# Accurate Debye–Waller Factors of $^7$LiH and $^7$LiD by Neutron Diffraction at Three Temperatures

By Jean Pierre Vidal and Geneviève Vidal-Valat

*Groupe de Dynamique des Phases Condensées (LA CNRS 233), Université des Sciences et Techniques du Languedoc, 34060 Montpellier CEDEX, France*

## Abstract

Integrated neutron diffraction intensities of $^7$LiH and $^7$LiD single crystals were measured at 293, 160 and 93 K ($^7$LiH) or 83 K ($^7$LiD). Two different methods of analysis were used: a least-squares refinement procedure and an iterative Fourier method. The iterative process was found more efficient than the least-squares refinement in deriving the final structural parameters; high parameter correlations and strong dependencies of structural parameters on relatively weak structure factors tend to give convergency problems in the least-squares approach. The final thermal parameters from both treatments agree well with those of Calder, Cochran, Griffiths & Lowde [*J. Phys. Chem. Solids* (1962), **23**, 621–632] for the room-temperature data. Lattice-dynamical models have been used to compare the experimental and theoretical results. The agreement was found satisfactory.

## Introduction

Crystalline lithium hydride and deuteride are very interesting materials from both scientific and technological points of view. First of all they have the simplest electronic configuration of all ionic solids which has focused theoretical interest for first-principle calculations of these compounds. The lattice energy (Zhdanov & Polyakov, 1976; Norbeck & McWeeny, 1975; Kunz & Mickish, 1973), the lattice dynamics (Verble, Warren & Yarnell, 1968; Verma & Singh, 1971; Srivastata & Saraswat, 1975; Jaswal, Wolfram & Sharma, 1974; Singh, 1974), and the lattice statics (Bowman, 1974) have all been studied in the past.

Experimental investigations of thermal expansion (Smith & Leider, 1968; Anderson, Nasise, Philipson & Pretzel, 1970; Jex, 1974; Brückner, Kleinstück & Schulze, 1966), specific heat (Yates, Wostenholm & Bingham, 1974; Mel'nikova & Yakimovich, 1980), elastic properties (Haussühl & Skorczyk, 1969; Guinan & Cline, 1972; Terras, 1973; Gerlich & Smith, 1974; Vacher, Boissier & Laplaze, 1981), infrared and second-order Raman spectra (Jaswal, Sharma & Wolfram, 1972; Laplaze, 1979; Anderson & Lüty, 1983) have been undertaken at various temperatures;

attempts to correlate these observations within the terms of different lattice-dynamical models have met with some success.

Technologically, the high hydrogen content of LiH suggested it might be a promising material for laser-induced fusion work, and Wenzl (1980) showed that the efficiency of hydrogen generation by electrolysis might be improved by the storage of hydrogen in lithium.

Crystallographic work on lithium hydride has been performed by Calder, Cochran, Griffiths & Lowde (1962) at room temperature.

This paper reports on the results of a single-crystal neutron diffraction experiment on $^7$LiH and $^7$LiD at three different temperatures: 293, 160, 93 K for $^7$LiH, and 293, 160, 83 K for $^7$LiD. A complete X-ray study is under way.

## Experimental

The experiments were carried out in the same way for the two compounds. The crystals were synthesized from $^7$Li metal and hydrogen of 99% purity or deuterium of 99·5% purity. Typical boules were approximately cylindrical, 20–25 mm in diameter and 20–25 mm long with ⟨100⟩ parallel to the cylinder axis. The crystals as grown contained few low-angle grain boundaries and were slightly blue in color due to an excess of lithium in the crystal. From these boules, discs 5 mm deep were cut, and the lithium excess was removed by annealing for about 8 days under a hydrogen or deuterium atmosphere at a pressure of about 5·5 atm ($5·6 \times 10^5$ Pa) at approximately 773 K. The annealed samples were provided by Dr Mathew C. Delong (University of Utah) and were stored in anhydrous paraffin oil to prevent any damage by the atmosphere. The thermal and annealing treatments were performed to remove as completely as possible the excess lithium. The subsequent quenching reduced the extinction effects in the crystals (*cf.* Vidal, Vidal-Valat & Zeyen, 1985); the success of this treatment was indicated by their perfect transparency. From these discs parallelepipeds were cut for the neutron diffraction study.

Special precautions had to be taken in the experiments because of the high reactivity of the material;

the freshly cleaved crystals were sealed under vacuum in thin-walled quartz tubes. The diffraction measurements were carried out at the high-flux reactor of the Institut Laue–Langevin, Grenoble, on the *D*9 four-circle diffractometer at a wavelength of 0·5465 (2) Å. After an initial optical inspection, the quality of the crystals was further checked by recording some Bragg reflections using the $\omega$-scan technique. Due to the limited measuring time we chose deliberately to give priority to the measurements at 293 and 83 or 93 K, and to take only small data sets at the intermediate temperature 160 K. Data collection (~5 days/compound) was performed with one specimen of each compound; no sample deterioration was detected during this period as shown by regular checks of peak shape and intensity of 2 standard reflections, and a comparison of a small data set collected at the beginning and the end of the measurement. The temperature was maintained by a closed-loop single-stage Displex cryorefrigerator and controlled to ±1 K using an Au(0·07Fe)/Cr thermocouple (Allibon, Filhol, Lehmann, Mason & Simms, 1981). The difference in temperature for the $^7$LiH and $^7$LiD experiments arises from the X-ray studies in which we could not reach 83 K for both compounds. For the three temperatures, the cell parameters were determined by least-squares calculations using the centered $2\theta$ angles of selected reflections. They agree exactly with the values obtained in the X-ray study and they are listed in Table 1. The $\omega-2\theta$ step-scan mode (33 steps/reflection) was used with a measuring time of about 4 min per reflection. In the case of $^7$LiH, the highly incoherently scattering hydrogen provokes an absorption-like phenomenon, the magnitude of which is best determined experimentally. The determination of the corresponding linear absorption parameter was made using a simple translation system fixed to the front of the detector with additional variable slits to limit the beam to the crystal size. Several measurements were performed on platelets and on the sample itself and compared with the unweakened intensities. The result gives a 'mean' linear absorption coefficient $\mu = 0\cdot1257$ (±0·0003) mm$^{-1}$ for $^7$LiH. This value is used for the absorption correction.

