# Localization of Protons in $Li_{1-x}H_xIO_3$ by Single-Crystal Neutron Diffraction

J. Le Roy

*LSM, IUT, Université de Savoie, 9 rue de l'Arc en Ciel, B. P. 240, 74942 Annecy le Vieux Cedex, France*

C. Rosso and J. Bouillot

*L'EMFON, FAST, Université de Savoie, 41 av. de la Plaine, B. P. 806, 74016 Annecy Cedex, France*

J.-M. Crettez[1]

*LPS, UFR Sciences et Techniques, Université de Bourgogne, B. P. 138, 21004 Dijon Cedex, France*

and

J.-X. Boucherle and M. Bonnet

*CEA, Département de Recherche Fondamentale sur la Matière Condensée, SPSMS/MDN, CENG, B. P. 85X, 38041 Grenoble Cedex, France*

Structural parameters of lithium iodate–iodic acid solid solution $Li_{1-x}H_xIO_3$ ($x = 0.28$) have been refined at 60 K and at room temperature from single-crystal neutron diffraction data with a good reliability factor (about 2%). The lattice parameters are $a = 5.494(7)$ Å, $c = 4.924(2)$ Å at 60 K and $a = 5.514(3)$ Å, $c = 4.960(3)$ Å at RT. The proton does not replace the lithium atom but is located in a general position of the space group $P6_3$, $x = 0.240(4)$, $y = 0.299(4)$, and $z = -0.042(6)$ at RT, and its thermal ellipsoid is well defined. Hydrogen sites are located on three of the six lateral edges of the distorted oxygen octahedron around the lithium site. © 1995 Academic Press, Inc.

## INTRODUCTION

Single crystals of lithium iodate ($\alpha$-$LiIO_3$, space group $P6_3$, $Z = 2$) and hydrogen iodate ($HIO_3$, $P2_12_12_1$, $Z = 4$) have been intensively studied and are widely used in optical applications, owing to their nonlinear properties. The growth of both crystals is easily accomplished by isothermal controlled evaporation of supersaturated aqueous solutions. It is well known that the optical quality of $\alpha$-$LiIO_3$ crystals depends mainly on three parameters: the temperature, the evaporation rate, and the pH of the solution. Samples of the best quality are generally obtained from neutral or slightly acidic solutions (pH 6 to 7) with a slow evaporation rate, at about 315 K. Lowering the pH toward 1.5 by adding $HIO_3$ makes growth easier but crystals have less optical quality (dislocations, sometimes yellowish coloration). In such samples protons behave as impurities which probably replace some Li atoms, and most of physical properties are influenced by these impurities.

By studying the ternary system $LiIO_3$–$HIO_3$–$H_2O$ at 298 K, Ricci and Amron (1) pointed out the existence of the solid solution $Li_{1-x}H_xIO_3$ with $x$ varying continuously from 0.22 to 0.35. Some physical characteristics of these lithium iodate–iodic acid solid solutions, such as dielectric, vibrational, and piezoelectric properties have been already reported and show that these crystals are promising for applications (2–4). A full understanding and qualitative modeling of these properties depend on the accuracy of the structure data. Investigations from single-crystal X-ray and powder neutron diffraction have only given partial results (5, 6). The space group of $Li_{1-x}H_xIO_3$ (with $x = 0.33$) is $P6_3$, like $\alpha$-$LiIO_3$, and the lithium atom occupancy is two-thirds of that in $\alpha$-$LiIO_3$ (Wyckoff site $2a$), while protons are randomly distributed in general positions ($6c$) around an Li vacancy with an occupation factor of 0.33. From these experiments the accurate location of the proton is questionable and its thermal vibrations are only approximately accounted for by an isotropic temperature factor. Thus a single-crystal neutron diffraction experiment was performed, which is reported herein.

---

[1] To whom correspondence should be addressed.

