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Equation of state of lithium deuteride from neutron diffraction under high pressure

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Time-of-flight neutron-diffraction spectra of powder samples of ^{7}LiD have been recorded at 300 K, up to 10 GPa at the ISIS spallation source. The experimental setup consists of a 2.5-MN hydraulic press, 50 kg in mass, acting on a toroidal anvil cell. This allows compression of 100-mm^3 samples to over 10 GPa, with better stress homogeneity than flat-anvil devices. The equation of state of ^{7}LiD has been related to the NaCl pressure scale with a precision of 1.5×10^{-3} on the volume variation under pressure. Comparison of existing calculations with the present data shows variable agreement, depending on the calculational hypotheses. Reassessment of the divergent theoretical estimates for the pressure of band crossing in lithium hydrides reconciles them to a common prediction of about 180 GPa for the pressure of semimetallization. However, the present work cannot reduce the wide separation of the estimates for the $B1\rightarrow B2$ structural-transition pressure.

I. INTRODUCTION

Lithium hydrides form an interesting series where isotopic substitution from ^{6}LiH up to ^{7}LiT causes a very large relative variation of mass. In this respect, they are comparable to the hydrogen (H, D, T) or helium (^{3}He, ^{4}He) families. Because of the low masses of their constituent atoms, they represent a good case for calculations of the contribution of zero-point motion to the lattice enthalpy. Thus, observation of their equation of state (EOS) and phase stability should provide crucial tests for existing theories and calculational schemes currently used in condensed-matter studies. Lithium hydrides are isoelectronic to helium, and under high density their phase diagram is expected to show analogies with helium in the same way as alkali halides under pressure become analogous, if not identical, to their closest rare gas element, e.g., CsI and xenon.

A number of other features make the lithium hydrides a unique series of materials. Although they are largely ionic, they differ from alkali halides by their elastic constants: the C_{44}/C_{12} ratio is larger than 4 in LiH. This large deviation from the Cauchy relations implies a large, noncentral, contribution to interionic forces. Last, but not least, they should exhibit a phase transition from their $B1$ (NaCl) structure to the $B2$ (CsCl) structure under pressure and predictions of the transition pressure, if this transition does indeed exist, has been a favorite among theorists for several decades. An obvious reason for this is the apparent simplicity of the 1*s* electronic environment of the ions which should make them readily tractable by *ab initio* methods.

In view of these attractive features, the need for experimental data on the equation of state of lithium hydrides is all the more evident. The last direct measurement of the equation of state (molar volume) under static pressure[1] dates back several decades. In those experiments, the volume of the sample, in a tungsten carbide die, was indirectly estimated by calculating the expansion of the bore under pressure. The pressure itself was derived from the old fixed points pressure scale which has since been revised, and then abandoned. Thus, the authors' estimated error of ±4% on the bulk modulus is actually closer to 6% if the error on pressure is taken into account. This precision on an EOS is not sufficient to allow comparison with calculations. As will be shown later on in the present paper, most calculated equations of state for LiH do fall within this bracket up to 4 GPa, that is, to the highest pressure measured in Ref. 1, although they differ widely at higher pressures and lead to highly variable predictions for the transition pressure from $B1$ to $B2$.

In order to make a significant comparison with experiment, that is, one that allows a critical evaluation of the accuracy of the calculations, a precision at least 1 order of magnitude higher is required. For this reason, we chose to measure the equation of state of lithium hydride by neutron-scattering methods, which have better precision than x-ray methods especially for light elements, the x-ray cross section of which is small.

In this work, we will briefly describe the setup which was built on this occasion, then discuss the experimental values with reference to previous high-pressure[1] and ultrasonic[2,3] experiments, and finally compare them to existing theoretical calculations[4–13] on the equation of state and the phase transition.[14–16]

