Anomalies in the elastic properties of polycrystalline lanthanum at phase transitions under pressure

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A pulsed ultrasound technique is used to measure the velocities of longitudinal and transverse elastic waves in polycrystalline lanthanum under pressures up to 82 kbar at room temperature. The pressure dependence of the density, elastic constants, and Debye temperature are calculated. The anomalies found in the pressure dependence of the sound velocities reflect an additional anharmonicity of the longitudinal and transverse acoustic phonons at two phase transitions in the intervals 0–30 kbar and 60–80 kbar. A decrease in the transverse-sound velocity in the pressure range 18–23 kbar indicates the approach of a polymorphic transformation at which the lanthanum structure, as a result of a shift of individual close-packed layers, changes from double-hexagonal close-packed to face-centered cubic. On the basis of an anomalous increase observed in the compressibility at pressures 62–76 kbar, and in conjunction with band stucture-calculations and with x-ray data and data on the pressure dependence of the superconductivity transition temperature T_c and electrical resistance R, this transition can be ascribed to an electronic transition of order $2\frac{1}{2}$. However, a final conclusion as to whether this transition is an electronic–topological one can be reached on the basis of direct measurements of the topology of the Fermi surface.

According to its position in the periodic table, lanthanum under normal conditions is an electronic analog of the d-transition metals scandium and yttrium and, even though it heads the group of rare earth metals, has no f electrons. The conduction band of lanthanum is formed by two $6s$ electrons and one $5d$ electron. Unlike its analogs, lanthanum is a relatively high-temperature superconductor at atmospheric pressure: T_c is 5 K for the double-hexagonal close-packed (dhcp) phase and 6 K for the face-centered cubic (fcc) phase. Lanthanum has an anomalously low Debye temperature and melting point. At low temperatures it has a negative coefficient of thermal expansion and a high electronic specific heat. These peculiar physical properties of lanthanum can be explained by a high density of states at the Fermi level, as is typical of d-transition metals, and by a strong electron–phonon coupling and a relatively soft phonon spectrum.

The properties of lanthanum under pressure are also unusual. The temperature of its transition to the superconducting state increases substantially, reaching 13 K at 180 kbar. This can be attributed to a continuous increase in the density of states at the Fermi level and a softening of the short-wavelength phonons. In addition, the $T_c(p)$ curve exhibits anomalies due to linear pressure effects. In particular, above 70 kbar there is an anomalous increase in T_c, with $(\partial^2 T_c/\partial p^2)T > 0$ (Ref. 1). There is also an anomalous change in the electrical resistance R under pressure. Over the pressure interval 25–35 kbar on the 294 K isotherm there is a resistance decrease of 15% accompanying the dhcp–fcc transformation. From 60 kbar to the inflection point at 70 kbar the resistance increases $[(\partial^2 R/\partial p^2)_T > 0]$, and at pressures above 80 kbar the $R(p)$ curve saturates. Such a behavior of the electrical resistance in the interval 60–80 kbar has been attributed[1] to a rapid increase in the soft-phonon contribution.

A hypothetical phase diagram has been proposed[1] for lanthanum on the basis of the measured pressure dependence of T_c and R. This diagram was constructed by proceeding from the intuitive idea that the p–T diagram of lanthanum is isomorphic to that of cerium. It was also taken into consideration that the x-ray structural data[2] in the pressure range 30–120 kbar reveal only the fcc phase of La and do not show any volume anomalies. The dhcp–fcc transformation boundary and the melting curve on the hypothetical phase diagram for La can be considered firmly established.

Interest in the study of the elastic properties of lanthanum has been motivated by analysis of the pressure curves of T_c and R, the features of which have been attributed chiefly to anomalies in the phonon spectrum.[1] The ultrasound technique used in the present paper permits the study of the changes in the low-frequency acoustical part of the phonon spectrum and enables one to relate these changes to the nature of the phase transitions.

In the present experiments we used polycrystalline lanthanum with a purity of 99.76%. The velocities $v_{l,0}$ and $v_{t,0}$ of longitudinal and transverse elastic waves, respectively, were measured under normal conditions, and the density ($\rho = 6.16$ g/cm^3) was determined by the method of hydrostatic suspension. The propagation velocities of elastic waves at high pressures were studied in two stages by a pulsed-ultrasound technique. At pressures up to 30 kbar the measurements were made on a piezometric apparatus.[3] The diameter of the samples was 18 mm and the height was 5–7 mm. For measurements in the range 25–82 kbar a sample was placed in a modified high-pressure chamber of the "toroid" type.[4] In this case the length of the sample was 7 mm and the diameter was 14 mm. The pressure was measured during each trial by monitoring the jumps in the electrical resistance of the reference metals Bi, Ba, and Tl in accordance with Ref. 5.