## EXPERIMENTAL

### Sample Preparation

Working on the data of Ref. (1), the solid solution $Li_{1-x}H_xIO_3$ appears as a single crystallization product of the system $LiIO_3$–$HIO_3$–$H_2O$ when the ratio of weight percents $r = (\% \ LiIO_3)/(\% \ HIO_3)$ of the saturated solution is in the range 1.224 to 0.474. Then the $x$ parameter in the formula of the solid is in the range 0.224 to 0.355. A least-squares fitting based on their 17 data points yields the following linear relation: $r = 2.505-5.765x$. This relation can be used to define the $LiIO_3$ and $HIO_3$ concentrations to grow solid solution crystals with a given value of $x$. Small, long hexagonal rods of single crystals have been grown after several months at 295 K, and among them three crystals have been tested by using the X-ray Laue technique. A sample (3 mm in length, 0.7 mm in diameter) was cut from the sharply pointed end of the best crystal and used for the experiment.

### Data Collection and Structure Refinements

Neutron single-crystal diffraction measurements were made on the DN4 four-circle diffractometer running in the reactor SILOE (CEN Grenoble). The sample sticked inside a helium-filled aluminium can was placed in a three-stage refrigerator. Data were collected at 60 K and at room temperature using the $\omega$-scan technique with the wavelength 1.181 Å and the maximum value 0.546 of $\sin \theta/\lambda$. The scan width varied from 3° to 5° as a function of $\theta$, according to the resolution of the diffractometer with a constant number of steps (31 steps). The 3 0 0 reflection measured at regular time intervals did not vary significantly during the experiments.

The data were first reduced using the program COLL5 (7), which eliminates the background and gives integrated intensities, full width at half height, and statistical errors. There were 509 reflections at 60 K and 494 at RT. Then intensities of symmetrically equivalent reflections were put together by running the program ARRNGD with absorption corrections performed by the program DISTA3. These programs are based on the CCSL Library (8). The linear absorption coefficient of the material, calculated from the data of Ref. (9) is $\mu = 1.2 \ cm^{-1}$. The number of nonequivalent reflections was then 90 at 60 K and 89 at RT.

The structure refinements based on $F^2$ with the weighting scheme $w = 1/\sigma$ were done by running the program MXD (10). Correction of the extinction effects (11) was applied. This extinction was chosen isotropic because of the regular hexagonal shape of the sample. Moreover, the correction related to the $\lambda/2$ contamination with the fixed rate of 0.5% in intensity was taken into account. Refinements started with Li in position $2(a)$: 0, 0, $z$; I in $2(b)$:

1/3, 1/3, 1/2; and O and H in general positions $6(c)$: $x, y, z$ of the space group $P6_3$, with reduced atomic coordinates of Ref. (6). The four atoms in the model were allowed to vibrate anisotropically, within the harmonic approximation.

## RESULTS AND DISCUSSION

Lattice constants obtained from the positions of 23 reflections are: $a = 5.494(7)$ Å, $c = 4.924(2)$ Å at 60 K and $a = 5.514(3)$ Å, $c = 4.960(3)$ Å at RT. According to the linear relation between $x$ and the $c/a$ ratio, $x = 5.985-6.335 \ c/a$ given in Ref. (5), the calculated proton concentration is $x = 0.28(1)$ for the crystal under investigation. Starting with a different value of $x$, and refining $x$ among other parameters, refinements at both 60 K and RT lead to the same concentration value $x = 0.28(1)$, which shows the self consistency. The final structural parameters are given in Table 1 for atomic position coordinates and in Table 2 for anisotropic thermal parameters. Refinements indicators of the order of 2% are reported in Table 1.

