulk modulus results in large errors in  $B$ . The values of  $C$ (emp) and  $C$ (theo) agree quite well, the empirical value of  $\Omega dB/d \ln \Omega$  is surprisingly near the experimental value. One would have expected the breakdown of the assumptions regarding the Frohlich-Bardeen equation of state to have yielded an empirical value appreciably less than the experimental value.<sup>22</sup>

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### Crystal Structure of Ferroelectric $\text{LiH}_3(\text{SeO}_3)_2$ <sup>†</sup>

K. VEDAM, Y. OKAYA, AND R. PEPINSKY

*Crystal Research Laboratory, Department of Physics, The Pennsylvania State University, University Park, Pennsylvania*

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The structure of the room-temperature ferroelectric  $\text{LiH}_3(\text{SeO}_3)_2$  has been determined by x rays, using the heavy-atom method, and refined on the IBM 704. The crystals are monoclinic, with space group  $Pn$  and  $a=6.25$  Å,  $b=7.88$  Å,  $c=5.43$  Å,  $\beta=105.2^\circ$ . Fairly strong O—H···O bonds with distances 2.52, 2.56, and 2.57 Å are found, nearly perpendicular to the polar direction. The O—Se—O angles in one of the two selenite ions are rather similar; in the other ion these angles are unequal, as in the structure of  $\text{H}_2\text{SeO}_3$ . Possible positions for the Li ions are given based on crystal-chemical considerations.

#### I. INTRODUCTION

FERROELECTRICITY is observed in lithium trihydrogen selenite,  $\text{LiH}_3(\text{SeO}_3)_2$ , over the temperature range from  $-196^\circ\text{C}$  to  $90^\circ\text{C}$ .<sup>1</sup> The spontaneous polarization is the largest yet observed in a water-soluble crystal:  $15 \mu\text{coul}/\text{cm}^2$ . The coercive field, 1400 volts/cm, is disadvantageously high when compared to that of  $(\text{glycine})_3 \cdot \text{H}_2\text{SO}_4$ : 220 volts/cm.<sup>2</sup>

A recent structure analysis of  $(\text{glycine})_3 \cdot \text{H}_2\text{SO}_4$ , utilizing both x-ray<sup>3</sup> and neutron<sup>4</sup> diffraction and the x-ray anomalous dispersion method<sup>5-7</sup> for establishment

of the absolute configuration of the polar crystal, has permitted assignment of a polarization and switching mechanism for that ferroelectric.

The x-ray analysis reported here is a first step in the development of similar understanding of the polarization and switching mechanism in  $\text{LiH}_3(\text{SeO}_3)_2$ . No attempt has been made in this study to locate hydrogen atoms, which would be very difficult if not impossible in the presence of the heavy selenium atom. A neutron analysis at the Brookhaven reactor, and an anomalous dispersion study similar to that accomplished for  $(\text{glycine})_3 \cdot \text{H}_2\text{SO}_4$ , are in progress.

#### II. EXPERIMENTAL

The crystals of  $\text{LiH}_3(\text{SeO}_3)_2$  used in the present x-ray study were grown from aqueous solution of lithium hydroxide or lithium carbonate and selenious acid in stoichiometric ratios. These crystallize in the monoclinic system, with space group  $Pn$  and cell dimensions

\* This analysis has been supported by contracts with the Air Force Office of Scientific Research, Air Research and Development Command and with the U. S. Atomic Energy Commission.

<sup>1</sup> R. Pepinsky and K. Vedam, Phys. Rev. **114**, 1217 (1959).

<sup>2</sup> B. T. Matthias, C. E. Miller, and J. P. Remeika, Phys. Rev. **104**, 849 (1956).

<sup>3</sup> S. Hoshino, Y. Okaya, and R. Pepinsky, Phys. Rev. **115**, 323 (1959).

<sup>4</sup> S. Hoshino, Mitsui, Y. Okaya, and R. Pepinsky (to be published).

<sup>5</sup> Unterleitner, Y. Okaya, and R. Pepinsky (to be published).

<sup>6</sup> R. Pepinsky and Y. Okaya, Proc. Natl. Acad. Sci. U. S. **42**, 286 (1956).

<sup>7</sup> R. Pepinsky, Record Chem. Progr. Kresge-Hooker Sci. Lib. **17**, 145 (1956).

$a=6.25_8$  Å,  $b=7.88_6$  Å,  $c=5.43_3$  Å,  $\beta=105.2^\circ$ . There are two chemical units per cell.