II. EXPERIMENT

The high-pressure setup has been briefly described before[17] and will be fully discussed in a forthcoming paper.[18] The high-pressure cell is an opposed toroidal anvil device[19] (Fig. 1). The sample volume is a spheroid about 100 mm^3 in volume, which is adequate for neutron measurements on powders. Gaskets are made of pyrophyllite and beryllium copper. Tungsten carbide anvils are supported with hard steel (maraging steel) binding rings and partly hollowed out at the back, to decrease the absorption of incident neutrons. Neutrons are scattered at a fixed 90° angle and analyzed by time-of-flight methods. This geometry has been devised specifically for use at the ISIS spallation facility at the Rutherford Appleton Laboratory (U.K). Since the total area of the sample and gasket arrangement is about 2.5 cm^2 in area at 10 GPa, this requires a thrust of ~120 tons (1.2 MN) to reach this pressure and almost twice as much to reach pressures of the order of ~15 GPa, which can be envisaged with large sintered diamond anvils. A 250-tonnes (2.5-MN) press was therefore built (Fig. 2). This includes a hydraulic ram allowing *in situ* variation of the pressure, which is more practical than fixed-pressure clamp devices.[17] Since space is limited in neutron facilities, the size had to be less than 40 cm in all dimensions. Finally, the total mass was kept down to 50 kg,[20] because the setup has to be taken in and out, tilted, and otherwise manipulated in the loading and unloading operations, and therefore should not be too massive for an average operator. Existing presses of the same capacity currently have masses over 1000 kg and are therefore not suitable. Details of the finite-element calculation of the hydraulic ram will be published elsewhere.[18]

Samples of ^{7}LiD contained less than 1% ^{6}Li and were mixed with NaCl in approximately 20% ^{7}LiD–80% NaCl proportion by mass to give comparable intensities of the diffraction peaks. Precompression of the 175-mg pellets to ~1 GPa and loading of the cell were done in a glove box under nitrogen gas, which had been thoroughly desiccated with P_2O_5, because of the reactivity of lithium hydride with OH groups. The choice of ^{7}Li and deuterium is imposed by the neutron technique since ^{6}Li and hy-

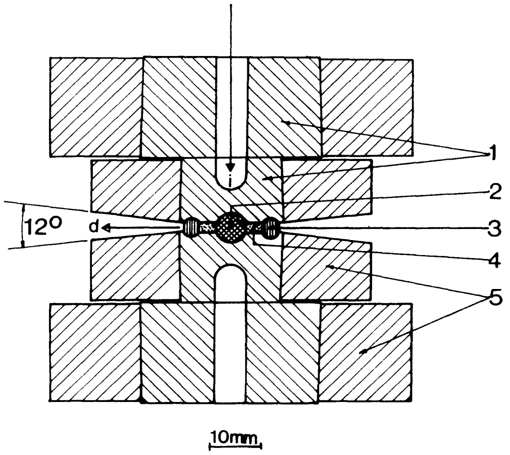

FIG. 1. Cross section of high-pressure anvils and sample volume. (1) Tungsten carbide anvils and anvil seats. The 6-mm-diam hole reduces the incident neutron absorption. (2) Sample space. The sample space is typically a 6-mm-diam spheroid. Pellets of the sample powder (^{7}LiD in the present case) are precompressed under ~1.2 GPa with the required amount of the calibrant (NaCl) to reach adequate compactness before the run. (3) Toroidal gasket. Soft beryllium copper gaskets are machined to the correct section, then shaped by compression in their grooves, and finally aged at 320 °C to full hardness (42 RC). (4) Pyrophyllite gaskets 1–2 mm in thickness depending on the final pressure. (5) Maraging steel rings are heat-treated to full hardness (52 HRC) and the tungsten carbide cores are pushed in, on a 1.5° angle, to the maximum tensile strength of the steel at the carbide-steel face (1600 MPa). The incident neutron beam (i) is precollimated by a 6-mm-diam B_4C collimator. The diffracted beam (d) can be collected over a 12° angle in 2θ: 90°±6°. The faces and sides of the anvil binding rings are coated with gadolinium oxide paint.