In the course of the experiments we determined the changes with pressure of the transit times $\Delta t_l(p)$ and $\Delta t_t(p)$ of longitudinal and transverse ultrasonic waves, respective-

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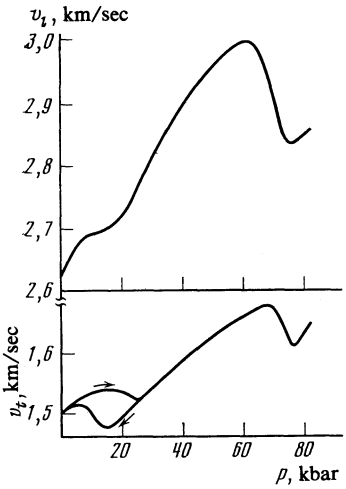

FIG. 1. Pressure dependence of the velocities v_l and v_t of longitudinal and transverse ultrasonic waves, respectively, in polycrystalline lanthanum.

ly, at frequencies of 3–5 MHz and also the change in the sample length $\Delta l(p)$. The corrections to the measured quantities due to the deformation of the chamber were determined by a special series of experiments. The measurements permitted calculation of the pressure dependence of the sound velocities $v_l(p)$ and $v_t(p)$ (Fig. 1), the bulk modulus $K_T(p)$, the shear modulus $G(p)$, the Debye temperature $\Theta(p)$ (Fig. 2), and the relative volume change $V/V_0(p)$ (Fig. 3) in lanthanum at pressures of up to 82 kbar. In the calculation the adiabatic–isothermal correction was taken to be independent of pressure.

Figure 1 shows the pressure dependence of the velocities of longitudinal and transverse elastic waves in lanthanum at room temperature under pressures of up to 82 kbar. One can discern two regions, 0–30 kbar and 60–80 kbar, in which the monotonic growth of the velocities is disrupted. It is known that in a stable structure the speed of ultrasound should increase monotonically with pressure, with a negative second derivative $(\partial^2 v/\partial p^2)_T$. The decrease of the transverse sound velocity v_t in the pressure interval 18–23 kbar

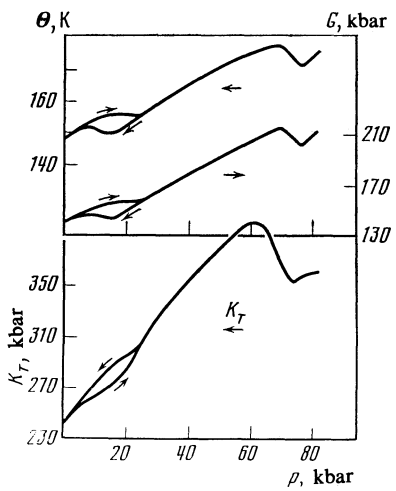

FIG. 2. Pressure dependence of the bulk modulus K_T, shear modulus G, and Debye temperature Θ for polycrystalline lanthanum.

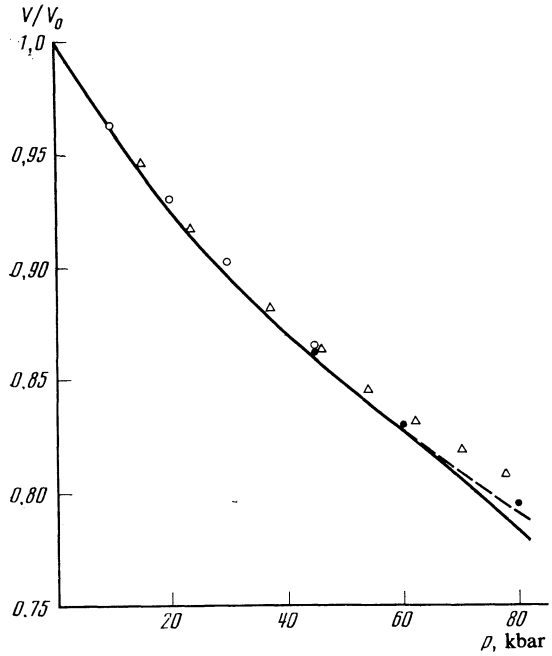

FIG. 3. Pressure dependence of the reduced volume V/V_0 for polycrystalline lanthanum. The solid curve represents the data of the present experiment, the filled circles the data of Ref. 2, the open circles the data of Ref. 6, and the triangles the data of Ref. 7.