Three-dimensional intensity data were obtained from equi-inclination Weissenberg photographs using  $\text{CuK}\alpha$  radiation and the multiple-film technique (6 sheets of Ilford Industrial, Type G, x-ray film). The crystals were rotated around the  $a$  axis ( $h=0$  to 5), around the  $b$  axis ( $k=0$  to 6) and around the  $c$  axis ( $l=0$ ). In all, 576 nonequivalent reflections were recorded. The intensities were visually estimated by comparison with a standard scale, and were corrected for Lorentz and polarization factors. Although the radii of the cylindrical specimens were very small (radius less than 0.04 mm and  $\mu$  absorption factor less than 0.73), absorption corrections were computed with the IBM 704 machine using the program of Vand and Pepinsky.<sup>8</sup> Some reflections with strong intensities were affected by extinction. Corrections for secondary extinction were made in the refinement stage through comparison with calculated structure factors, in a manner described below.

TABLE I.  $\text{LiH}_3(\text{SeO}_3)_2$ : coordinates of Se and O atoms, with standard deviations  $\sigma$  (in fractions of cell edges) and temperature factors  $B$  (in Å<sup>2</sup>).

Atoms	$x$	$\sigma(x)$	$y$	$\sigma(y)$	$z$	$\sigma(z)$	$B$
Se <sub>I</sub>	0.233	0.001	0.394	0.000	0.088	0.001	1.17
Se <sub>II</sub>	0.266	0.001	0.901	0.000	0.413	0.001	1.08
O <sub>1</sub>	0.210	0.005	0.229	0.003	0.863	0.005	1.19
O <sub>2</sub>	0.314	0.004	0.725	0.003	0.599	0.004	1.06
O <sub>3</sub>	0.305	0.006	0.268	0.004	0.353	0.006	2.47
O <sub>4</sub>	0.191	0.006	0.807	0.004	0.130	0.006	2.69
O <sub>5</sub>	0.485	0.005	0.466	0.003	0.061	0.005	1.07
O <sub>6</sub>	0.021	0.006	0.993	0.004	0.418	0.006	3.10

### III. STRUCTURE DETERMINATION

With two molecules in the space group  $Pn$ , coordinates of all atoms in the chemical unit had to be determined. Since the  $(0k0)$  reflections with  $k=\text{odd}$  were very weak, and because the polar direction can be reversed electrically, the structure cannot differ greatly from that in the centrosymmetric space group  $P2_1/n$ , which has four-fold general positions. The contribution of the lithium and the hydrogen is negligible compared to the oxygens and selenium. Therefore in the first stage of the analysis only one  $\text{SeO}_3$  group was treated as an asymmetric unit for the space group  $P2_1/n$ .

The conventional heavy-atom method was followed. Projections of the Patterson function along the  $a$  and  $b$  axis were computed on X-RAC, and the coordinates of selenium atoms in the approximate space group  $P2_1/n$  were determined as (0.23, 0.15, 0.09).

Assigning the signs of the selenium contribution to the observed structure factors, the  $a$ ,  $b$ , and  $c$  axis projections of the electron-density function were computed on X-RAC to determine approximate

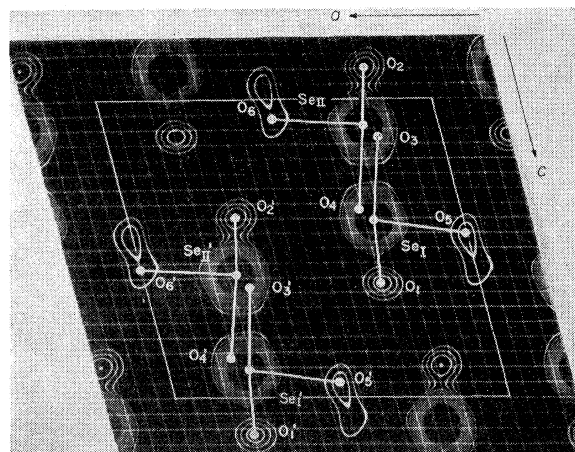


FIG. 1.  $\text{LiH}_3(\text{SeO}_3)_2$ : electron density projection along the  $b$  axis.

coordinates for the oxygens. After several iterated structure factor and electron density calculations on S-FAC and X-RAC, the structure appeared to converge properly.

At this stage the deviation of the structure from the centrosymmetric space group became apparent, evidenced by unreasonable elongation of the electron density of some of the oxygens. Accordingly, the provisional two-fold screw-axis symmetry was removed and the noncentrosymmetric space group  $Pn$  was adopted for further analysis.

