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Lithium at high dynamic pressure

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Abstract

Experimental investigation of lithium compressed by multiple shock waves up to a pressure 210 GPa demonstrates an abnormal dependence on electric resistivity. As against normal behaviour of a metal, the resistivity monotonically increases in the pressure range 30–150 GPa from typical metallic values at ambient conditions by more than 15 times, returning to metallic values at pressures higher than 160–210 GPa. The obtained results demonstrate the anomalous resistivity of lithium both in solid and liquid states. This effect is explained by theoretical calculations done with the use of the linear muffin-tin orbital method.

High-pressure studies play an important role in understanding the fundamental physical properties of condensed matter. The conventional point of view in condensed-matter physics [1] predicts that, as density and pressure increase, structural phase transitions occur in a solid, a closest-packed phase with the maximum coordination number appears, insulators become conductors and a pressure ionization effect takes place under extreme conditions. Numerous experiments and theoretical models seem to support this general picture. Lithium, like other alkali metals, has long been considered as a prototypical ‘simple’ metal with metallic bonding. At ambient conditions, alkali metals occur in simple body-centred-cubic or close packed lattices. But modern sophisticated quantum mechanical calculations by Neaton and Ashcroft [2] predict much interesting behaviour of matter at high pressures. The theory [2] shows that lithium under pressure transforms from a typical metal at ambient pressure to an orthorhombic phase at 50 GPa. At higher pressure the lithium nuclei form pairs, producing a molecular semimetallic structure near 100 GPa, finally transforming back to monoatomic metal at very high pressures. Preliminary experiments carried out in diamond anvil cells [3, 4] at a pressure of 60 GPa have demonstrated a number of interesting optical anomalies, but they do not take measurements of the electric resistivity—the basic indicator of metal–insulator transitions. Recent x-ray diffraction studies to 50 GPa pressure [5], done at a temperature of

200 K to overcome the unusual reactivity of lithium with the diamond anvil under pressure, found a sequence of phase transitions. According to these measurements, near 39 GPa lithium transforms from a high-pressure face-centred-cubic (fcc) structure through an intermediate rhombohedral phase to a cubic body-centred unit cell with 16 atoms (Pearson symbol *cI16*). The total energy calculations [5] performed by means of the linear muffin-tin orbital method predicted that this phase, observed in elements for the first time, is stable to a pressure of 165 GPa. In our previous work [6] we reported direct measurements of the electric resistivity ρ of lithium compressed by dynamic methods by a factor of ~ 3 to a pressure of 60 GPa, which revealed its anomalous increase, by more than ten times. We present in this paper new results obtained for lithium, quasi-isentropically compressed in multistep shock experiments up to a pressure of 210 GPa and density of 2.3 g cm^{-3} , which significantly extends the region of densities studied in previous investigations [3–6].

High pressures and densities in a substance can be generated by isothermal, isentropic or dynamic (shock-wave) compression techniques. The maximum pressure achieved in static compression experiments is limited by the strength in the diamond anvil, while the pressure limits for the shock-wave method depend only on the driver's power. So the shock-wave experiments provide for a simple and effective means of investigating the electrical properties and phase transitions in matter at high pressure and temperature. As the characteristic time of the shock-wave experiments is of the order of 10^{-6} s or less, the diffusion processes and chemical interaction between the compressed material and surrounding media play a much less destructive role than in static experiments [3–5], in which the characteristic time is of the order of hours or more.

The method of multiple shock compression [7] is used in the present investigation to decrease the effects of irreversible heating in the front of the shock wave. It allows one to generate the thermodynamic states that can be considered as quasi-isentropic. The lithium sample is placed in an insulator between steel baseplates. The impact of the striker accelerated up to 5 km s^{-1} by the detonation products of high explosives produces the intense shock wave initiating the compression process. Due to the higher dynamic impedance of steel the shock wave in lithium is progressively reflected from the baseplate, reshocking the sample. The sequence of reverberating shocks between baseplates leads to reaching some final state with a higher pressure and lower temperature in comparison to the case of a single shock [7]. Note that a partition of a single shock into successive small shocks substantially decreases the final temperature and increases the final density, making the process more 'isentropic'. Such a specially designed process of multistep shock compression can be treated as a quasi-isentropic one. For example, the estimated temperature of lithium multistep compressed up to 100 GPa between stainless steel anvils is ~ 10 times less than would be achieved by a single shock to the same pressure.