The structure refinement confirms the position coordinates obtained from high-resolution powder neutron diffraction (6), particularly concerning the hydrogen atoms. The localization of proton is verified by a difference Fourier map $F_{obs} - F_{calc}$, where the highest value of residual peaks does not exceed 5% of the hydrogen peak observed in an $F_{obs}$ Fourier map. Interatomic distances and angles are reported in Table 3. The proton and its two nearest oxygens form a quasi-linear O–H=O bond which corresponds to a very slightly bound proton in this compound. The nonsymmetrical position of H between

### TABLE 1

Reduced Atomic Coordinates ($\times 10^3$) in $Li_{1-x}H_xIO_3$ ($x = 0.28$) and Reliability Factors from Single-Crystal Neutron Diffraction

|  | Temperature (K) | | |
|---|---|---|---|
|  | 60 | RT | 295 (Ref. 6)[a] |
| Li($z$) | 439(2) | 433(2) | 444(4) |
| H($x$) | 237(4) | 240(4) | 229(5) |
| H($y$) | 303(3) | 299(4) | 290(4) |
| H($z$) | −49(5) | −42(6) | −45(4) |
| O($x$) | 350.8(2) | 351.5(1) | 353.6(2) |
| O($y$) | 263.0(2) | 261.2(1) | 264.3(3) |
| O($z$) | 173.3(6) | 170.7(6) | 173.6(5) |
| $R_{w.abs}$ | 2.4 | 2.0 | 5($R_N$) |
| $R_{w.lsq}$ | 2.0 | 2.0 | 3.8 ($R_W$) |

[a] In the last column results from high-resolution powder neutron diffraction (Ref. 6) and extrapolated at 295 K are reported ($x = 0.34$).

**TABLE 2**
Anisotropic Thermal Parameters
$(\times 10^3 \text{ Å}^2)$ in $Li_{1-x}H_xIO_3$ (x = 0.28)

| | Temperature (K) | | |
|---|---|---|---|
| | 60 | RT | 295 (Ref. 6)[a] |
| $Li(U_{11})$ | 9(2) | 21(1) | 13(1) |
| $Li(U_{33})$ | 47(3) | 77(7) | 91(3) |
| $Li(B_{iso}^{eq})$ | 1.6 | 3.1 | 3.1 |
| $H(U_{11})$ | 14(11) | 23(9) | — |
| $H(U_{22})$ | 39(11) | 63(12) | — |
| $H(U_{33})$ | 18(17) | 47(20) | — |
| $H(U_{12})$ | 14(8) | 16(8) | — |
| $H(U_{13})$ | 4(8) | 17(11) | — |
| $H(U_{23})$ | 2(11) | −5(14) | — |
| $H(B_{iso}^{eq})$ | 1.8 | 3.7 | $1.9(B_{iso})$ |
| $I(U_{11})$ | 7.3(6) | 14.6(5) | 17.4(6) |
| $I(U_{33})$ | 13(2) | 24(1) | 28.6(4) |
| $H(B_{iso}^{eq})$ | 0.7 | 1.4 | 1.7 |
| $O(U_{11})$ | 9.8(4) | 17.7(4) | 17.1(3) |
| $O(U_{22})$ | 12.8(5) | 25.3(5) | 29.4(4) |
| $O(U_{33})$ | 26.7(8) | 41.1(9) | 47.2(2) |
| $O(U_{12})$ | 5.6(3) | 10.0(3) | 11.5(3) |
| $O(U_{13})$ | 4.7(7) | 6.6(7) | 5.8(7) |
| $O(U_{23})$ | 0.7(6) | −2.0(6) | −3.6(6) |
| $O(B_{iso}^{eq})$ | 1.3 | 2.2 | 2.5 |

[a] In the last column results from high-resolution powder neutron diffraction (Ref. 6) and extrapolated at 295 K are reported (x = 0.34). Only an isotropic temperature factor was refined for hydrogen.

the oxygen atoms may be related to the lone pair electrons associated to the iodine atoms.