All the atomic coordinates except those for the lithium and the hydrogen atoms, as obtained by the procedure described above, were subjected to least squares refinement of the three-dimensional data, using the automatic refinement Program PS XR3 of Vand and Pepinsky<sup>9</sup> on the IBM 704. In the course of these refinements it was found that several reflections with strong intensities were affected considerably by extinction. The  $F_{\text{obs}}$  values for these were corrected for

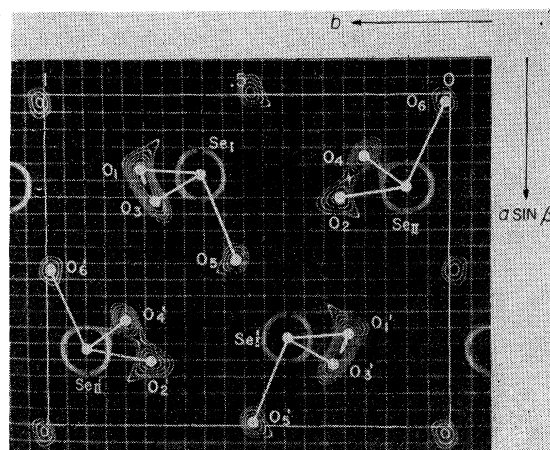


FIG. 2.  $\text{LiH}_3(\text{SeO}_3)_2$ : electron density projection along the  $c$  axis.

<sup>8</sup> V. Vand, Van den Hende, and R. Pepinsky (to be published).

<sup>9</sup> V. Vand and R. Pepinsky, *Z. Krist.* **111**, 46 (1958).

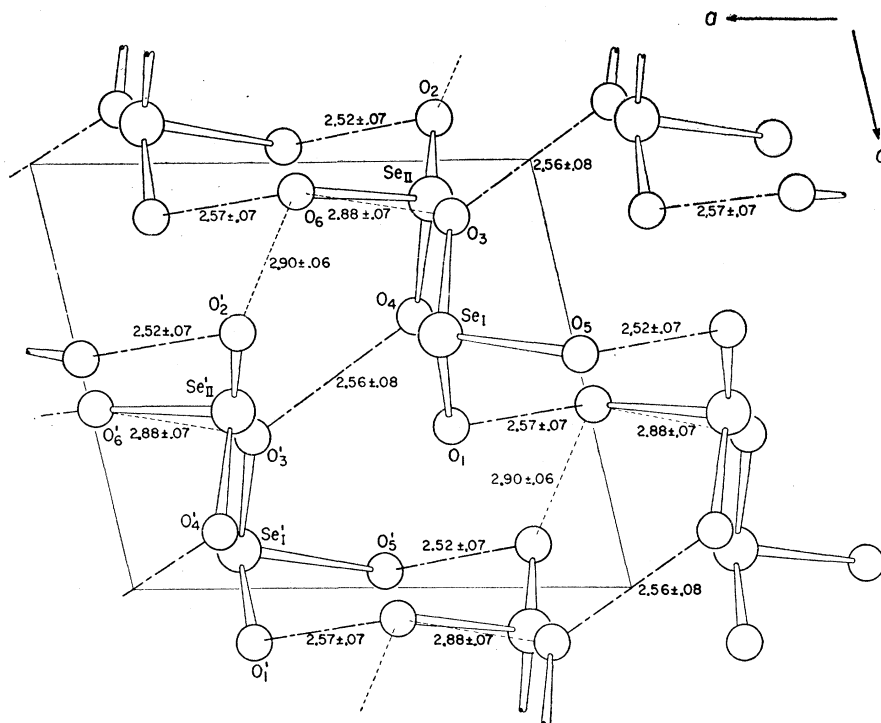


FIG. 3.  $\text{LiH}_3(\text{SeO}_3)_2$ : projection of the structure along the  $b$  axis.

secondary extinction with the usual formula

$$F_{\text{obs}}^{\text{corrected}} = F_{\text{obs}} \exp(g \cdot F_{\text{calc}}^2 \cdot \text{LPF})$$

(all symbols have the usual meanings), with  $g = 0.65 \times 10^{-5}$ . After six cycles the disagreement factor

$$R = \frac{\sum ||F_{\text{obs}}| - |F_{\text{calc}}||}{\sum |F_{\text{obs}}|}$$

dropped to 0.127 for the three-dimensional data.

The final set of atomic coordinates and isotropic temperature factor are given in Table I. The standard deviations of the atomic coordinates have been estimated using the formula by Cruickshank<sup>10</sup> and are also listed in Table I.<sup>10a</sup> The electron density projection along the  $b$  and  $c$  axes, using the final set of the phases of the structure factors, are shown in Figs. 1 and 2, respectively. Here all the atoms designated with a prime are related to the corresponding unprimed atoms by the operation of the  $n$  glide.