The multiple shock compression of lithium up to megabar pressures was performed by special high explosive generators (see figure 1, illustrating the experimental set-up for the regime of multistep shock compression). The impact of a plane steel projectile initiated the sequence of shock waves in the baseplate–insulator–lithium–insulator–baseplate system. The stainless steel impactor with 3–4 mm thickness is accelerated up to 5 km s^{-1} by detonation products of the high explosive. The impactor strikes the stainless steel baseplate (2–4 mm thickness) initiating the shock wave. Lithium foil (0.07–0.15 mm thickness) is placed between polyethylene or Teflon insulating plates (0.8–1.0 mm). The shock in the sample then reverberates back and forth between the baseplate and the reflector through insulating plates and the lithium specimen until the pressure reaches a value equal to the pressure incident initially from the steel. A pulsed generator produces square pulses of magnitude 8.5 A in low-resistance loads. Electric signals from the lithium and a piezoresistive manganin gauge are

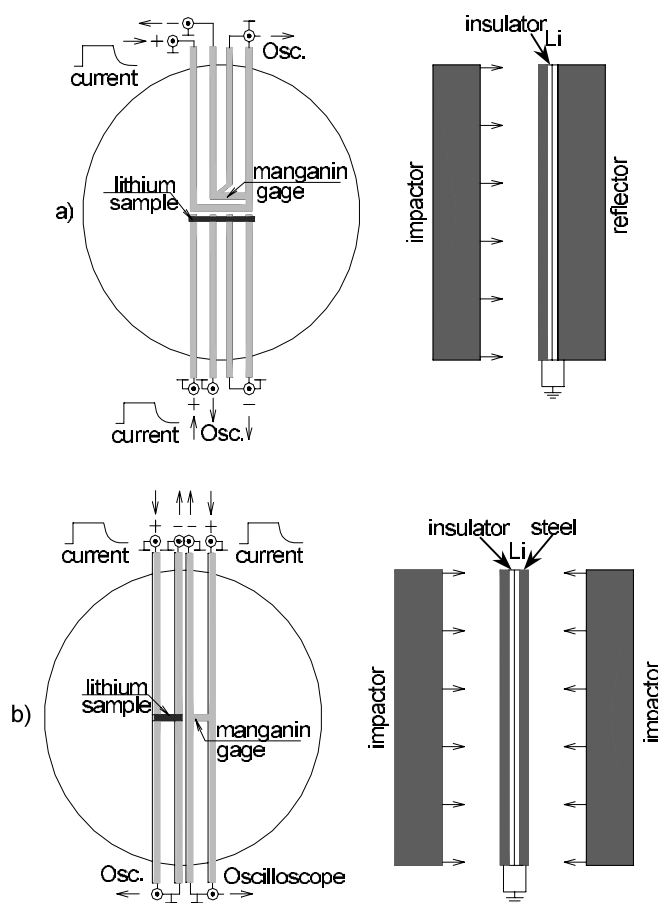


Figure 1. Experimental set-up. (a) Traditional scheme, (b) symmetrical scheme.

recording with a Tektronix TDS744A digital oscilloscope in the frequency band 0–1 GHz with a 2 ns sampling time. Pressure is measured by a four-point manganin gauge made of 35 μm thick manganin foil and electrodeposited with a 5 μm copper layer, excepting its bridge. The use of a four-point scheme excludes any influence due to resistance of the contacts and input leads. The cell was designed such that the lithium specimen and the bridge of the pressure gauge were in the region free from edge effects induced by hydrodynamic disturbances. The assembling of the cell was made in an argon dry box. All gaps were filled with a vacuum lubricant. The pressure range to 100 GPa has been investigated at liquid nitrogen (77 K) and room (293 K) initial temperatures. In the second series of measurements the symmetrical ('front collision') scheme of compression was used, with two high velocity impactors striking baseplates simultaneously from opposite directions. It made it possible to achieve much higher pressures, up to 210 GPa.