More interesting in this experiment are the refined anisotropic thermal parameters for H, which were not refinable in our previous structural studies. The thermal ellipsoids including nuclear probability densities greater than 70% have been obtained using the program GRETEP

**TABLE 3**
Interatomic Distances (Å) and Angles (°) in
$Li_{1-x}H_xIO_3$ (x = 0.28)

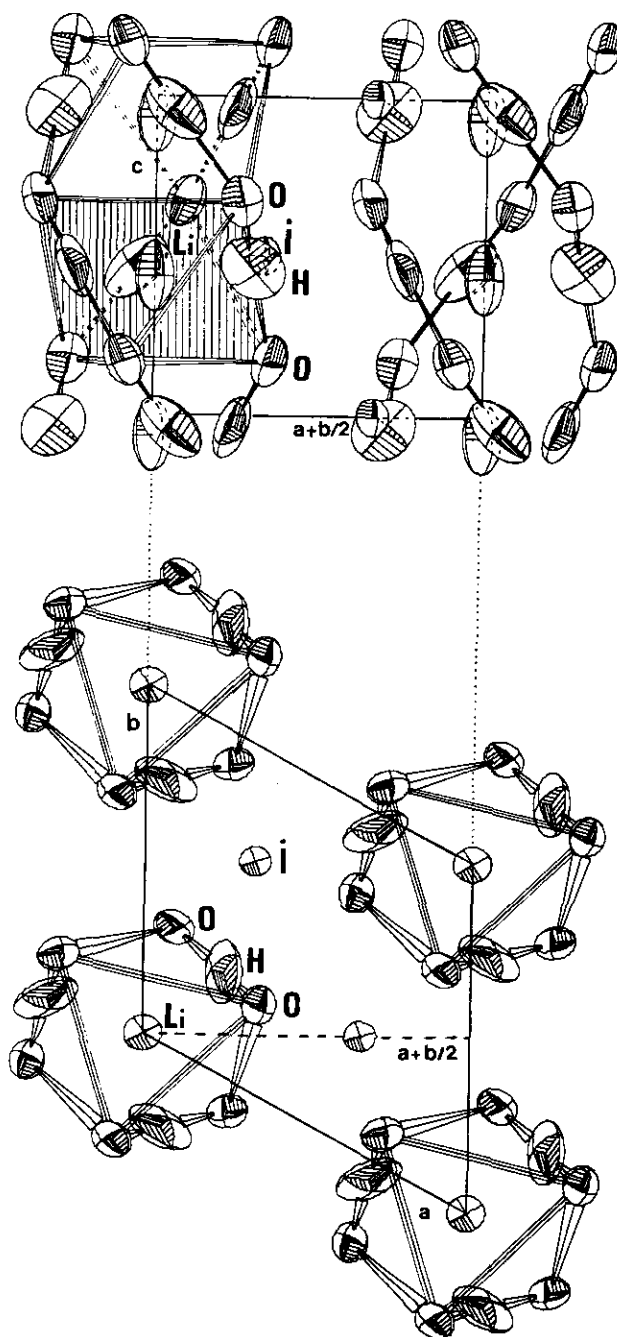| | | Temperature (K) | |
|---|---|---|---|
| | | 60 | RT |
| $IO_3$ group | I–O | 1.794(2) | 1.789(2) |
| | ⟨O–I–O | 99.24(8) | 99.46(8) |
| $IO_6$ octahedron | I═O | 2.780(2) | 2.811(2) |
| | ⟨O═I═O | 89.87(6) | 89.63(5) |
| $LiO_6$ octahedron | Li–O | 2.085(6) | 2.104(6) |
| | Li═O | 2.175(6) | 2.175(6) |
| "H bonding" | O–H | 1.33(2) | 1.29(3) |
| | O═H | 1.68(2) | 1.74(3) |
| | ⟨O–H═O | 179(2) | 180(2) |



FIG. 1. Perspective drawings of the thermal ellipsoids of atoms in $Li_{1-x}H_xIO_3$ at room temperature. The basic planes are respectively (a + b/2, c) and (a, b) in the upper and lower parts of the figure. In this last view, only octahedra $Li(H_3)O_6$ with z values between 0.1 and 0.6 are shown.