An almost multiple-scattering effect was removed by setting the crystallographic and diffractometer axes differently. Moreover, the small sizes and the broad mosaic character of the thermally treated samples may further reduce any extraneous intensity effects. However, as a check, Renninger scans were performed on $^7$LiH on the 006 reflection. No significant effect was detected.

Bragg scattering of harmonics or subharmonics of the fundamental wavelength can occur in a neutron experiment. Considering the $\lambda/2$ contamination in $^7$LiH, the weak corresponding effect was evaluated theoretically to be around 0·5% on the 111 reflection. This estimation is surely higher than the true value

## Table 1. *Crystallographic characteristics*

| | $^7$LiH | $^7$LiD |
|---|---|---|
| Sample sizes (mm) | 1·956 × 1·831 × 1·304 | 1·555 × 1·505 × 1·254 |
| Cell parameters (Å) | | |
| at 300 K | 4·0752 (11) | 4·0615 (10) |
| 160 K | 4·0647 (12) | 4·0515 (11) |
| 93 K | 4·0609 (11) | |
| 83 K | | 4·0447 (12) |
| Space group | Fm3m | Fm3m |
| Linear absorption coefficient (mm$^{-1}$) | 0·1257 (±0·0003) (measured) | |
| Nuclear scattering amplitude (×10$^{-14}$ m) | * Li$^7$: −0·2197 (0·0010) †H: −0·3741 (0·0004) | * Li$^7$: −0·2197 (0·0010) ‡D: 0·6674 (0·0006) |
| $z$ | 4 | 4 |
| $\lambda$ used (Å) | 0·5465 | 0·5465 |
| Calculated density (Mg m$^{-3}$) | 0·7798 | 0·8876 |

* $^7$Li: Koester (1978).
† H: Koester (1975).
‡ D: Koester (1977).

because of the short wavelength used and the large mosaic spread of the samples.

## Data analysis

Lorentz, background and counter dead-time corrections were applied on the observed intensities. The background was calculated using the method of Lehmann & Larsen (1974). Effective path-length values were computed for all reflections for both samples to correct for absorption ($^7$LiH only) and extinction effects; absorption corrections of $^7$LiD were estimated to be negligible so no correction was applied. For $^7$LiH the data were corrected for absorption using a Gaussian integration method (Busing & Levy, 1957). Thermal-diffuse-scattering corrections were made using the procedure of de With, Harkema & Feil (1976) on neutrons having a speed exceeding the velocity of sound in the crystal (Willis & Pryor, 1975). The elastic constants of Terras (1973) were used for $^7$LiH at 293, 160 and 93 K. The elastic constants of LiD were only known at room temperature (Haussühl & Skorczyk, 1969). For the lower temperatures, they were estimated from the LiH values on the basis of Haussühl & Skorczyk's observations. The calculated corrections were found to be the greatest for room-temperature $^7$LiD measurements in which they lay between $\alpha_{111} = 0\cdot002$ and $\alpha_{800} = 0\cdot092$. This latter value is of the same order of magnitude as the corresponding standard deviation $[\sigma(F_o)/F_o]$.

Two different types of refinement were employed in the data analysis. First, the latest version of *LINEX* (Becker & Coppens, 1975) was used, which allows the treatment of extinction in terms of different models, together with harmonic thermal parameters and a scale factor. The scattering lengths are those of Koester (1978) for $^7$Li, of Koester (1975) for hydrogen and of Koester (1977) for deuterium; they were not refined during the analysis. The weighting scheme is inversely proportional to the variance of the reflection intensity and the ignorance factor is estimated

at 1% for all data sets. The refinements were based on $F_{hkl}$.

A second data analysis was carried out using the iterative Fourier method of Vahvaselkä & Kurki-Suonio (1975) to determine the isotropic thermal parameters and the scale factor (Vidal-Valat 1975). This procedure is based on the criterion that the optimum values of the parameters are reached when the deviation of the experimental density from the model, *i.e.* the difference Fourier series, is as smooth as possible at the atomic centres (Kurki-Suonio & Meisalo, 1966). In this iterative Fourier method, no extinction corrections are included and the intensities must be corrected beforehand. In the present work, the extinction corrections given by the *LINEX* program were used.