The time-resolved characteristics in the experiments carried out are pressure, measured by the manganin gauge, and voltage (and, therefore, resistance) measured with the use of four-point contact probes. The average errors for pressure and resistance are of the order of 5%. 1D numerical modelling has been done to obtain the density d and temperature T of lithium under conditions of the dynamic experiment. It has been carried out with the use of a semiempirical multiphase equation of state (EOS) [8]. The EOS model has been modified to

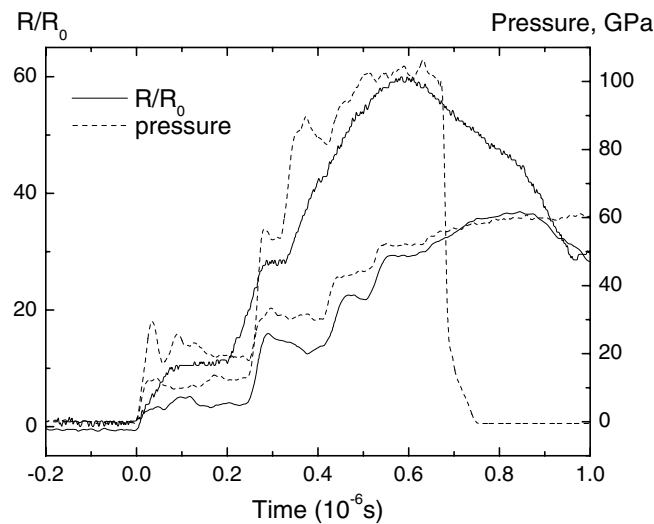


Figure 2. Relative resistance (left axis) and pressure (right axis) profiles as a function of time in multishock-compression experiments.

the full Debye model of a crystal [9] to adequately account for the low-temperature states; the obtained EOS of lithium describes the thermodynamic properties of solid, liquid and plasma states as well as high pressure melting, evaporating and ionization. We used resistance data, direct measurements of pressure to 100 GPa and results of computer simulation to obtain d , ρ and T , while at higher pressures, which are outside the region of applicability of the manganin gauge, these values resulted from computer simulation only. The change in thickness of the lithium samples under pressure, resulting in a corresponding correction of the resistivity ratio ρ/ρ_0 (where ρ_0 is the resistivity at ambient conditions), was also taken into account in analysing the experimental data. Estimated errors for pressure, density, resistivity and temperature are roughly 5%.

In agreement with the general theory of solid state [1], the lithium resistivity at moderate dynamic pressure $P < 10$ GPa slightly increases as pressure and temperature increase. The anomalous region occurs at a dynamic pressure of 40 GPa and above at normal [6] and low (77 K) initial temperatures. Two experimental resistivity histories for lithium and the appropriate pressure profiles obtained by the manganin gauge are plotted in figure 2. The analysis shows that 4–5 steps of the sample resistance and associated pressure steps can be resolved in the experimental recordings. Typically in the other experiments we can also resolve 4–5 individual pressure steps and measure lithium resistivity in each of them. It is evident that the pressure increases in steps corresponding to reflections of a shock wave from the steel baseplates. It is important that the resistivity of lithium increases synchronously with pressure in both experiments. Finally, the lithium resistivity decreases when the compressed sample begins to expand in the release wave.

The ‘front collision’ experiments with two impactors (figure 1(b)) allows one to achieve very high pressure. The maximum pressure in a lithium sample placed in polyethylene plates was about 160 GPa and in a sample in Teflon plates it was about 212 GPa, respectively. These experiments have been carried out at ambient conditions. The original resistance $R(t)/R_0$ recordings and corresponding pressure profile from a manganin gauge obtained in a 212 GPa experiment are plotted in figure 3. Teflon becomes a conductor at such high pressures, which results in an appearance of an additional load in the experimental circuit.

