Lithium: anomalies of its elastic properties under high pressures up to 1.6 GPa at 78 K

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The propagation rates of longitudinal and transverse waves in polycrystalline lithium have been measured by a pulsed ultrasonic method at $T=78$ K under pressures up to 1.6 GPa. The equation of state and elastic properties of lithium as a function of the pressure have been determined. It has been postulated that the sharp softening ($\approx 14\%$) of the shear modulus $G(p)$ of lithium in response to the first application of pressure at 78 K is caused by accumulation of the low-temperature martensitic phase. © *1994 American Institute of Physics.*

1. INTRODUCTION

Lithium, the lightest alkali metal and the first metal in the periodic table, has continually attracted the attention of both theoreticians and experimentalists. The equation of state of this substance has been determined,[1–4] the phonon spectrum and the elastic modulus have been calculated and measured as a function of the pressure and temperature,[5–11] and the stability of the lithium crystal lattice, which has a bcc structure under ordinary conditions, has been investigated[5,12–15] in numerous studies. The results of some investigations have created contradictions, calling for additional experimental data. This applies, in particular, to the martensitic phase transformation of lithium at low temperatures.[14,16–18] Investigation employing diffraction and elastic and inelastic neutron scattering methods have established that bcc lithium is partially ($\approx 50\%$) transformed during this transition into a rhombohedral close-packed $9R$ structure (of the samarium type) with the presence of a considerable number of polytypes with fcc and hcp packing of the atoms.[15,17,19,20] The transition temperature at atmospheric pressure has been recorded in the 68–78 K range by different investigators, and a dependence on the history of the sample and the possibility of stimulating this transition by cold working or pressure have been noted.[7,14,18,19]

According to Ref. 12, the phase transition from the bcc structure to the close-packed structure is preceded by processes resulting in a loss of stability of the crystal lattice with respect to displacement in the (110) plane in the $[1\bar{1}0]$ direction, which can be determined from the elastic constant $c'=(c_{11}-c_{12})/2$. In this case the expected premartensitic softening of the TA1[110] mode near the phase transition can be observed in ultrasonic investigations. Ultrasonic measurements performed on lithium single crystals under pressures up to 0.20 GPa (Ref. 8) and 0.35 GPa (Ref. 8) in the 85–300 K temperature range did not reveal a softening effect; it was shown that the derivatives of the shear elastic constants in this (p,T) region remained positive, although they were small. In our investigation[11] of the elastic properties of lithium at $T=295$ K and pressures up to 2.5 GPa revealed softening of the elastic characteristics of lithium at $p>1.0$ GPa, which demonstrated the appearance of some instability in the lithium bcc lattice long before the phase transition at 6–7 GPa. The performance of ultrasonic investigations of lithium at $T=78$ K and high pressures up to 1.6 GPa should provide additional information on the stability of the crystal lattice in the region of the martensitic transformation and reveal the features of the baric dependence of the elastic characteristics of lithium.

The ultrasonic piezometer[21] was modified to carry out investigations at low temperatures. To achieve the temperature $T=78$ K, a high-pressure unit consisting of a matrix and two plungers made from an alloy steel was completely immersed in a vessel filled with liquid nitrogen, which had the form of a thermally insulated stainless steel container hermetically sealed to the lower plunger of the high-pressure unit. A miniature 300-ton press[22] was used to create the force. The temperature was measured using copper-constantan thermocouples. The measurements of the changes in the transit times of longitudinal $[\Delta t_l(p)]$ and transverse $[\Delta t_t(p)]$ ultrasonic pulses with a duration of 2–3 μs and a carrier frequency of 3 or 5 MHz were determined with an accuracy to 2–3 ns by the pulse-echo-overlap method.[23] The variation of the height of the sample $\Delta l(p)$ was determined using dial-type micron indicators, whose mechanical parts were located outside of the low-temperature zone.

Lithium of type ÉL-1 with a content of the main substance equal to 99% was used in the experiments. Since lithium exhibits high anisotropy $[2c_{44}/(c_{11}-c_{12})\sim 10]$ and, like many metals previously investigated by us, for example, Bi and Cs,[24,25] forms ingots consisting of coarsely crystalline grains, the measurements were performed on samples prepared from a substance that was melted and then rapidly cooled by immersion in liquid nitrogen. The x-ray diffraction patterns showed polycrystalline grains no larger than 0.2 mm, ensuring, as in Refs. 24 and 25, convergence of the experimental results.