(12). Drawings are given in Fig. 1. The proton ellipsoid appears to be rather flat and the analysis of its main directions shows that the orientation of the two longest axes vary between 60 K and RT. For both temperatures the smallest axis is approximately perpendicular to the

LE ROY ET AL.

O–H=O line (97° at 60 K and 91° at RT), whereas the longest one never lies along this line. This result suggests a single-well potential between the oxygen atoms, at least from low temperature up to RT. The equivalent isotropic thermal parameter of the proton calculated from the same data is 3.7 $Å^2$ at RT, i.e., about twice the value of $B_{iso}$ refined with a poor accuracy in powder diffraction experiments (6). Concerning the other atom species, the $U_{ij}$ of I and O are quite similar for both experiments, whereas the thermal ellipsoid of Li, which is of revolution around the $c$-axis, is less elongated along $c$ when $x = 0.28$ instead of 0.34 (Ref. 6). Indeed the eccentricity which was 2.6 at RT when $x = 0.34$ becomes 1.9 when $x = 0.28$, at the same temperature. This tendency agrees with the fact that in pure lithium iodate $LiIO_3$, the Li thermal ellipsoid is rather isotropic, with $U_{33}$ slightly smaller than $U_{11}$ (13, 14). So the anisotropy of the Li thermal vibrations seems directly related to the $(1 - x)$ occupancy of the Li site.

In conclusion, the reduced atomic coordinates as well as the anisotropic thermal parameters are now precisely defined for all the atoms in $Li_{1-x}H_xIO_3$, at low temperature and at RT. The accuracy of the anisotropic thermal parameters of the proton makes the occurrence of another proton site highly improbable. Nevertheless, further experimental investigations on structural parameters above room temperature are needed for understanding the mechanism of the partial decomposition beginning at about 398 K and which is responsible for the decrease of the iodic acid mole fraction $x$ (15).

## REFERENCES

1. J. E. Ricci and I. Amron, *J. Am. Chem. Soc.* **73**, 3613 (1951).
2. S. A. Hamid, G. Kunze, and G. Reuter, *Acta Crystallogr. Sect. A* **33**, 261 (1977).
3. S. A. Hamid and G. Kunze, *Acta Crystallogr. Sect. A* **33**, 264 (1977).
4. S. A. Hamid, *Phys. Status Solidi A* **43**, K29 (1977).
5. J. Le Roy, J.-M. Crettez, E. Coquet, and J. Bouillot, *Solid State Commun.* **75**(7), 539 (1990).
6. J.-M. Crettez, E. Coquet, J. Bouillot, J. Le Roy, and J. Pannetier, *J. Solid State Chem.* **105**, 336 (1993).
7. M. S. Lehmann and F. K. Larsen, *Acta Crystallogr. Sect. A* **30**, 580 (1974).
8. P. J. Brown and J. C. Matthewman, "The Cambridge Crystallographic Subroutine Library," RAL-87-010.
9. G. E. Bacon, "Neutron Diffraction," 3rd ed. Clarendon Press, Oxford, 1979.
10. P. Wolfers, *J. Appl. Crystallogr.* **23**, 554 (1990).
11. P. J. Becker and P. Coppens, *Acta Crystallogr. Sect. A* **31**, 417 (1975).
12. J. Laugier, D.R.F.M.C., CEN Grenoble, private communication.
13. E. Coquet, J.-M. Crettez, J. Pannetier, J. Bouillot, and J.-C. Damien, *Acta Crystallogr. Sect. B* **39**, 408 (1983).
14. C. Svensson, J. Albertsson, R. Liminga, Å. Kvick, and S. C. Abrahams, *J. Chem. Phys.* **78**(12), 7343 (1983).
15. J. Bouillot, E. Coquet, J. Pannetier, and J.-M. Crettez, *Physica B* **136**, 493 (1986).