No attempt has been made to locate lithium ions in the structure. From packing and coordination considerations, a probable position at (0.65, 0.075, 0.23) can be assigned. The problem of certain establishment of Li

positions will not be solved easily in this structure until the neutron analysis is accomplished. The neutron scattering cross section for lithium in natural isotopic ratio is small and negative ( $-0.18 \times 10^{-12}$  cm). The negative phase will be useful; but the use of the  $\text{Li}^6$  isotope ( $f = 0.7 \times 10^{-12}$  cm) will be more helpful, and resort will be had to this for the analysis.

#### IV. DISCUSSION OF THE STRUCTURE

The structure of  $\text{LiH}_3(\text{SeO}_3)_2$  is comprised of  $\text{SeO}_3^{2-}$  ions joined together by a system of  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bonds, and positive lithium ions. In Fig. 3 various hydrogen bonds, proposed on the basis of short O—O separations, are illustrated by chain lines; dashed lines indicate other short approaches. Interatomic distances greater than 2.90 Å are not entered in the figure. Table II gives the interatomic distances (with standard deviations) and the Donohue angles for the proposed hydrogen bonds.

It is seen that the hydrogen bonds appear to be

TABLE II.  $\text{LiH}_3(\text{SeO}_3)_2$ : short interatomic distances, with standard deviations, and related Donohue angles. Primes refer to atoms in a neighboring  $\text{SeO}_3$  ion.

Distances in Å	Donohue angles (in degrees)
$\text{O}_1-\text{O}_6': 2.57 \pm 0.07$	$\text{Se}_I-\text{O}_1-\text{O}_6': 119$
$\text{O}_3-\text{O}_4': 2.56 \pm 0.08$	$\text{O}_1-\text{O}_6'-\text{Se}_{II}': 109$
$\text{O}_5'-\text{O}_2: 2.52 \pm 0.07$	$\text{Se}_I-\text{O}_3-\text{O}_4': 104$
	$\text{O}_3-\text{O}_4'-\text{Se}_{II}': 130$
	$\text{Se}_I-\text{O}_5-\text{O}_2': 123$
	$\text{O}_5-\text{O}_2'-\text{Se}_{II}': 115$

<sup>10</sup> D. W. J. Cruickshank, *Acta Cryst.* **2**, 65 (1949).

<sup>10a</sup> A table listing the observed and calculated structure factors has been deposited as Document No. 6242 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting \$2.50 for photoprints or \$1.75 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

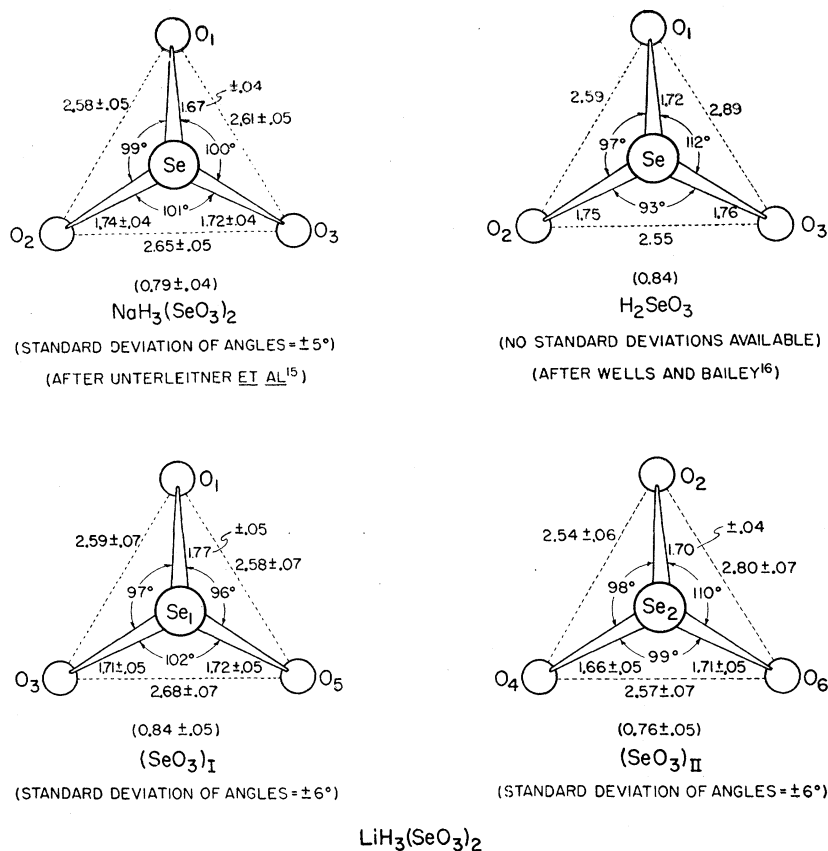


FIG. 4. Size and shape of selenite ions. Distances from selenium to plane of three oxygens shown in parentheses.