(with a simultaneous drop in the signal amplitude) is indicative of an increase in the shear compliance of the lattice and in the anharmonicity of the atomic vibrations. When the amplitude of these vibrations reaches a certain critical value, the shear strain causes the original dhcp lattice of the lanthanum to convert to an fcc lattice.

Our measurements have yielded estimates of the pressure interval in which the groundwork is laid for the polymorphic transformation (18–23 kbar for increasing pressure and 15–10 kbar for decreasing pressure) and of the pressures at the onset of the dhcp–fcc ($\sim$22–23 kbar) and fcc–dhcp ($\sim$10 kbar) transformations. A large hysteresis ($\sim$13 kbar) is thus in evidence; calculations[6] show that this is due to the small difference in the specific volumes of the coexisting phases. In fact, as in the analogous measurements of Ref. 7, we were unable to detect a volume discontinuity from the piezometer readings. The data of Bridgman[8] give this discontinuity as about 0.26%. The pressure dependence of the longitudinal-sound velocity $v_l(p)$ does not exhibit hysteresis.

In a study[9] of the pressure dependence of the electrical resistance of alloys of lanthanum with cerium it was suggested that the dhcp–fcc transformation in lanthanum is electronic, analogous to the γ–α transformation in cerium. However, we did not observe near this phase transition in lanthanum the anomalous decrease in v_l that preceded the isomorphic transition in cerium.[10] Nevertheless, the $v_l(p)$ curve did exhibit a change in the sign of the second derivative from minus to plus at a pressure of $\sim$12 kbar. We believe that this feature can be attributed to some qualitative change which occurs in the electron spectrum of lanthanum, triggering the dhcp–fcc structural transition. Such an explanation seems logical since lanthanum, being a rather high-tem-

perature superconductor, has a strong electron–phonon coupling. In addition, a self-consistent calculation of the band structure of fcc lanthanum has shown that in the 0–50 kbar range there is a change in the connectivity of the Fermi surface, whereupon instead of a connecting neck a packet of electrons forms in the L–U–W–K plane.[11]

Beginning at about $62 \pm$ kbar the longitudinal wave slows down (see Fig. 1), and a 72 kbar there is an inflection point on the $v_l(p)$ curve. At pressures of 70–72 kbar the ultrasound signal is noticeably attenuated for this wave. The slowing down of the transverse wave begins at a higher pressure ($\sim$68 kbar). Throughout the slowing region of the transverse wave there is a substantial attenuation of the ultrasound signal, with the maximum decrease in its amplitude occurring near the $v_t(p)$ minimum at 76 ± 1 kbar. Above 76 kbar there is a rather rapid increase in both sound velocities and a simultaneous increase in the signal amplitude. It should be pointed out that there are no discontinuities or hysteresis in the curves in the pressure range 60–80 kbar.

We have thus detected a softening of the longitudinal and transverse long-wavelength acoustical phonons in lanthanum at 62–76 kbar.

The decrease with pressure of the longitudinal-sound velocity results in an increase in the compressibility (a decrease in the bulk modulus K_T) of lanthanum in the interval 62–74 kbar (Fig. 2). The pressure dependence of the reduced volume V/V_0 (Fig. 3) exhibits a change in slope at about 62 kbar on account of the subsequent increase in the compressibility. The dashed line shows an extrapolation of the initial part (0–62 kbar) of the experimental $V/V_0(p)$ curve. The difference in the values of the reduced volume corresponding to these two curves is around 0.006 at 80 kbar. Obviously, in view of the small size of this effect the x-ray measurements[2] in the range 30-120 kbar revealed no anomalies in the compressibility nor any changes in the crystal structure of lanthanum.

Quite recently Grosshans, Vohra, and Holzapfel[12] managed to detect a gradual change in the fcc lattice of lanthanum at pressures above 70 kbar by means of the more sensitive technique of energy-dispersive diffraction. They assumed that the distortion of the fcc lattice starts out as a soft mode, which then freezes into a static distortion. They classified this phenomenon as a second-order phase transition. It seems natural to suppose that the anomalous decrease which we have observed in the transverse-sound velocity at pressures above 68 kbar, with the concomitant substantial signal attenuation, is just a reflection of the onset of this soft mode. Such a supposition is supported by the decrease with pressure of the transverse-wave velocity v_t in our experiment near the polymorphic transformations, implying an increase in the shear compliance of the lattice (see, e.g., Refs. 10 and 13). It is noteworthy that within the accuracy of the experiment $v_t(p)$ exhibits no hysteresis in the range 60–80 kbar, indicating[6] that the specific volumes of the fcc and distorted fcc structures are indistinguishable, in contradiction to the assumption of a first-order phase transition. But this is not a second-order phase transition (which is characterized by the absence of a volume discontinuity) either, since the elastic properties of lanthanum exhibit no discontinuities. Thus the absence of discontinuities and the lack of hysteresis in the curves $v_l(p)$, $v_t(p)$, $K_T(p)$, and $V/V_0(p)$ in the interval from 60 to 80 kbar are grounds for assuming that the transition in lanthanum is neither first-order nor second-order.

