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Anomalous resistivity of lithium at high dynamic pressure

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Experimental investigation of lithium compressed by multiple shock waves up to the pressure 210 GPa demonstrates the abnormal dependence of electric resistivity. As against normal behavior of metal, the resistivity monotonically increases in the pressure range 30–150 GPa from typical metallic value at ambient conditions in more than 15 times, returning back to metallic one at pressure higher then 160–210 GPa. The obtained results demonstrate anomalous resistivity of lithium both in solid in liquid states.

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High-pressure studies play an important role in understanding 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 solid, a closest-packed phase with the maximum coordination number appears, insulators become conductors, and 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 prototype "simple" metal with metallic bonding. At ambient conditions, alkali metals occur in simple body-centered-cubic or close packed lattices. But modern sophisticated quantum mechanical calculations by Neaton and Ashcroft [2] predict much reach and interesting behavior of matter at high pressure. 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's nuclei form pairs producing 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] to pressure 60 GPa have demonstrated a number of interesting optic anomalies, but they do not contain measurements of the electric resistivity – the basic indicator of metal – insulator transitions. Recent X-ray diffraction studies to 50 GPa pressure [5], done at reduced to 200 K temperature 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 high-pressure face-centred-cubic (f.c.c.) 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 linear muffin-tin orbital method predicted that this phase, observed in elements first time, is stable to 165 GPa pressure. In our previous work [6] we reported direct measurements of the electric resistivity ρ of lithium compressed by dynamic methods by factor of $\sim$3 to 60 GPa, which revealed its anomalous, more than in 10 times, increase. We present in this paper new results obtained for lithium, quasi-isentropically compressed in multistep shock experiments up to pressure of 210 GPa and density of 2.3 g/cm^3, which significantly extends the region of densities studied in prevoius 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 shock wave method depend only on the driver's power. So the shock-wave experiments provide for simple and effective means in the investigation of electrical properties and phase transitions in matter at high pressure and temperature. As characteristic time of the shock-wave experiments is of the order 10^{-6} s or less, the diffusion processes and chemical interaction between the compressed material and surrounding media play much less destructive role than in static experiments [3 – 5], in which characteristic time is hours or more.

The method of multiple shock compression [7] is used in present investigation to decrease effects of irreversible heating in the shock wave front. It allows one to generate the thermodynamic states that can be considered as quasi-isentropical. The lithium sample is placed in

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insulator between steel baseplates. The impact of the striker accelerated up to 5 km/s by detonation products of high explosive produces the intense shock wave initiating the compression process. Due to higher dynamic impedance of the 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 of some final state with higher pressure and lower temperature in comparison with the case of 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 specially designed process of multistep shock compression can be treated as quasi-isentropic one. For example, 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 Fig.1, illustrating the experimental setup for the regime of multistep shock compression). The impact of 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 by detonation products of high explosive. The impactor strikes 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).