The reflections with obviously erroneous values due to shadowing by the Displex equipment were discarded. The profile of each reflection was recorded in the course of the experiment and was used as a guide to choose the best reflections for further analysis. Our studies on compounds with high symmetry and a few atoms per unit cell (Vidal-Valat, Vidal & Kurki-Suonio, 1978; Vidal-Valat, Vidal, Zeyen & Kurki-Suonio, 1980; Vidal, Vidal-Valat, Galtier & Kurki-Suonio, 1981, 1982) lead us to the working assumption that anomalous features in the profiles indicate unreliable reflections independent of their integrated intensities. The choice of suitable reflections is then based on the shape of different profiles of the same reflection taken at least three times. All reflections with symmetric profiles of the expected full width at half-height and full width at background were selected first. Since first refinements clearly showed the extinction to be isotropic, the observed structure factor of a reflection was taken to be the mean of the remaining symmetry-related reflections and was used in the final refinements. However, for some reflections, and particularly the high-angle reflections, the count rates obtained were very low. Some intensities were not sufficiently greater than the background to give accurate measurements. This effect is more important in $^7$LiH than in $^7$LiD (see below). In these special cases, the selection of the reflections was carried out in two steps. Firstly, the most regular profile among the reflections was chosen for a further analysis. The iterative Fourier procedure was then used with which it is possible to treat each reflection independently. If the introduced reflection was seen to be internally consistent with the entire data set, it was retained for the final analysis. Otherwise the reflection was excluded from the final analysis and a visually discarded equivalent one might be used if its test of internal consistency was positive (Kurki-Suonio & Ruuskanen, 1971). However, almost all reflections with sin $\theta/\lambda \geq 1$ Å$^{-1}$ are very weak and the cut-off for the refinement was set to 1 Å$^{-1}$ accordingly.

Simple structures of high symmetry (like the rock-salt structure of $^7$LiH and $^7$LiD) have no free positional, and only very few thermal, parameters. On the other hand, the number of independent reflections is small and, moreover, they group into subsets which contain similar information on the structural parameters. There are two such subsets in $^7$LiH and $^7$LiD: *hkl* with *h*, *k*, *l* all even, and *hkl* with *h*, *k*, *l* all odd. Due to the similar magnitude of the scattering length of $^7$Li and H, the contributions of these atoms cancel out to some extent for the odd reflections. The similarity of information in each of the subsets causes correlation problems in the least-squares refinements: scale and extinction factors are highly correlated with the thermal parameters. These correlations are less of a problem if the iterative Fourier method is used. The correlation problem is aggravated in the case of $^7$LiH by the fact that one subset is almost extinguished. Straightforward inclusion of all these weak, and therefore less precisely determined, reflections, which in principle carry valuable information on the difference in the thermal motions of $^7$Li and H, might lead the least-squares refinement to take account mainly of the errors; slight systematic errors will give rise to considerable changes in the refined thermal parameters and care has to be taken to obtain a suitable set of reflection intensities and their proper standard deviations. The selection procedure described above was found to be very efficient in this case. A routine treatment including all measured data without careful checking of profiles resulted in strong correlation effects and eventually ended up in a different and clearly wrong minimum in *R*-factor space indicated by the temperature dependency of the thermal parameters in the case of $^7$LiH.

The results of the least-squares refinements are listed in Table 2. The extinction model leading to the lowest *R* factor is type I, characterized by a Gaussian mosaic parameter *g*. Table 3 gives the experimental structure factors, their relative errors $\sigma(F_o)/F_o$, where $\sigma(F_o)$ is the estimated standard deviation of $F_o$, and extinction coefficients.

The same experimental data were used in the least-squares procedure and in the iterative process. The results of the iterative procedure are listed in Table 4.

In order to assess the accuracy of the thermal and scale parameters obtained, the calculation was repeated with different cut-offs ranging from sin $\theta/\lambda = 0.5$ up to 1 Å$^{-1}$. No particular trend could be observed in the dependence of the *B* values on the cut-off and the asymptotic thermal-parameter values are reached largely before the cut-off 1 Å$^{-1}$ in sin $\theta/\lambda$. A similar study was also made for the least-squares treatment. It must be said that the asymptotic behavior is reached more rapidly with the iterative process than with the least-squares refinement. Moreover, the iterative Fourier method handles the problem of weak intensities better than the least-squares refinement.

Table 2. *Least-squares-refined parameters of $^7$LiD and $^7$LiH at 293, 160, 83 or 93 K*

|  | $^7$LiD | $^7$LiD | $^7$LiD | $^7$LiH | $^7$LiH | $^7$LiH |
|---|---|---|---|---|---|---|
|  | 293 K | 160 K | 83 K | 293 K | 160 K | 93 K |
| $R$ | 0·012 | 0·006 | 0·008 | 0·008 | 0·008 | 0·006 |
| $wR$ | 0·014 | 0·008 | 0·010 | 0·008 | 0·010 | 0·006 |
| $U_{Li}(Å^2)$ | 0·0133 (2) | 0·0087 (1) | 0·0075 (1) | 0·0151 (2) | 0·0097 (3) | 0·0081 (1) |
| $U_{D\,or\,H}(Å^2)$ | 0·0183 (2) | 0·0151 (1) | 0·0139 (1) | 0·0217 (2) | 0·0197 (4) | 0·0188 (2) |
| Scale factor, $k$ | 12.2 (1) | 12.14 (7) | 11·96 (7) | 14.49 (9) | 14·6 (2) | 14·4 (1) |
| Extinction parameter, $g$ ($\times 10^4$) | 0·19 (1) | 0·19 (1) | 0·168 (9) | 0·49 (2) | 0·47 (4) | 0·44 (3) |
| Lowest extinction coefficient, $y$ | 0·687 | 0·681 | 0·702 | 0·622 | 0·622 | 0·715 |
|  | (111) | (111) | (111) | (200) | (200) | (200) |

This advantage is due to the decrease of correlation effects in the case of the iterative procedure caused by the different weighting schemes of the two procedures. Using only checked observations, the least-squares method gives thermal parameters in good agreement with the iterative Fourier approach; the results for both methods are presented in Table 4 and Fig. 1 gives the temperature dependence of the thermal parameters. The differences for the two approaches are less than 1% and are always less than the experimental error.

## Lattice dynamics consideration

To compare the experimental results with theory, we consider lattice-dynamical models for $^7$LiH and $^7$LiD.