The experimental plots of $\Delta t_l(p)$ and $\Delta t_t(p)$ have several special features (Fig. 1). First, these dependences are partially irreversible, i.e., one of the branches corresponds to the raising of the pressure in the first cycle, and the other branch corresponds to removal of the load in the first cycle and all subsequent loading cycles, i.e., the steady state of the substance. On the other hand, the dependence of $\Delta l(p)$ is identical for all the cycles. Second, the plots of $\Delta l(p)$, $\Delta t_l(p)$, and $\Delta t_t(p)$ do not show any abrupt changes or discontinuity over the entire range of pressures. It follows from this that a martensitic transition with a partial bcc-to-$9R$

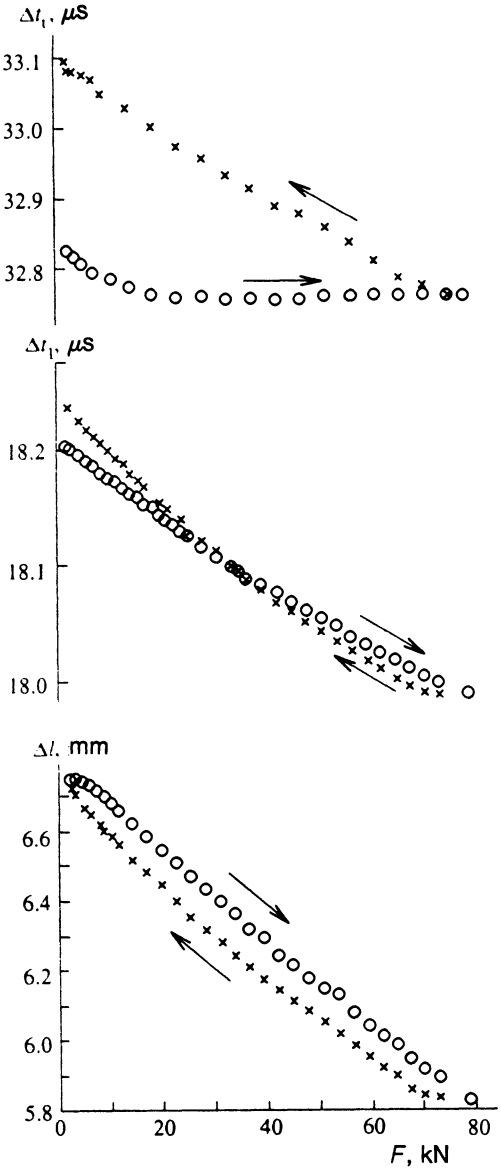

FIG. 1. Experimental plots of the transit times of longitudinal [$t_l(p)$, experiment No. 8] and transverse [$t_t(p)$, experiment No. 9] ultrasonic waves and of the sample length [$l(p)$, experiment No. 8] as functions of the press force: ○—as the pressure is increased, ×—during repeated loadings.

transition probably occurred already under the conditions of the stressed state needed to ensure acoustic contact at the beginning of the experiment, i.e., when “cold working was simulated” by lowering the temperature to 78 K.[7,14,18,19] Third, after removal of the pressure and warming to $T=295$ K, the same features in the behavior of $\Delta t_l(p)$ and $\Delta t_t(p)$ were repeated in the subsequent experiments at $T=78$ K.

The experimental plots of $\Delta l(p)$, $\Delta t_l(p)$, and $\Delta t_t(p)$ were used to determine the baric dependences of the propagation rates of longitudinal [$v_l(p)$] and transverse [$v_t(p)$] ultrasonic waves in lithium at $T=78$ K up to pressures of 1.6 GPa for the two branches (Fig. 2). The calculation was performed for the initial values v_{l0} and v_{t0} obtained from the elastic moduli of a lithium single crystal at 78 K (Ref. 26) by averaging according to Peresada's method.[27] Corrections determined in special measurements for the variation of the sample length as the temperature is lowered, as well as for the deformation of the high-pressure chamber under the conditions of the experiment, were taken into account. These plots of the propagation rates versus the pressure nearly coincided with the plots obtained by averaging the results of 10 experiments performed on samples cut from an ingot without preliminary treatment. The largest deviations from the averaged plot with consideration of all the samples are equal to 0.3% for $v_l(p)$ and 2.6% for $v_t(p)$ when the pressure is raised and to 0.6 and 2.5% when the pressure is removed, respectively.