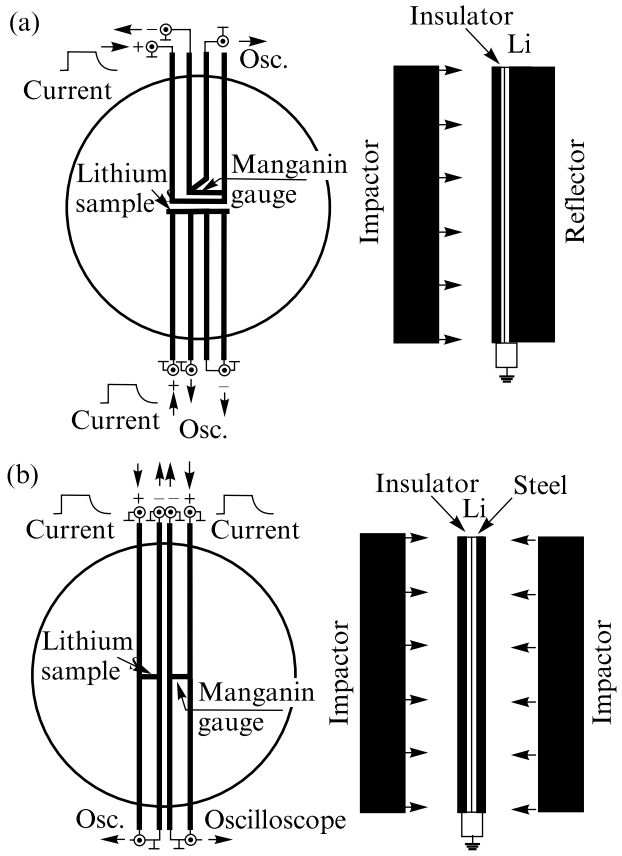

Fig.1. Experimental setup. a) Traditional scheme; b) Symmetrical scheme

The shock in the sample then reverberates back and forth between the base plate and the reflector through insulating plates and lithium specimen until the pressure reaches the value equal to the pressure incident initially from the steel. Pulsed generator produces square pulses of magnitude 8.5 A in low-resistance loads. Electric signals from lithium and piezoresistave manganin gauge are recording with Tektronix TDS744A digital oscilloscope in the frequency band 0–1 GHz with a 2 ns sampling time. Pressure is measured by four-points manganin gauge made of 35 μm thick manganin foil and electrodeposited with a 5 μm copper layer excepting its bridge. The usage of a four-point scheme excludes any influence due to resistance of 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 in 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 used was the symmetrical ("front collision") scheme of compression with two high velocity impactors striking baseplates synchronically from opposite directions. It made it possible to achieve much higher pressures up to 210 GPa.

The time-resolved characteristics in carried out experiments 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 5%. 1D numerical modeling has been done to obtain density d and temperature T of lithium under conditions of dynamic experiment. It has been carried out with the use of semiempirical multiphase equation of state [8] (EOS). The EOS model has been modified to the full Debye model of a crystal [9] to account for adequately the low-temperature states; the obtained EOS of lithium describes 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 of thickness of lithium samples under pressure, resulting in corresponding correction of the resistivity ratio ρ/rho_0 (where ρ_0 is the resistivity at ambient conditions) was also taken into account in analyzing the experimental data. Estimated errors for pressure, density, resistivity and temperature are roughly 5%.

In agreement with general theory of solid state [1], the lithium resistivity at moderate dynamic pressure $P < 10$ GPa slightly increases as pressure and temperature grow. The anomalous region occurs at dynamic pressure of 40 GPa and higher at normal and low (77 K) initial temperature. Two experimental resistivity histories for lithium and the appropriate pressure profiles obtained by the manganin gauge are plotted on Fig.2. The analysis shows that 4–5 steps of the sample resis-

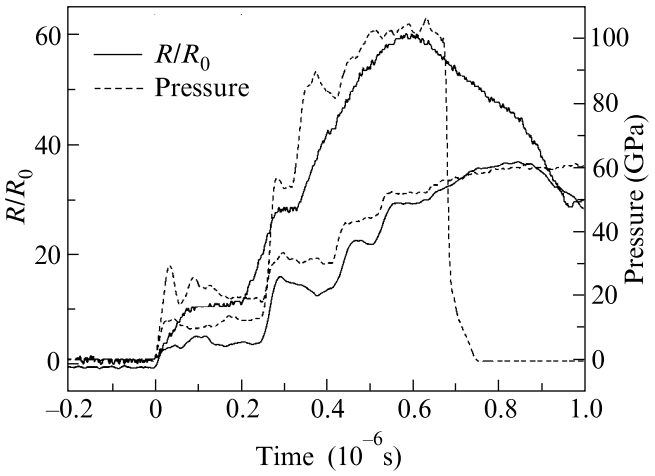

Fig.2. Relative resistance (left axis) and pressure (right axis) profiles as function of time in multishock-compression experiments

tance and associated pressure steps can be resolved in the experimental recordings. Typically in the other experiments we also can resolve 4–5 individual pressure steps and measure lithium resistivity in each of them. It is evident that the pressure grows in steps corresponding to reflections of a shock wave from steel baseplates. It is important, that the resistivity of lithium grows synchronously with the pressure in both experiments. Finally, lithium resistivity decreases when the compressed sample becomes to expand in release wave.

The "front collision" experiments with two impactors (Fig.1b) allows one to achieve very high pressure. The maximum pressure in lithium sample placed in polyethylene plates was of 160 GPa and in sample in teflon plates of 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 manganin gauge obtained in 212 GPa experiment are plotting on Fig.3. Teflon becomes a conductor at such high pressure, which results

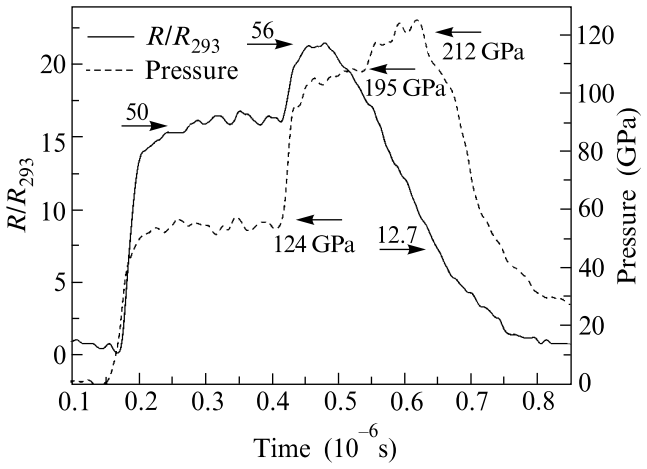

Fig.3. Relative resistance (left axis) and pressure (right axis) profiles as function of time recorded in 212 GPa experiment. Numbers near arrows correspond to corrected values (see text)