The vibrations of an atom in a crystal lattice, moving in a harmonic potential field, can be characterized by a symmetric tensor **U**, with six independent components. The mean-square amplitude of vibration in the direction of a unit vector **1** with components $l_\alpha$ is given by (Cruickshank, 1956):

$$\langle u^2 \rangle = \sum_{\alpha\beta} \langle u_\alpha u_\beta \rangle l_\alpha l_\beta.$$

To calculate the quantities $\langle u_\alpha u_\beta \rangle$, we adopt the formulae and notations given by Vidal *et al.* (1981) in
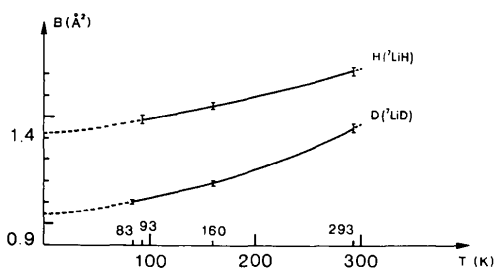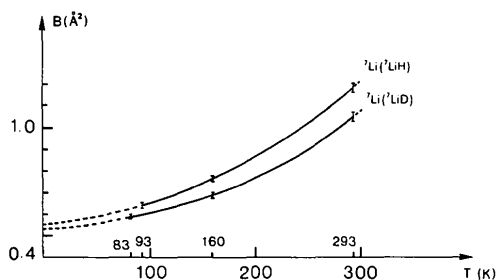


Fig. 1. Temperature dependence of the thermal parameters.

the Appendix. Not having at our disposal a complete set of experimental frequencies and polarization vectors, measured by inelastic neutron diffraction, we have divided the calculations into two parts, acoustic and optical.

### (1) *Acoustic contribution*

We take a spherical volume $V$ centered on the center of the Brillouin zone ($\Gamma$ point). The acoustic contribution from this volume is then, in the Debye approximation:

$$\frac{\hbar v_m}{(2\pi)^3} |K_m|^2 \sum_a \int [1/C_a(\Omega)] t_{\alpha,a}(\Omega) t^*_{\beta,a}(\Omega)$$

$$\times \varphi[\hbar C_a(\Omega) K_m / K_b T]\, d\Omega.$$

$v_m$ is the cell volume. $K_m$ is the radius of the sphere chosen to ensure the correct number of modes (Willis & Pryor, 1975). $C_a(\Omega)$ is one of the three velocities of sound in the direction $\Omega$; $t_{\alpha,a}(\Omega)$ are the corresponding components of the polarization vectors. The function $\varphi$ is defined by:

$$\varphi(x) = \frac{1}{x^2} \int_0^x \{[1/(e^u - 1)] + \tfrac{1}{2}\} u \, du.$$

50 points are taken in the reduced Brillouin zone which is 1/16 of the total zone. The experimental elastic constants at room temperature for $^7$LiD and $^7$LiH are taken from Haussühl & Skorczyk (1969). At low temperatures those of Terras (1973) are considered for $^7$LiH. Concerning the $^7$LiD elastic constants at low temperatures, their values were estimated from the $^7$LiH values on the basis of Haussühl & Skorczyk's observations.

### (2) *Optical contribution*

The thermal mean-square displacements can be calculated as a sum in reciprocal space:

$$u_{\alpha\beta}(J) = \sum_{K,S} \frac{\hbar}{NM_J} \cdot \frac{1}{\omega(K,S)} \text{Re}\,[ V_{J,\alpha}(K,S) V^*_{J,\beta}(K,S)]$$

$$\times \{[\exp(\hbar\omega / K_b T) - 1]^{-1} + \tfrac{1}{2}\},$$

where $J = 1, 2, \ldots, g$ atoms in the unit cell, Re = real part of [ ], and $\alpha = 1, 2, 3, \beta = 1, 2, 3$ refer to Cartesian axes. $M_J$ is the mass of atom $J$ and $V_{J,\alpha}(\mathbf{K}, S)$ are

Table 3. *Experimental ($F_o$) and calculated ($F_c$) structure factors of $^7$LiH and $^7$LiD with relative deviations [$\sigma(F_o)/F_o$], extinction parameters ($y$) and b ($=2\sin\theta/\lambda$)*

d: discarded; u: unobserved

**$^7$LiH (293 K)**

| h k l | b | $F_c$ | $F_o$ | $\sigma(F_o)/F_o$ | y |
|---|---|---|---|---|---|
| 1 1 1 | 0·42502 | 0·5520 | 0·5621 | 0·011 | 0·967 |
| 2 0 0 | 0·49077 | -2·1675 | -2·1712 | 0·004 | 0·622 |
| 2 2 0 | 0·69406 | -1·9788 | -1·9739 | 0·004 | 0·780 |
| 3 1 1 | 0·81386 | 0·4054 | 0·4084 | 0·021 | 0·988 |
| 2 2 2 | 0·85004 | -1·8070 | -1·8090 | 0·005 | 0·844 |
| 4 0 0 | 0·98155 | -1·6504 | -1·6464 | 0·005 | 0·889 |
| 3 3 1 | 1·06962 | 0·2920 | 0·2836 | 0·040 | 0·996 |
| 4 2 0 | 1·09740 | -1·5078 | -1·5129 | 0·006 | 0·910 |
| 4 2 2 | 1·20214 | -1·3778 | -1·3621 | 0·007 | 0·931 |
| 3 3 3 | 1·27507 | 0·2047 | 0·2034 | 0·090 | 0·998 |
| 5 1 1 | 1·27507 | 0·2047 | 0·2115 | 0·093 | 0·998 |
| 4 4 0 | 1·38812 | -1·1514 | -1·1607 | 0·011 | 0·959 |
| 5 3 1 | 1·45173 | 0·1381 | 0·1367 | 0·190 | 0·999 |
| 4 4 2 | 1·47232 | -1·0529 | -1·0517 | 0·014 | 0·962 |
| 6 0 0 | 1·47232 | -1·0529 | -1·0625 | 0·014 | 0·966 |
| 6 2 0 | 1·55196 | -0·9630 | -0·9668 | 0·016 | 0·971 |
| 5 3 3 | 1·60911 | u 0·0877 | | | |
| 6 2 2 | 1·62771 | -0·8811 | -0·8771 | 0·020 | 0·973 |
| 4 4 4 | 1·70009 | -0·8065 | -0·8024 | 0·025 | 0·980 |
| 5 5 1 | 1·75241 | u 0·0500 | | | |
| 7 1 1 | 1·75241 | u 0·0500 | | | |
| 6 4 0 | 1·76951 | -0·7380 | -0·7324 | 0·026 | 0·982 |
| 6 4 2 | 1·83631 | -0·6757 | -0·6705 | 0·030 | 0·987 |
| 5 5 3 | 1·88485 | u 0·0222 | | | |
| 7 3 1 | 1·88485 | u 0·0222 | | | |
| 8 0 0 | 1·96309 | -0·5668 | -0·5765 | 0·038 | 0·991 |