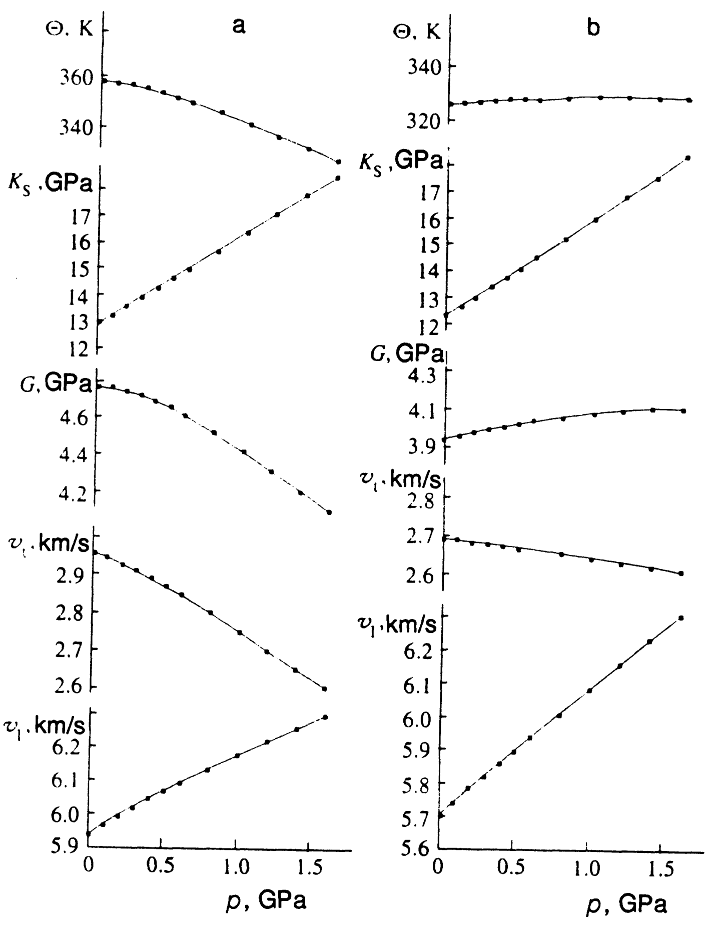

FIG. 2. Elastic characteristics of lithium during the first application of pressure to 1.6 GPa at $T=78$ K (a) and during repeated loadings ($1.6\rightleftarrows 0$ GPa) at $T=78$ K (b).

We note the special features in the behavior of the experimental plots of $v_l(p)$ and $v_t(p)$ as the pressure is raised in the first cycle, viz., nonlinearity of the variation of $v_l(p)$ and a strong decrease in $v_t(p)$ ($\approx 12\%$), which demonstrate the structural instability of the medium under investigation under the present conditions. In the cases in which lithium is in the steady state, i.e., when the pressure is removed in the first and subsequent loadings, v_l increases nearly linearly with the pressure, and v_t decreases weakly ($\approx 3.0\%$), possibly due to the softening of the shear TA1[110] mode of the acoustic part of the phonon spectrum of bcc lithium.

The adiabatic bulk modulus $K_S(p)$, the shear modulus $G(p)$, the Debye temperature $\Theta(p)$, and the compression $V(p)/V_0$ calculated from the experimental dependences of

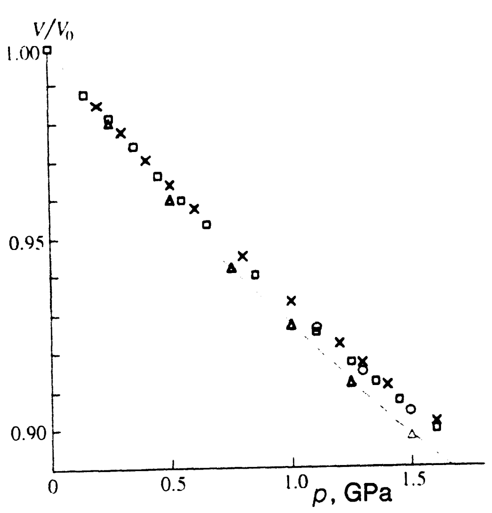

FIG. 3. Compression of lithium to 1.6 GPa. Present work (ultrasonic method): *1)* △—$T=295$ K (Ref. 11); *2)* □—first application of pressure, $T=78$ K; *3)* ×—subsequent pressure cycles, $T=78$ K. Data of Anderson and Swenson[1] (piezometric measurements): *4)* ○—extrapolation to $T=78$ K.