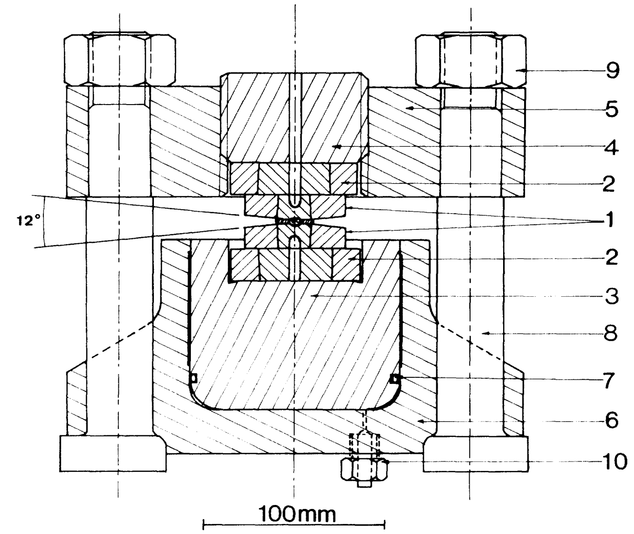

FIG. 2. Cross-sectional sketch of the 2.5-MN press. (1) Anvils and sample assembly. (2) Anvil seats and supporting rings. (3) Main piston (35 NCD 16 steel—52 HRC), 100 cm^2 in diameter to provide a ~2.5-MN thrust under 250 MPa oil pressure. (4) Front breech (same material) has two functions: to make assembling of the sample and anvils possible without disassembling the tie rods, and to provide a flat resting surface for the seats by being mechanically decoupled through the thread from the plate (5) which bends outwards under load. (5) Top plate [same steel as (3)]. (6) Hydraulic ram [same material as (3)]. Its unusual shape has been calculated (Ref. 20) to provide compensation of strains and negligible deformation under load at the level of the gasket (7) and of guide ring (top of piston). (7) Neoprene O ring. This is leak tight to well above 200 MPa because the diameter of the oil chamber (6) does not vary under pressure. (8) Tie rods. Marval 18 maraging steel (51 HRC—tensile strength: 1800 MPa). (9) Retaining nuts [same metal as (8)]. (10) Hydraulic oil inlet connected to a 280-MPa pump.

drogen are neutron absorbers and/or incoherent scatterers, and they would give rise to an unacceptably low signal-to-noise ratio.

The press was mounted in the POLARIS station of the ISIS facility, with the axis (Fig. 2) in the horizontal plane. A supporting jig gave adequately reproducible alignment with the incident neutron beam which was collimated down to a diameter of 6 mm by a B_4C collimator. Gadolinium oxide coating of the faces and sides of the anvil binding rings eliminated CW diffraction peaks. Exposure times were between 4 and 6 h and data were collected by an array of 20 ^{4}He tubes, 2 cm in diameter, at 2 m distance, giving a resolution of about 7×10^{-3}. This apparatus was used above 2 GPa only. At lower pressure, we used a clamp-type piston-cylinder system with a biconical supported alumina cylinder[21] and Fluorinert as a pressure transmitting medium for the NaCl:LiD sample.

III. RESULTS

Spectra recorded in the toroidal anvil system are shown in Fig. 3. They are normalized to the incident neutron flux at all energies. The form of the background is due to incoherent scattering from the cell and its environment. The decrease in signal with increasing pressure is due to the closing of the gap between the anvils under increasing thrust. At the highest pressure ($\sim$10 GPa) the load was 126 tonnes (1.24 MN). A noteworthy feature is that the linewidth of the peaks does not increase measurably between 3 and 10 GPa. A statistical line-shape analysis of the NaCl and LiD peaks shows that, at the highest load, the pressure broadening is equivalent to 0.4±0.1 GPa. This is smaller than the broadening which is usually observed in Bridgman-type flat-anvil systems, where biaxial components of strain lead to inhomogeneous stress conditions and large pressure gradients. The reason must be that the compression in this setup has quasi-spherical geometry, and thus maintains comparatively uniform conditions in the center of the spheroid which is precisely the diffracting part of the sample. Since the sample under study and the calibrant are intimately mixed, both undergo identical conditions, provided that they have comparable mechanical properties and the applied pressure is a sizable ($\sim$10%) fraction of their bulk moduli, which is the case here.

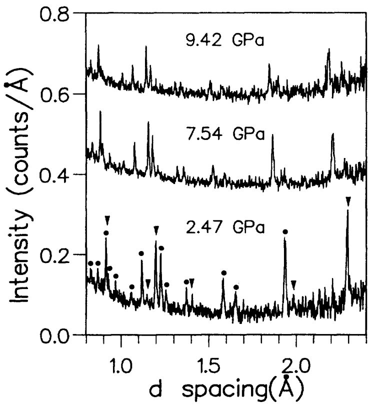

FIG. 3. Spectra taken at three different pressures (4–6 h exposure on the POLARIS station). The number of counts is relative to the incident neutron flux at all wavelengths. The form of the background comes from the press absorption and scattering. Diffraction lines are identified by solid circles (NaCl) and inverted triangles (^{7}LiD). The upper two spectra have been shifted upwards for clarity.