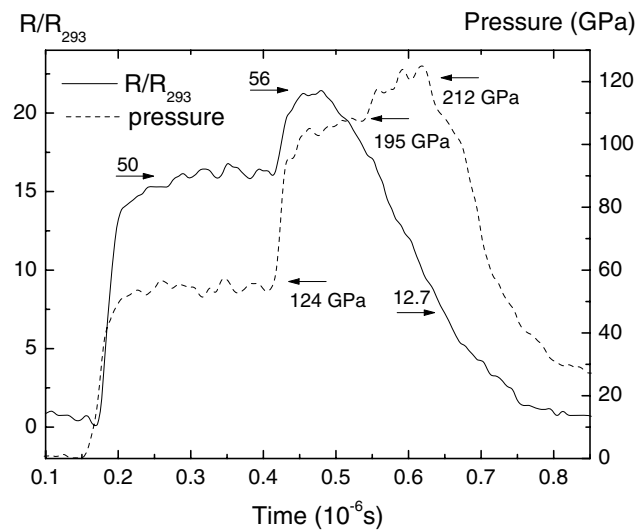


Figure 3. Relative resistance (left axis) and pressure (right axis) profiles as a function of time recorded in a 212 GPa experiment. Numbers near the arrows correspond to corrected values (see text).

It influences both the resistivity of the manganin gauge and lithium sample. The known dependence of manganin resistance on pressure allows one to account for the influence of surrounding media on the resistances of the gauge and sample. The corrected resistance of the lithium sample and pressure obtained from computer simulation are also plotted in figure 3. The experimental recordings demonstrate that the lithium resistance increases as the pressure increases up to 195 GPa and then it decreases even as the pressure reaches its maximum value of 212 GPa. An analogous result has been obtained in another multistep-compression experiment to 160 GPa. As is seen from figures 2, 3, lithium demonstrates anomalous behaviour under high compression. Its resistance changes weakly at pressures less than 40 GPa, rises anomalously to ten times in the pressure range 40–120 GPa and returns to its metallic value at 160–190 GPa.

A summary of the data obtained is given in figure 4 in the form of lithium specific resistivity ρ/ρ_{293} as a function of density. As one can see the specific resistivity increases monotonically with increasing density for all experiments at initial temperatures 77 and 293 K, corresponding to a maximum pressure of 100 GPa. The data obtained at higher pressures (160 and 212 GPa experiments) also agree with these measurements in the investigated density range up to 1.75 g cm^{-3} . At higher densities, of the order of $2.0\text{--}2.3 \text{ g cm}^{-3}$, the specific resistivity decreases dramatically. Lithium melts under conditions of the dynamic experiment in the first or in second shock waves in the region of pressure $<7.3 \text{ GPa}$ and temperature $<530 \text{ K}$, which depends on the intensity of the incident shock wave. The final states of dynamically compressed lithium, according to the results of 1D numerical modelling with real EOS, correspond to a liquid state at temperatures from 955 to 2833 K. At normal pressures, the estimated thermal component of the lithium specific resistivity ρ/ρ_{293} is about 20–25% of the total value at maximum density. So the main reason for change in the lithium resistivity is the effect of high pressure. Apparently, the anomalous region occurring at 40 GPa and $1.1\text{--}1.2 \text{ g cm}^{-3}$ corresponds to a fcc-*cI16* transition, in accordance with recent results [5]. The high pressure phase having poor conductivity can be a *cI16* or *oC8* (*Cmca* ‘paired-atom’ predicted by Neaton and Ashcroft [2]) phase.