**$^7$LiD (293 K)**

| h k l | b | $F_c$ | $F_o$ | $\sigma(F_o)/F_o$ | y |
|---|---|---|---|---|---|
| 1 1 1 | 0·42646 | -3·3620 | -3·3445 | 0·003 | 0·687 |
| 2 0 0 | 0·49243 | 1·6446 | 1·6017 | 0·006 | 0·917 |
| 2 2 0 | 0·69640 | 1·4877 | 1·5046 | 0·008 | 0·948 |
| 3 1 1 | 0·81660 | -2·8555 | -2·8969 | 0·005 | 0·858 |
| 2 2 2 | 0·85291 | 1·3452 | 1·3372 | 0·010 | 0·965 |
| 4 0 0 | 0·98486 | 1·2157 | 1·1974 | 0·012 | 0·976 |
| 3 3 1 | 1·07322 | -2·4263 | -2·4460 | 0·007 | 0·907 |
| 4 2 0 | 1·10110 | 1·0981 | 1·1029 | 0·016 | 0·979 |
| 4 2 2 | 1·20620 | 0·9914 | 0·9724 | 0·020 | 0·986 |
| 3 3 3 | 1·27937 | -2·0626 | -2·0577 | 0·010 | 0·945 |
| 5 1 1 | 1·27937 | -2·0626 | -2·0673 | 0·010 | 0·946 |
| 4 4 0 | 1·39280 | 0·8066 | 0·7948 | 0·034 | 0·991 |
| 5 3 1 | 1·45662 | -1·7543 | -1·7626 | 0·015 | 0·965 |
| 4 4 2 | 1·47729 | 0·7269 | 0·7312 | 0·040 | 0·993 |
| 6 0 0 | 1·47729 | 0·7269 | 0·7098 | 0·040 | 0·994 |
| 6 2 0 | 1·55720 | 0·6546 | 0·6836 | 0·043 | 0·995 |
| 5 3 3 | 1·61454 | -1·4927 | -1·4762 | 0·020 | 0·976 |
| 6 2 2 | 1·63320 | 0·5890 | 0·5862 | 0·050 | 0·996 |
| 4 4 4 | 1·70582 | 0·5297 | 0·5518 | 0·054 | 0·997 |
| 5 5 1 | 1·75832 | -1·2708 | -1·2626 | 0·024 | 0·982 |
| 7 1 1 | 1·75832 | -1·2708 | -1·2655 | 0·024 | 0·983 |
| 6 4 0 | 1·77548 | 0·4759 | 0·4651 | 0·067 | 0·998 |
| 6 4 2 | 1·84250 | 0·4272 | 0·4220 | 0·075 | 0·998 |
| 5 5 3 | 1·89121 | -1·0824 | -1·0791 | 0·029 | 0·988 |
| 7 3 1 | 1·89121 | -1·0824 | -1·0866 | 0·030 | 0·988 |
| 8 0 0 | 1·96972 | 0·3433 | 0·3596 | 0·095 | 0·999 |

**$^7$LiH (160 K)**

| h k l | b | $F_c$ | $F_o$ | $\sigma(F_o)/F_o$ | y |
|---|---|---|---|---|---|
| 1 1 1 | 0·42612 | 0·5454 | 0·5510 | 0·013 | 0·969 |
| 2 0 0 | 0·49204 | -2·2008 | -2·1960 | 0·004 | 0·622 |
| 2 2 0 | 0·69585 | -2·0406 | -2·0685 | 0·004 | 0·776 |
| 3 1 1 | 0·81596 | 0·3817 | 0·3845 | 0·026 | 0·992 |
| 2 2 2 | 0·85224 | -1·8930 | -1·8788 | 0·005 | 0·836 |
| 4 0 0 | 0·98408 | -1·7572 | -1·7356 | 0·005 | 0·845 |
| 3 3 1 | 1·07238 | d 0·2523 | | | |
| 4 2 0 | 1·10024 | -1·6319 | -1·6453 | 0·006 | 0·900 |
| 4 2 2 | 1·20525 | -1·5164 | -1·5092 | 0·007 | 0·908 |
| 3 3 3 | 1·27836 | d 0·1507 | | | |
| 5 1 1 | 1·27836 | 0·1507 | 0·1496 | 0·180 | 0·999 |
| 4 4 0 | 1·39170 | -1·3116 | -1·2950 | 0·010 | 0·940 |
| 5 3 1 | 1·45548 | u 0·0717 | | | |
| 4 4 2 | 1·47612 | -1·2209 | -1·2340 | 0·012 | 0·956 |
| 6 0 0 | 1·47612 | -1·2209 | -1·2362 | 0·012 | 0·945 |
| 6 2 0 | 1·55597 | -1·1370 | -1·1167 | 0·014 | 0·964 |
| 5 3 3 | 1·61326 | u 0·0109 | | | |
| 6 2 2 | 1·63192 | -1·0596 | -1·0618 | 0·016 | 0·968 |
| 4 4 4 | 1·70448 | -0·9879 | -0·9922 | 0·020 | 0·972 |
| 5 5 1 | 1·75694 | u -0·0351 | | | |
| 7 1 1 | 1·75694 | u -0·0351 | | | |
| 6 4 0 | 1·77408 | -0·9216 | -0·9242 | 0·002 | 0·975 |
| 6 4 2 | 1·84105 | -0·8603 | -0·8718 | 0·025 | 0·978 |
| 5 5 3 | 1·88972 | u -0·0694 | | | |
| 7 3 1 | 1·88972 | u -0·0694 | | | |
| 8 0 0 | 1·96816 | -0·7509 | -0·7435 | 0·030 | 0·986 |