Separate Rietveld profile refinements were done on NaCl and LiD, taking into account baseline and attenuation corrections for the cell, which had been determined in separate experiments. At the present stage, this only gives a qualitative estimate of the thermal parameters (Debye-Waller factors), but yields a *relative* precision of 3×10^{-4} or better on lattice constants (Table I). Since there are no other free parameters than the lattice constant in the $B1$ (NaCl) structure, this fully defines the atomic positions in this case.

In Fig. 4, the experimental points are fitted to a Birch equation of state of the form

$$P=\tfrac{3}{2}B_0[(V_0/V)^{7/3}-(V_0/V)^{5/3}] \times\{1+\tfrac{3}{4}(B'-4)[(V_0/V)^{2/3}-1]\} \quad (1)$$

with P the pressure in GPa, B_0 the room-pressure bulk modulus, V and V_0 the volume, and B', $[dB/dP]$ the derivative of the bulk modulus. The parameters of the fit are V_0: 0.067 53(4) nm^3, B_0: 31.7±0.4 GPa, and B': 3.4±0.1.

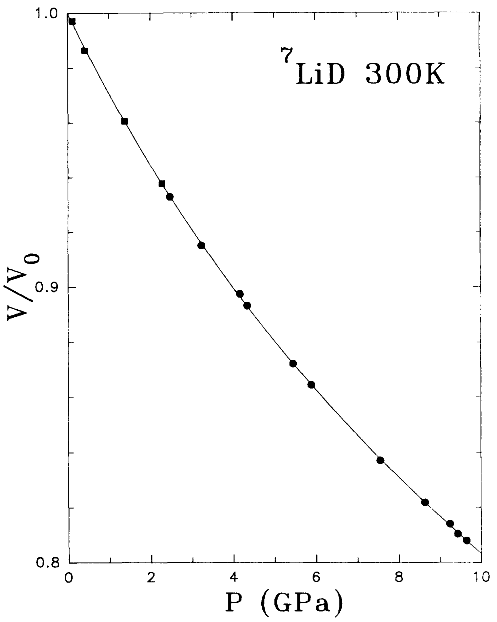

FIG. 4. Relative volume change under pressure (V/V_0) of ^{7}LiD at ambient temperature (Table I). Solid squares: measurement in a clamp-type McWhan press, with Fluorinert as a pressure transmitting medium. Solid circles: measurements from three separate runs, with the anvils and press of Figs. 1 and 2. Solid line: best fit with a Birch equation of state (BEOS) and the following parameters: $V_0=0.067\,53(4)$ nm^3 [$a_0=0.4072(1)$ nm], $B_0=31.7\pm0.4$ GPa, and $B'=3.4\pm0.1$. The Decker equation of state for NaCl has been used in all cases for pressure calibration.

TABLE I. The lattice parameter *a* of ^{7}LiD versus the lattice parameter of NaCl in four separate runs all at 294±2 K. The errors given are the standard deviations from the Rietveld refinement and do not include instrumental errors and/or other experimental uncertainties. The values for pressure are taken from the lattice parameter of NaCl and the Decker equation of state (Ref. 22), and do *not* imply a precision of four figures on the absolute pressure.

Run No.	Type of cell and run	Applied load (kN)	a(^{7}LID) (nm)	a(NaCl) (nm)	Pressure (GPa)
1	McWhan cell	10	0.406 83(6)	0.563 88(10)	0.115
		40	0.405 37(6)	0.561 1(1)	0.414
		80	0.401 78(7)	0.554 8(7)	1.368
		120	0.398 6(1)	0.549 6(2)	2.278
2	Paris-Edinburgh cell	300	0.397 90(5)	0.548 6(6)	2.467
		600	0.392 18(6)	0.539 96(8)	4.338
		770	0.392 8(1)	0.540 67(1)	4.161
3	Paris-Edinburgh cell	460	0.395 35(9)	0.544 85(9)	3.230
		750	0.389 08(6)	0.535 62(7)	5.447
4	Paris-Edinburgh cell	700	0.387 91(5)	0.534 05(6)	5.883
		900	0.383 79(3)	0.528 52(4)	7.544
		1000	0.381 43(6)	0.525 3(1)	8.628
		1100	0.380 22(6)	0.523 59(8)	9.232
		1160	0.379 66(4)	0.523 08(5)	9.424
		1240	0.379 28(7)	0.522 5(1)	9.642