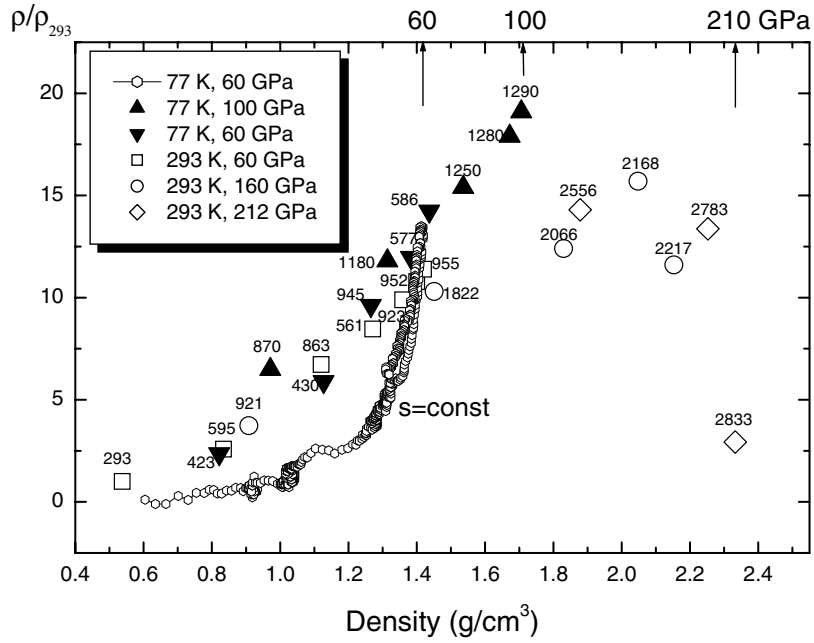


Figure 4. Resistivity of lithium as a function of density from multishock-compression experiments. The legend includes initial temperature and maximum pressure, while numbers near the points show calculated temperature.

The band structure calculations [2, 5] demonstrate that both phases are rather poor metals, possessing, for example, much lower values of the electron density of states at the Fermi level compared to the fcc or bcc phases. In this work we also carried out band structure calculations for the lithium *cI16* phase which is expected to be stable in the pressure range 48–165 GPa [5]. It is in this pressure range that most of our experimental data fall.

It is quite easy to estimate the behaviour of electrical resistivity under pressure in the lithium solid phase using the well-known expression for the resistivity of a metal:

$$\rho(p, T) = \frac{4\pi}{\omega_{\text{pl}}^2(p)} \frac{1}{\tau(p, T)}. \quad (1)$$

Here ω_{pl} is the electron plasma frequency defined as

$$\omega_{\text{pl}}^2 = \frac{4\pi e^2}{3V_0} \sum_{\mathbf{k}} |v_{\mathbf{kF}}|^2 \delta(E_{\mathbf{k}} - E_{\text{F}}) \quad (2)$$

where $v_{\mathbf{kF}}$ is the electron velocity at the Fermi surface and V_0 is the unit cell volume. $\frac{1}{\tau}$ is the relaxation rate due to the electron–phonon interaction. At $T > \Theta_{\text{D}}/5$ (Θ_{D} is the appropriate Debye temperature), $1/\tau$ is defined as

$$\frac{1}{\tau(p, T)} = 2\pi\lambda(p)T \quad (3)$$

where λ is the constant of electron–phonon coupling. In the above expression for $\rho(p, T)$, there are two pressure-dependent quantities, the plasma frequency $\omega_{\text{pl}}(p)$ and the constant of electron–phonon coupling $\lambda(p)$.