to an appearance of additional load in experimental circuit. It influences on the resistivity of both 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 gauge and sample. The corrected resistance of lithium sample and pressure obtained from computer simulation are also plotted on Fig.3. The experimental recordings demonstrate that the lithium resistance grows as pressure increases up to 195 GPa and then it decreases even the pressure reaches the maximum value of 212 GPa. Analogous result has been obtained in another multistep-compression experiment to 160 GPa. As it is seen from Figs.2,3, lithium demonstrates anomalous behaviour under high compression. Its resistance changes weakly at pressures less then 40 GPa, rises anomalously in tens times in the pressure range 40–120 GPa and becomes back metallic at 160–190 GPa.

The summary of obtained data is given on Fig.4 in the form of lithium specific resistivity ρ/ρ_{293} as function of density. As one can see the specific resistivity increases monotonically with density increase for all experiments at initial temperatures 77 K and 293 K corresponding to maximum pressure 100 GPa. The data obtained at higher pressures (160 GPa and 212 GPa experiments) also agree with these measurements in inves-

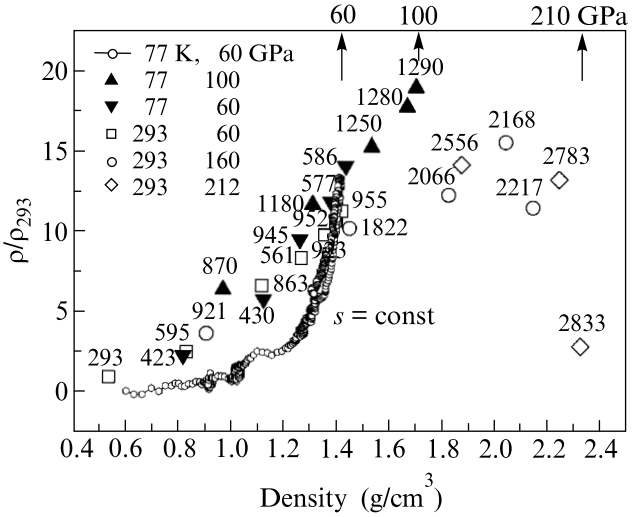

Fig.4. Resistivity of lithium as function of density from multishock-compression experiments. The legend of points includes initial temperature and maximum pressure, numbers near points show calculated temperature

tigated density range to 1.75 g/cm^3. At higher densities of the order of 2.0–2.3 g/cm^3 the specific resistivity decreases dramatically. Lithium melts under conditions of dynamic experiment in first or in second shock waves in the region of pressure < 7.3 GPa and temperature < 530 K, which depends on the intensity of incident shock wave. Final states of dynamically compressed lithium, according to results of 1D numerical modeling with real EOS, correspond to liquid state at temperatures from 955 to 2833 K. The estimated thermal component of lithium specific resistivity ρ/ρ_{293} is of the order of 20–25 % from total value at the maximum density. So the main reason of change of lithium resistivity is decreasing of interatomic distance. Apparently the anomalous region occurring at 40 GPa and 1.1–1.2 g/cm^3 corresponds to f.c.c.-cI 16 transition, in accordance with recent results [5]. The high pressure phase having poor conductivity can be cI 16 or oC 8 (Cmca 'paired-atom' predicted by Neaton and Ashcroft [2]) phase. One should note that the dependence of resistivity on density is similar in both solid (quasi-isentropic compression data s = const from previous work [6] on Fig.4) and liquid states. Another interesting and unusial fact is that under conditions of dynamic experiments liquid lithium is poor conductor to 160 GPa (for example, crystal germanium and silica are typical semiconductors while these materials have good conductivity in liquid state). It seems that compressed liquid lithium has orederd structure which is broken at 160 GPa and lithium becames back a "good" metal, see Fig.4.

Thus, the electrical conductivity of lithium at megabar dynamic pressure demonstrates the anomalous behavior. It changes from typical to metal values to semiconductor one's and then back to metallic. The analysis of experimental data proves that lithium, first metal in the periodic system of elements having one valence electron, can not more be considered as a "simple" metal at high pressure. We plan to continue the experimental investigation of these exotic effects by performing similar experiments at lower temperatures and high pressures, and also exploring other alkali metals. First experiments carried out for sodium proved the existence of the effect.

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