The value of V_0 corresponds to an ambient lattice parameter for ^{7}LiD of 0.4072(1) nm, which was treated as a variable parameter of the fit rather than being constrained to match published room-temperature values. This was done in order not to introduce the absolute errors of the instrumental setup into this measurement, since only the variation of volume under pressure is of interest. The experimental data consist of four experiments (solid squares) with a clamp-type cell[21] and three separate runs with the toroidal anvil system, performed at an interval of several months (solid circles). Nevertheless, the scatter (mean-square deviation) of the experimental points with respect to the calculated fit is less than 5×10^{-5} nm.

Unfortunately, this level of accuracy cannot be claimed on the equation of state because of current limits on the accuracy with which pressure can be defined. The pressure was evaluated here from the Decker equation of state[22] of 1971, which is the best reference, at the present time, since the so-called ruby fluorescence scale which is a widely accepted standard for pressures between 5 and 100 GPa is based on the Decker EOS. The absolute accuracy of the Decker equation of state has never been *directly* checked, since the only comparison with experiment in Decker's paper[22] relies on unpublished piston-cylinder data (see Ref. 36 quoted in the above paper). Therefore, no precise figure may be given for the (in)accuracy on pressure. So, although the relative error on the lattice parameter of NaCl is the same as on ^{7}LiD, the uncertainty on the absolute pressure must be that of the international pressure scale, which is at least 10^{-2} at 10 GPa. Experimental data are thus given here with no evaluation of the error on pressure, which is that of the NaCl equation of state.[22]

The data can also be fitted to a first-order Murnaghan equation of state of the form

$$P=(B_0/B')[(V_0/V)^{B'}-1] \tag{2}$$

with B_0: 32.1±0.3 GPa and B': 3.05±0.1. The best-fit parameters are different from Eq. (1) and this is no surprise: the functional form and physical hypotheses underlying Eqs. (1) and (2) are not the same and, therefore, the meaning of the parameters, particularly B, is different in the two equations. In view of this, comparison with other experimental data and theoretical calculations will be made on the full $V(P)$ dependence over the relevant pressure interval.

IV. COMPARISON WITH OTHER EXPERIMENTAL DATA

As noted in the Introduction, published experimental data on the EOS of lithium hydrides are scarce. The only reported results under static high pressure are those of Ref. 1 for hydrides and deuterides of ^{6}Li and ^{7}Li, and of Ref. 2 for LiH to 200 MPa. In addition, a number of reports from military institutions exist on the equation of state of lithium hydrides because of their use in thermonuclear devices. Those reports are not referred to in the present paper since most of them are not available to the public and have not appeared in refereed journals or open conference proceedings.

The experimental values for $V(P)$ of ^{7}LiD and ^{7}LiH taken from Ref. 1 are shown for comparison in Fig. 5. The difference between the two is much smaller than the experimental uncertainty reported by the authors of Ref.

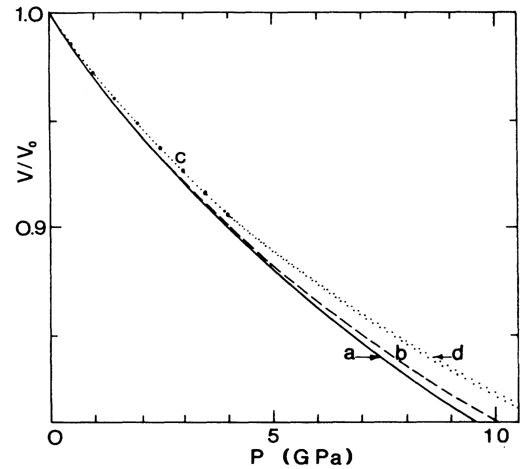

FIG. 5. Comparison with experimental data. (a) Solid line, our 300-K data fitted to the BEOS. (b) Dashed line, 300-K Murnaghan equation of Gerlich and Smith (Ref. 2) $B_0=31$ GPa, $B'=3.8$. (c) Solid circles, experimental values of Stephens and Lilley (Ref. 1) for ^{7}LiH and ^{7}LiD. The two sets of values differ by less than 0.5% on $\Delta V/V_0$ at 4 GPa. (d) Dotted lines are the Murnaghan equations of Ref. 1 for ^{7}LiH ($B_0=33.6$ GPa) and ^{7}LiD ($B_0=34.0$ GPa) and $B'=4$.