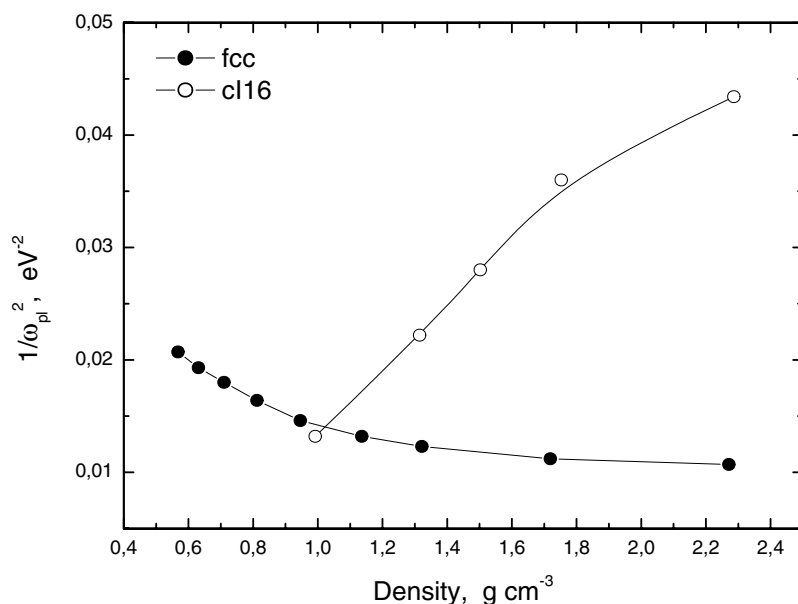


Figure 5. Dependence of $1/\omega_{pl}^2$ on lithium density for the fcc and *cI16* phases.

Figure 5 shows the pressure dependence of $1/\omega_{pl}^2$ for the fcc and *cI16* phases. In the fcc phase, $1/\omega_{pl}^2$ decreases smoothly upon compression, in accordance with the increase in electron charge density. In the *cI16* phase, however, $1/\omega_{pl}^2$ increases with increasing pressure. The estimate [10] shows that, in the *cI16* phase, the pressure dependence of λ is not too strong. The combined effect of increasing $1/\omega_{pl}^2$ and temperature upon compression could explain, at least qualitatively, our experimental data.

One should note that the dependence of electrical resistivity on density is similar in both solid (quasi-isentropic compression data $s = \text{constant}$ from previous work [6] in figure 4) and liquid states. Another interesting and unusual fact is that, under conditions of dynamic experiments, liquid lithium is a poor conductor to 160 GPa (for example, crystalline germanium and silica are typical semiconductors while these materials have good conductivity in the liquid state). It seems that compressed liquid lithium has an ordered structure which is broken at 160 GPa when it returns to being a 'good' metal, see figure 4. Only two crystalline structures of lithium are known to have electron excitation spectra corresponding to a 'bad' metal. These are the *cI16* and *oC8* phases. It is still a question which of them is more stable at higher temperatures, even in the solid state. It is all the more obscure which of these two phases would preserve the short-range order upon transition to the liquid state.

Thus, the electrical conductivity of lithium at megabar dynamic pressures demonstrates anomalous behaviour. It changes from typical values to metallic values to semiconductor ones and then back to metallic. The analysis of the experimental data proves that lithium, the first metal in the periodic system of elements having one valence electron, can no longer be considered as a 'simple' metal at high pressure. We plan to continue the experimental and theoretical investigation of these exotic effects by performing similar experiments at lower temperatures and higher pressures, and also exploring other alkali metals. We also plan to consider the phase diagrams of alkali metals at non-zero temperature and to estimate the pressure dependence of the melting temperature. Our first experiments carried out for sodium proved the existence of the effect.

Acknowledgments

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References

- [1] Ashcroft N W and Mermin N D 1976 *Solid State Physics* (New York: Holt, Rinehart and Winston)
- [2] Neaton J B and Ashcroft N W 1999 *Nature* **400** 141
- [3] Struzhkin V V *et al* 1999 *Bull. Am. Phys. Soc.* **44** 1489
- [4] Mori Y and Ruoff A L 2000 *Science and Technology of High Pressure* ed M H Manghnani, W J Nellis and M F Nichol (Hyderabad: University Press) p 75
- [5] Hanfland M, Syassen K, Christensen N E and Novikov D L 2000 *Nature* **408** 174
- [6] Fortov V E *et al* 1999 *JETP Lett.* **70** 628
- [7] Postnov V N *et al* 1983 *Fiz. Goren. Vzryva* **5** 160 (in Russian)
- [8] Bushman A V, Kanel G I, Ni A L and Fortov V E 1993 *Thermophysics and Dynamics of Intense Pulse Loadings* (London: Taylor and Francis)
- [9] Landau L D and Lifshits E M 1976 *Statistical Physics* (New York: Pergamon)
- [10] Christensen N E and Novikov D L 2001 *Phys. Rev. Lett.* **86** 1861