**$^7$LiD (160 K)**

| h k l | b | $F_c$ | $F_o$ | $\sigma(F_o)/F_o$ | y |
|---|---|---|---|---|---|
| 1 1 1 | 0·42750 | -3·4053 | -3·3960 | 0·004 | 0·681 |
| 2 0 0 | 0·49363 | 1·6648 | 1·6242 | 0·007 | 0·917 |
| 2 2 0 | 0·69810 | 1·5241 | 1·5174 | 0·009 | 0·938 |
| 3 1 1 | 0·81860 | -2·9929 | -3·0057 | 0·005 | 0·845 |
| 2 2 2 | 0·85500 | 1·3942 | 1·4013 | 0·012 | 0·962 |
| 4 0 0 | 0·98726 | 1·2744 | 1·2698 | 0·012 | 0·973 |
| 3 3 1 | 1·07585 | -2·6324 | -2·6609 | 0·007 | 0·897 |
| 4 2 0 | 1·10379 | 1·1638 | 1·1694 | 0·016 | 0·979 |
| 4 2 2 | 1·20915 | 1·0618 | 1·0671 | 0·020 | 0·984 |
| 3 3 3 | 1·28249 | -2·3171 | -2·3244 | 0·010 | 0·931 |
| 5 1 1 | 1·28249 | -2·3171 | -2·3189 | 0·010 | 0·932 |
| 4 4 0 | 1·39620 | 0·8612 | 0·8691 | 0·033 | 0·989 |
| 5 3 1 | 1·46018 | -2·0411 | -2·0380 | 0·015 | 0·953 |
| 4 4 2 | 1·48090 | 0·8014 | 0·7956 | 0·039 | 0·992 |
| 6 0 0 | 1·48090 | 0·8014 | 0·7956 | 0·039 | 0·992 |
| 6 2 0 | 1·56100 | d 0·7280 | | | |
| 5 3 3 | 1·61848 | -1·7994 | -1·7988 | 0·017 | 0·965 |
| 6 2 2 | 1·63719 | 0·6603 | 0·6620 | 0·047 | 0·995 |
| 4 4 4 | 1·70999 | 0·5981 | 0·6131 | 0·051 | 0·996 |
| 5 5 1 | 1·76262 | -1·5876 | -1·5758 | 0·020 | 0·972 |
| 7 1 1 | 1·76262 | -1·5876 | -1·5972 | 0·020 | 0·975 |
| 6 4 0 | 1·77982 | 0·5409 | 0·5449 | 0·059 | 0·997 |
| 6 4 2 | 1·84700 | d 0·4883 | | | |
| 5 5 3 | 1·89583 | -1·4019 | -1·3924 | 0·021 | 0·980 |
| 7 3 1 | 1·89583 | -1·4019 | -1·3948 | 0·023 | 0·980 |
| 8 0 0 | 1·97453 | 0·3956 | 0·3921 | 0·090 | 0·999 |

**$^7$LiH (93 K)**

| h k l | b | $F_c$ | $F_o$ | $\sigma(F_o)/F_o$ | y |
|---|---|---|---|---|---|
| 1 1 1 | 0·42652 | 0·5447 | 0·5492 | 0·014 | 0·971 |
| 2 0 0 | 0·49250 | -2·2125 | -2·2039 | 0·004 | 0·715 |
| 2 2 0 | 0·69650 | -2·0626 | -2·0821 | 0·004 | 0·784 |
| 3 1 1 | 0·81672 | 0·3780 | 0·3810 | 0·029 | 0·993 |
| 2 2 2 | 0·85304 | -1·9241 | -1·9172 | 0·005 | 0·842 |
| 4 0 0 | 0·98500 | -1·7960 | -1·7978 | 0·005 | 0·883 |
| 3 3 1 | 1·07338 | 0·2445 | 0·2514 | 0·052 | 0·998 |
| 4 2 0 | 1·10127 | -1·6775 | -1·6765 | 0·006 | 0·884 |
| 4 2 2 | 1·20638 | -1·5678 | -1·5573 | 0·007 | 0·919 |
| 3 3 3 | 1·27956 | 0·1384 | 0·1338 | 0·188 | 0·999 |
| 5 1 1 | 1·27956 | 0·1384 | 0·1368 | 0·190 | 0·999 |
| 4 4 0 | 1·39300 | -1·3722 | -1·3682 | 0·010 | 0·939 |
| 5 3 1 | 1·45684 | u 0·0546 | | | |
| 4 4 2 | 1·47750 | -1·2850 | -1·2776 | 0·011 | 0·950 |
| 6 0 0 | 1·47750 | -1·2850 | -1·2933 | 0·011 | 0·955 |
| 6 2 0 | 1·55743 | -1·2041 | -1·2056 | 0·013 | 0·960 |
| 5 3 3 | 1·61477 | u -0·0108 | | | |
| 6 2 2 | 1·63344 | -1·1291 | -1·1312 | 0·015 | 0·967 |
| 4 4 4 | 1·70608 | -1·0594 | -1·0538 | 0·020 | 0·970 |
| 5 5 1 | 1·75858 | u -0·0612 | | | |
| 7 1 1 | 1·75858 | u -0·0612 | | | |
| 6 4 0 | 1·77574 | -0·9947 | -1·0036 | 0·021 | 0·973 |
| 6 4 2 | 1·84277 | -0·9345 | -0·9310 | 0·024 | 0·976 |
| 5 5 3 | 1·89149 | u -0·0994 | | | |
| 7 3 1 | 1·89149 | u -0·0994 | | | |
| 8 0 0 | 1·97001 | -0·8265 | -0·8306 | 0·028 | 0·984 |