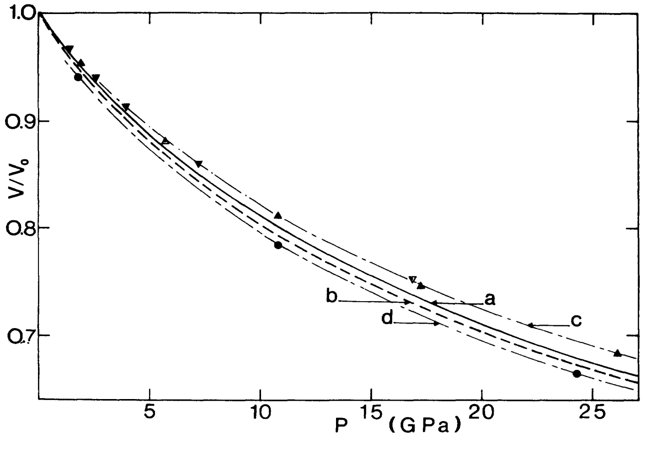

FIG. 6. Comparison with calculations at 0 K. (a) Solid line, Birch equation of state at 0 K with $B_0=33.5$ GPa and $B'=3.4$, deduced from our 300-K results (Fig. 4) with a 6% increase on B_0 (Ref. 2). (b) Dashed line, our results at 300 K (Fig. 4) and Martins's calculation at 0 K (BEOS with $B_0=31$ GPa and $B'=3.5$, Ref. 12) happen to coincide over this pressure range. (c) Triangles pointing up, Gou, Wang, and Meng (Ref. 11) and inverted triangles, Hama and Kawakami (Ref. 9). In the latter reference, values for V/V_0 from these authors were taken directly from their Table 2 using their calculated V_0 at $P=0$, i.e., 9.58 cm^3/mol.$^{-1}$ Both sets of values then are in very close coincidence and are joined by a dash-dotted line which is only a guide to the eye. (d) Solid circles from Perrot (Ref. 5). Dash-dotted line as above.

1. For this reason, and lack of contrary evidence, we shall, from now on, take our equation of state for ^{7}LiD to be representative of that of "natural" LiH which contains over 90% ^{7}Li. At 4 GPa, the decrease of volume is reported in Ref. 1 to be 9.4% instead of 10% according to our measurements. This difference is consistent with a 10% overestimate of the actual pressure due to the use of the "fixed-points" pressure scale at the time (1968) of the measurements.

The elastic moduli of LiH single crystals and their pressure derivatives were measured[2] by ultrasonic methods up to 160 MPa by Gerlich and Smith. Using values for $B_0=31$ GPa and $B'=3.8$, which also fit with other ultrasonic data,[3] they derived the equation of state of LiH at 300 K via a Murnaghan relation. This is shown in Fig. 5 and does compare very well with our data up to 5 GPa, within 1% on $\Delta V/V_0$. At higher compressions, the difference between this Murnaghan EOS (MEOS) and our data rapidly increases. This is expected, since a MEOS should not be used for pressures more than ~10 or 20 % of the bulk modulus. Also, as noted at the end of the preceding section, direct comparison of the bulk modulus and its pressure derivative between two sets of results would be completely misleading: although the set of parameters used in a first-order MEOS are different in our case and in Ref. 2, the $V(P)$ dependence is identical within experimental error over the range (a few GPa) where it is applicable. This is not unexpected: ultrasonic data *do* give the bulk modulus and its pressure derivative at zero pressure, exactly, but do *not* allow extrapolation of a first-order MEOS to high pressure. On the contrary, in our case, a Murnaghan EOS *does* represent the experimental data well in the range of pressures under study—as well as other *ad hoc* mathematical forms would—but the bulk modulus and its derivative are then only best-fit parameters to the experimental data and should *not* be taken at face value to measure the ambient pressure properties exactly.