fairly strong, and, furthermore, they are nearly parallel to the  $c$  plane, the perpendicular to which is the polar direction. The presence of strong  $\text{O}-\text{H}\cdots\text{O}$  bonds perpendicular to the polar direction is also observed in the structures of potassium dihydrogen phosphate<sup>11-14</sup> and (glycine)<sub>2</sub>· $\text{H}_2\text{SO}_4$ .<sup>3</sup>

The two selenite ions are pyramidal, as expected, and their shape and size are shown in Fig. 4. Similar data found in the structure of  $\text{NaH}_3(\text{SeO}_3)_2$ <sup>15</sup> and  $\text{H}_2\text{SeO}_3$ <sup>16</sup> are shown for comparison. The two  $(\text{SeO}_3)_\text{I}$

and  $(\text{SeO}_3)_\text{II}$  are dissimilar.  $(\text{SeO}_3)_\text{I}$  has three fairly equal  $\text{O}-\text{Se}-\text{O}$  angles; in  $(\text{SeO}_3)_\text{II}$  the inequality of these angles is clearly seen. In this respect  $(\text{SeO}_3)_\text{II}$  is similar to the  $\text{SeO}_3$  ion in  $\text{H}_2\text{SeO}_3$ .<sup>16</sup>

Distances between the selenium atom and the plane of these oxygen atoms are also shown in Fig. 4. They are all 0.80 Å within  $\pm 0.04$  Å.

## V. ACKNOWLEDGMENTS

We are grateful to Professor V. Vand, Dr. J. Van den Hende and Evelyn Pratt for assistance in IBM 704 calculations. These calculations were accomplished in the Atomic Energy Commission Computing and Applied Mathematics Center, Institute of Mathematical Sciences, New York University. X-RAC and S-FAC computations were supported by a contract with the Office of Naval Research.

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<sup>12</sup> B. C. Frazer and R. Pepinsky, Acta Cryst. **6**, 10 (1953).

<sup>13</sup> S. W. Peterson, H. A. Levy, and S. H. Simonsen, J. Chem. Phys. **21**, 2084 (1953).

<sup>14</sup> G. E. Bacon and R. S. Pease, Proc. Roy. Soc. (London) **A220**, 397 (1953).

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<sup>16</sup> A. F. Wells and M. Bailey, J. Chem. Soc. 1282 (1949).

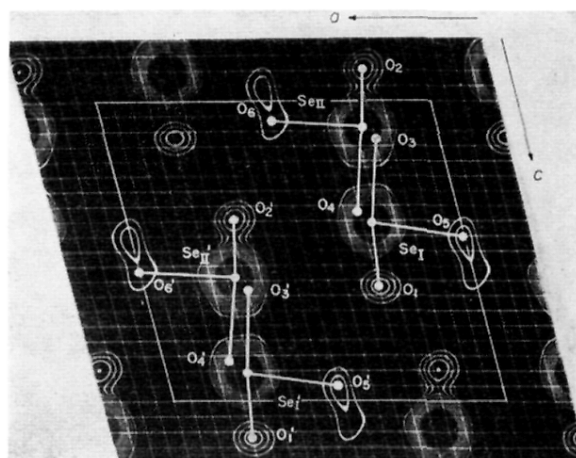


FIG. 1.  $\text{LiH}_3(\text{SeO}_3)_2$ : electron density projection along the  $b$  axis.

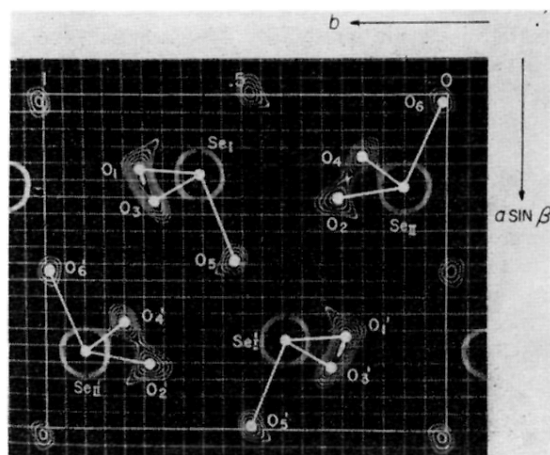


FIG. 2.  $\text{LiH}_3(\text{SeO}_3)_2$ : electron density projection along the  $c$  axis.