**$^7$LiD (83 K)**

| h k l | b | $F_c$ | $F_o$ | $\sigma(F_o)/F_o$ | y |
|---|---|---|---|---|---|
| 1 1 1 | 0·42823 | -3·4187 | -3·4193 | 0·003 | 0·702 |
| 2 0 0 | 0·49447 | 1·6730 | 1·6489 | 0·006 | 0·922 |
| 2 2 0 | 0·69929 | 1·5392 | 1·5636 | 0·008 | 0·943 |
| 3 1 1 | 0·81999 | -3·0366 | -3·0373 | 0·004 | 0·855 |
| 2 2 2 | 0·85645 | 1·4149 | 1·4245 | 0·009 | 0·965 |
| 4 0 0 | 0·98895 | 1·2996 | 1·2890 | 0·011 | 0·975 |
| 3 3 1 | 1·07768 | -2·6991 | -2·6874 | 0·006 | 0·908 |
| 4 2 0 | 1·10568 | 1·1926 | 1·2014 | 0·014 | 0·980 |
| 4 2 2 | 1·21121 | 1·0934 | 1·0878 | 0·018 | 0·985 |
| 3 3 3 | 1·28468 | -2·4011 | -2·4298 | 0·009 | 0·933 |
| 5 1 1 | 1·28468 | -2·4011 | -2·3838 | 0·009 | 0·934 |
| 4 4 0 | 1·39858 | 0·9161 | 0·9015 | 0·029 | 0·989 |
| 5 3 1 | 1·46267 | -2·1376 | -2·1532 | 0·011 | 0·954 |
| 4 4 2 | 1·48342 | 0·8370 | 0·8373 | 0·034 | 0·993 |
| 6 0 0 | 1·48342 | 0·8370 | 0·8389 | 0·034 | 0·993 |
| 6 2 0 | 1·56366 | 0·7638 | 0·7529 | 0·041 | 0·994 |
| 5 3 3 | 1·62124 | -1·9046 | -1·8993 | 0·015 | 0·965 |
| 6 2 2 | 1·63999 | 0·6961 | 0·6906 | 0·042 | 0·995 |
| 4 4 4 | 1·71291 | 0·6333 | 0·6359 | 0·047 | 0·996 |
| 5 5 1 | 1·76563 | -1·6984 | -1·7033 | 0·018 | 0·975 |
| 7 1 1 | 1·76563 | -1·6984 | -1·7006 | 0·018 | 0·973 |
| 6 4 0 | 1·78285 | 0·5753 | 0·5675 | 0·055 | 0·997 |
| 6 4 2 | 1·85015 | 0·5216 | 0·5272 | 0·060 | 0·998 |
| 5 5 3 | 1·89906 | -1·5158 | -1·5152 | 0·020 | 0·980 |
| 7 3 1 | 1·89906 | -1·5158 | -1·5020 | 0·021 | 0·980 |
| 8 0 0 | 1·97790 | 0·4262 | 0·4453 | 0·076 | 0·998 |

Table 4. *Comparison of the thermal parameters* (Å$^2$) *of $^7$LiD and $^7$LiH, obtained by different methods*

| | $^7$LiD | | | $^7$LiH | | |
|---|---|---|---|---|---|---|
| | 293 K | 160 K | 83 K | 293 K | 160 K | 93 K |
| *LINEX* | | | | | | |
| $B_{Li}$ | 1·048 | 0·684 | 0·591 | 1·191 | 0·766 | 0·640 |
| $\sigma(B_{Li})$ | (0·016) | (0·011) | (0·008) | (0·016) | (0·024) | (0·008) |
| $B_{D \text{ or } H}$ | 1·449 | 1·188 | 1·100 | 1·711 | 1·553 | 1·485 |
| $\sigma(B_{D \text{ or } H})$ | (0·016) | (0·010) | (0·008) | (0·016) | (0·034) | (0·016) |
| Iterative method | | | | | | |
| $B_{Li}$ | 1·037 | 0·681 | 0·592 | 1·195 | 0·761 | 0·643 |
| $B_{D \text{ or } H}$ | 1·439 | 1·179 | 1·101 | 1·715 | 1·550 | 1·483 |
| Calder *et al.* (1962) | | | | | | |
| $B_{Li}$ | | | | 1·22 ± 0·10 | | |
| $B_H$ | | | | 1·80 ± 0·03 | | |

the components of the polarization vectors, obeying the orthogonality relations:

$$\sum_{J\alpha} V_{J\alpha}(\mathbf{K}, S) V_{J\alpha}^*(\mathbf{K}, S') = \delta(S, S')$$

$$\sum_{S} V_{I\alpha}(\mathbf{K}, S) V_{J\beta}^*(\mathbf{K}, S) = \delta(I, J)\delta(\alpha, \beta).$$