In the same paper, Gerlich and Smith measured the temperature dependence of the elastic constants of LiH and evaluated the adiabatic bulk modulus at 0 K to be some 6% higher than at 300 K. This was used here to estimate the equation of state of ^{7}LiD at 0 K from our 300-K data, as shown in Fig. 6, where the isothermal bulk modulus of Eq. (1) has been increased by 6%, B' remaining the same. This procedure is admittedly only approximate, since both dB/dP and the ratio of isothermal to adiabatic moduli should decrease with temperature, but this will be a second-order correction and the real EOS at 0 K must lie in between the dashed (300 K) and solid (corrected to 0 K) lines in Fig. 6, closer to the latter which will be used, in the next section, for comparison with theoretical calculations, since these are done, as a rule, at zero temperature.

V. COMPARISON WITH CALCULATIONS

A number of calculations using various methods have been performed previously to predict the high-pressure behavior of LiH. In many cases, the motivation was to investigate the evolution towards conducting behavior either by band contact[5,9,16] (semimetal) or by band overlap[5] (metallization). The structural transition from the $B1$ to the $B2$ structure was also studied in a number of calculations.[7,11–15] Variations in the calculated metallization pressure[5,9,16] are only moderate, from 200 to 400 GPa. In contrast, the transition from $B1$ to $B2$ has attracted an astonishingly wide range of predictions over the years, being located at pressures ranging from 0.4 (Ref. 14) to 660 GPa,[13] or being altogether absent.[7,15] Since neither phenomenon has been observed to date,[16] up to some 50 GPa, the only test of the accuracy of calculations is their ability to predict the equation of state of the cubic (NaCl) structure in the observable range of pressure.

A number of published equations of state, when explicitly given, strongly differ from experimental values even below 10 GPa with initial compressibilities being much too low.[8,10,13] Four other equations of state[5,9,11,12] show better agreement with our experiments and are shown in Fig. 6.

Calculations by Hama and Kawakami[9] and by Martins[12] used the local-density-functional theory with different treatment of the contributions of lattice vibrations. To compare their calculations with our data, we took account of the following.

(i) In Ref. 9, V_0 is taken to be the calculated value of 9.58 cm^3/mol for $P=0$, when the zero-point energy is taken into account, although this is 5% smaller than the experimental V_0. Values for V/V_0 as P increases are then taken from Table 2 in Ref. 9. The values that we quote here for V/V_0 are, for this reason, quite different from those shown by the authors of Ref. 9 themselves in their Fig. 4, especially in the "low-pressure" region since they chose to use, in this figure, a value of 10.30 cm^3/mol for the initial volume V_0 which is *not* their calculated equilibrium molar volume.

(ii) In Ref. 12, the values calculated by Martins in the quasiharmonic approximation are retained. The calculated volume at equilibrium is only 3.5% smaller than the actual value and the Birch EOS parameters given in Table I of this reference ($B_0=31$ GPa, $B'=3.5$) are used to draw the EOS shown in Fig. 6. It should be noted here that this curve is identical to our room-temperature values and differs from it only when the low-temperature correction to our data is applied.

(iii) A completely different method was used by Gou, Wang, and Meng in Ref. 11, using a variational method to compute the crystal energy in an ionic overlap-compression model. Their results (Table 3 in Ref. 11) are also rather close to the actual values and precisely fit, up to the highest pressures, with those of Ref. 9, as interpreted here [see (i)].

(iv) Finally, one of the first equations of state, calculated by Perrot[5] is worth mentioning. He used an augmented-plane-wave (APW) scheme for the electronic contribution and a Debye model for the lattice vibrations. Although the initial bulk modulus (Fig. 6) is too small by some 18%, the calculated volume becomes identical with our EOS within 1% in $\Delta V/V_0$ between 20 and 100 GPa.