$v_l(p)$ and $v_t(p)$ are illustrated by Figs. 2 and 3. The value of the density of lithium $\rho_0=0.545$ kg/m^3 at $T=78$ K from Ref. 9 and the adiabatic isothermal correction $\Delta=0.01$ (Ref. 1) were taken in the calculations.

The bulk modulus K_S, which characterizes the repulsion potential in the lattice, increases monotonically with the pressure, its value during the first application of pressure differing from the value during the repeated loadings by more than 1%, despite the significant difference between $v_l(p)$ and $v_t(p)$ in the two cases. The value of the derivative of the isothermal bulk modulus $(\partial K_T/\partial p)_{p=0}=3.60\pm0.1$, which we determined for the steady state of lithium, agrees differently with the values obtained by Anderson and Swenson at $T=82$ K and $T=61$ K, i.e., before and after the martensitic transformation, which are equal to 3.57 ± 0.08 and 3.58 ± 0.21, respectively.

The anomalous behavior of lithium at the temperature of liquid nitrogen is manifested especially clearly in the character of the dependence of the shear modulus G on the pressure (Fig. 2). During the first application of pressure, the loss of resistance of the crystal lattice to shear is demonstrated by a considerable decrease in G (14.0%). The slight increase in the shear modulus and the weakening of the dependence on the pressure at $p>1.0$ GPa during the repeated loadings attest to the existence of soft shear modes in the phonon spectrum of lithium. It is noteworthy that the value of 0.216, which we determined for the derivative $(\partial G/\partial p)_{p=0}$ at $T=78$ K, is in good agreement with the value of 0.225 measured on single-crystalline lithium samples at $T=100$ K in Ref. 9. The agreement between the derivatives of the shear modulus in the present case may be attributed to the fact that after the transition the lithium bcc lattice makes a large contribution to the behavior of the shear elastic characteristics of Li in the initial range of pressures.

Analyzing the dependences obtained, we may postulate that lithium undergoes changes in two stages under the action of pressure at the temperature of liquid nitrogen: during the first application of pressure, the low-temperature phase continually accumulates at the expense of the quantity of the bcc phase in addition to the 45–50% of martensite which forms at atmospheric pressure when the temperature is lowered to $T=78$ K. It was noted in Ref. 20 that lowering the temperature to 4.2 K increases the amount of the $9R$ phase to 75%. The quantity of the new phase is probably determined by the maximum pressure in the particular experiment $p_{\max}$. In the second stage, in which the baric dependences $v_l(p)$ and $v_t(p)$ are reversible, lithium has a steady phase composition. In this case the character of the variation of the shear modulus $G(p)$ (Fig. 2b) possibly attests not only to the fact that the bcc-to-low-temperature phase transition did not go to completion, but also to the fact that another structural phase transition to a more stable, possibly an fcc, phase occurs in lithium at higher pressures.

The plots presented in Fig. 3 of the compression $V(p)/V_0$ during the first application of pressure and subsequent cycles, which we obtained by the ultrasonic method, are in good agreement with the results in Ref. 1, which were determined by piston-displacement measurements at 4 and 294 K and were extrapolated to $T=78$ K. Such agreement is based on the fact that the energies of the lithium bcc, fcc, hcp, and $9R$ lattices differ only slightly from one another.[10,13,28] It follows from this that the p-V dependences of the different lithium phases are nearly identical and that the volume jumps accompanying the phase transitions are very small.[1,29] A comparison of the compression of lithium at room temperature[11] and at the temperature of liquid nitrogen reveals a decrease in the compression of the lithium crystal lattice with decreasing temperature.

In the future it would be interesting to investigate lithium at $T=78$ K and various values of $p_{\max}$ by the ultrasonic method for the purpose of obtaining information on the volume ratios between the lithium bcc and low-temperature phases, as well as to investigate the elastic properties of lithium at temperatures somewhat below 78 K for the purpose of determining the anomalies in the elastic properties accompanying the martensitic phase transition.

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