$V_{J\beta}^*(\mathbf{K}, S)$ is the conjugate transpose of $V_{J\beta}(\mathbf{K}, S)$ $S = 1, 2, \ldots, 3g$ labels the different lattice modes of wavevector $\mathbf{K}$ and $N$ is the number of cells in the crystal. The work of Verble *et al.* (1968) gives the calculated dispersion curves of $^7$LiH and $^7$LiD and the different frequencies of the optic modes along the main directions $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ only. The lack of polarization vectors imposes the taking of characteristic points of the Brillouin zone such as $\Gamma$, $X$, $L$ and $K$ at 293 K, for which it is possible to derive the form of the polarization vectors.

Finally we add the two parts, acoustic and optic, to calculate the atomic mean-square amplitudes. The results are listed in Table 5.

The main difficulty in determining a simple lattice-dynamical model results from the lack of experimental data concerning both elastic constants and frequency magnitudes.

## Discussion

### (1) *Theoretical and experimental Debye-Waller factors*

To check whether our approximation and our model give physically meaningful results we have calculated the Debye-Waller coefficients at high temperatures $(T > \theta_D/2)$ and we observe that the ratio of $^7$Li to H or D Debye-Waller factors tends to 1 as indicated by Willis & Pryor (1975) and Huiszoon & Groenewegen (1972). A calculation at the 0 K point shows that the agreement between the calculated and the extrapolated experimental values fits to about 2 to 5%. In the light of the theoretical calculations, it seems that the main reason for the difference between the $B$ values of $^7$LiH and $^7$LiD is due to the change in mass. The change in force constants is generally

due to different electronic properties when comparing two compounds. In the case of $^7$LiH and $^7$LiD, the electronic configuration is exactly the same and the only difference is the addition of one neutron in $^7$LiD. There is therefore little possibility of seeing an important difference in force constants.

On the other hand, all properties connected with the mass and hence the vibration amplitudes must be affected by the isotope exchange. In our compounds, this is certainly the largest observable effect.

### (2) *Thermal-expansion coefficient*

The temperature dependence of the lattice parameters of $^7$LiH and $^7$LiD has already been studied by Smith & Leider (1968). The values found in our work are smaller than the lattice parameters of Smith *et al.* However, they reported that their crystals contained an excess of lithium and also that the cell parameters changed with the sample investigated. They argue that the presence of impurities enlarges the lattice parameters. The same observation was reported by Brückner *et al.* (1966).

Nevertheless, the thermal expansions obtained from the temperature dependency are in quite good agreement with those given by Smith & Leider (1968).

### (3) *Comparison with previous neutron diffraction results*

The earlier neutron diffraction results on LiH (natural Li) at room temperature of Calder *et al.* (1962) are shown in Table 4. The main difference between their and our studies comes from the presence of $^6$Li in their sample (natural Li contains ~7·46% $^6$Li). Our samples were therefore less absorbing and, moreover, the experimental determination of the absorption coefficient and the use of a physically meaningful extinction model should give better corrections than those of Calder *et al.* (1962). In addition, the $^7$Li neutron scattering length is now well known and does not have to be considered as a supplementary variable in our refinements. While the refinement value of the lithium temperature factor is in very good agreement with the result of Calder *et al.*, their value for H is larger than ours by 5%. A comparison of the structure factors measured by Calder *et al.* and ours, shows that the intensity of the reflection with $h$, $k$, $l$ all even is always greater by an almost constant value when compared with ours. This might be due to uncertainties in Calder's work arising from empirical corrections.

Only a few experimental studies of $^7$LiH and $^7$LiD with neutrons or X-rays have been undertaken in the last fifteen years, probably because of the reactivity and consequent experimental difficulties. This work represents the neutron part of a combined neutron-X-ray study which will deal with the electronic charge distribution around each ion in detail. To assess the true nature of the electronic deformations, a neutron

Table 5. *Comparison between lattice-dynamical and experimental Debye–Waller values*

| | Room temperature | | | 160 K | | | 83 K ($^7$LiD); 93 K ($^7$LiH) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Lattice dynamics | | | Lattice dynamics | | | Lattice dynamics | | |
| $^7$LiD | Acoustic part | Optic part | Iterative method | Acoustic part | Optic part | Iterative method | Acoustic part | Optic part | Iterative method |
| $B_{Li}$ (Å$^2$) | 0·887 | 0·223 | | 0·540 | 0·145 | | 0·450 | 0·143 | |
| | 1.110 | | 1·037 | 0·685 | | 0·681 | 0·593 | | 0·592 |
| $B_D$ (Å$^2$) | 0·887 | 0·481 | | 0·540 | 0·659 | | 0·450 | 0·651 | |
| | 1.368 | | 1·439 | 1·199 | | 1·179 | 1·101 | | 1·101 |
| **$^7$LiH** | | | | | | | | | |
| $B_{Li}$ (Å$^2$) | 1·078 | 0·161 | | 0·670 | 0·114 | | 0·541 | 0·114 | |
| | 1·239 | | 1·195 | 0·784 | | 0·761 | 0·655 | | 0·643 |
| $B_H$ (Å$^2$) | 1·078 | 0·562 | | 0·670 | 0·887 | | 0·541 | 0·884 | |
| | 1·640 | | 1·715 | 1·557 | | 1·550 | 1·425 | | 1·483 |

study of the thermal motions and their temperature dependency was found to be extremely useful.

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