Of the four EOS, that of Martins seems to be closest to our experimental data, since we expect the real EOS at 0 K to fall in between the experimental 300-K values (dashed line in Fig. 6) and the corrected 0-K values (solid line). Nevertheless, the agreement between extrapolation of our data and the four equations of state which we have examined is quite good up to some 100 GPa if one takes into account that the calculations were done with widely different methods and hypotheses. Up to 100 GPa, they all give the same $V/V_0=f(P)$ within $\pm 3\%$ on V/V_0. At this stage of the discussion, it should be stressed that the *extrapolation* of our Birch equation of state (BEOS) above 10 GPa is *not* presented here as an exact description of the $V(P)$ dependence. The BEOS is known to be well applicable to solids with ionic bonds such as NaCl, but we have no precise knowledge of its accuracy when extrapolated from $V/V_0=0.8$ to $V/V_0=0.3$. It certainly is better than a MEOS, but surely too soft in the high-pressure region. We use it here as the only experimental indication we have, for comparison with calculated values. Given this *caveat*, we can proceed to discuss the predictions on the insulator to conductor transition pressures. The direct X_1-X_4' energy gap of lithium hydride increases with pressure[16] and is expected to close down[5,9] at high pressure. This behavior is clearly different from the "metallization," which may occur at much higher pressure[5] when both lithium and hydrogen atoms will behave as one-electron alkali atoms. The gap-closing pressure has been predicted to be 200 GPa by Perrot,[5] 230 GPa by Hama,[9] and extrapolated to 400 GPa by Kondo and Asaumi.[16] If we relate these values to the different equations of state used by these authors, we find that they correspond to $V/V_0=0.34$ for Ref. 5, $V/V_0=0.35$ for Ref. 9, and $V/V_0=0.37$ for Ref. 16, where an unrealistic first-order Murnaghan EOS was used up to high compression. Thus, in this last case, $V/V_0=0.37$ is an upper value only. Using a common value of $V/V_0\sim 0.35$, which fits all three predictions and our extrapolated equation of state, we find that the band closing could take place as early as 150 GPa. Actually, our BEOS is surely too soft in the high-pressure region and a better estimate is to be found in the calculations of Ref. 12 which, at low pressure, fit best with measurements. In that case, a relative volume of 0.34–0.35 corresponds to pressures of 170–180 GPa, which still are in an experimentally accessible range of pressure.

The situation is less clear as regards the structural transition from the NaCl to CsCl structure which may be expected in LiH by analogy with the behavior observed in alkali halides. This transition has been predicted to occur at various pressures between 0.4 GPa, which is clearly inaccurate,[14] and 660 GPa.[13] Various authors[7,15] disclaim its occurrence at any pressure. Two of the equations of state examined here predict it at 85 (Ref. 11) and 500 GPa,[12] corresponding to $V/V_0\approx 0.5$ and $V/V_0\leq 0.25$, respectively. These values are too far apart to be reconciled, whatever the difference in the equations of state used. In this case both are in reasonable accord with experiment and the question will have to rely on future experimental evidence to be settled.

VI. CONCLUSION

Lithium hydrides, despite their apparent simplicity, thus appear not to be as well understood as most of their isoelectronic and isostructural neighbors such as alkali hydrides.[12] Among others, optical and structural studies above 100 GPa are badly needed to check directly the questions of gap closing and of the structural stability of the NaCl phase. Another point that should be addressed is the difference in the EOS between the various isotopic varieties. Small as this might be, it would provide a direct check on the contributions of lattice vibrations to the energy of the crystal. This contribution is treated in a very approximate manner in most calculations, since a complete treatment including the full phonon spectrum as a function of pressure would require heavy computational procedures.

As regards the experimental methods used here, it should be noted that a better understanding of absorption and background corrections is required to allow full structure refinements and therefore measurement of interatomic distances and thermal parameters. Nevertheless, the results show the value of neutron diffraction for studies of light-atom systems and demonstrate the precision achievable with time-of-flight methods. Neutron diffraction is especially useful for investigating hydrogen (deuterium) sublattices in such fundamental systems as H_2O, NH_3, or CH_4 , or any hydrogen compound for that matter, under high pressure. Hitherto there has been a pressure limit of about 3 GPa for accurate neutron-diffraction studies and nothing is known about the variation under high pressure of the bond length between hydrogen and any other atom, although this knowledge is absolutely necessary to understand the molecular stability and vibrational properties of such solids at high density. There is now the real prospect of applying neutron scattering to these and other light-atom structural problems, especially since, in our setup, the pressure range may, if needed, be extended well above 10 GPa by use of sintered diamond anvils instead of tungsten carbide.

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