The increase in the compressibility of lanthanum above 62 kbar in the present experiment is due to an additional screening of the ion–ion repulsion as a result of the anomalous growth of the density of states at the Fermi surface. To what can we attribute the features in the density of states of lanthanum as a function of pressure? It is known[14] that the total density of electron states is the sum of the states in the bands, so that the "turning on" of a new band (in the case of band overlap) is indistinguishable (as far as features in the density of states are concerned) from the appearance of a new cavity within the band or from the breaking of a connecting neck. As we have already mentioned, the conduction band of lanthanum is formed by two $6s$ electrons and one $5d$ electron. Upon compression the relatively free $6s$ states overlap more strongly than do the more localized $5d$ states. Under these conditions the s electrons prefer to go to the d band. The enhancement of the d character of the conduction band is a usual effect in metals with unfilled or partially filled d states. The s–d transitions play a decisive role in the systematics of the structural transitions of these metals under pressure.[15] Calculations have shown[16] that the experimentally observed sequence of structural transformations of rare earth metals under pressure (hcp–Sm-lattice–dhcp–fcc) is a result of the increase in the population of the d band. This sequence of structures under pressure is also observed in the $4d$ transition metal yttrium,[17] which has no f electrons.

Thus, on the one hand, the appearance of features in the density of states of lanthanum is made possible by the overlap of the s and d bands. On the other hand, self-consistence band-structure calculations for fcc lanthanum have shown[11] that at pressures between 50 and 120 kbar the second Brillouin zone touches the Fermi level on the Γ–K line, and the connecting neck in the hole part of the Fermi surface breaks off, i.e., the connectivity of the Fermi surface changes. Such a feature in principle leads[11] to an instability of the Lifshitz-Dagens type,[18,19] wherein the strong electron-phonon coupling in the metal destabilizes its crystal lattice as well. The change in the crystal lattice at such a transition can be very weak and continuous, as is seen for the transition in lanthanum.[12] The pressures at which the instability of the electronic structure and crystal lattice appear can, in principle, be different. It is possible that for this reason the softening of the longitudinal acoustical phonons in our experiments began at 62 kbar, whereas the softening of the transverse phonons was observed at pressures above 68 kbar. Unfortunately, no experimental data have been published on the topology of the Fermi surface of lanthanum under pressure. Our technique cannot be used to determine unambiguously which physical phenomenon (an s–d transition or a change in the connectivity of the Fermi surface) gives rise to the density-of-states anomalies responsible for the anomalous behavior of $v_l(p)$, $v_t(p)$, and $K_T(p)$ in the pressure range 62–76 kbar.

In discussing the nature of this transformation in lanthanum, we should consider the theoretical results of Lifshitz

et al.,[20] who obtained the equations of the theory of elasticity for fundamentally new nonlinear acoustic media such as a metal near the electronic–topological transition. They showed that near this transition the growth in the anharmonic constants is much stronger than the nonlinearities due to the usual cubic anharmonicity. Our experimental results indicate, in particular, that there is an appreciable ($\sim 18\%$) nonlinearity $K_T(p)$ in the interval 62–76 kbar [for the cubic anharmonicity $(\partial K_T/\partial p)_T$ should be constant]. The $K_T(p)$ curve which we obtained in the indicated pressure interval is qualitatively similar to the curve of $\partial p/\partial V$ versus z near an electronic–topological transition in the Lifshitz calculation (see Fig. 3a in Ref. 18).

It has been shown[21] on the basis of the simplest model of superconductivity that a possible cause of nonlinearity in $T_c(p)$ is a change in the topology of the Fermi surface under pressure: If, with increasing pressure, a closed Fermi surface goes over to an open surface or a new cavity forms, then T_c grows in a nonlinear manner. A change in T_c of this nature has been observed[1] in lanthanum at pressures above 70 kbar, and self-consistent band-structure calculations for lanthanum[12] have shown that in the interval 50–120 kbar a new cavity forms when the connecting neck is broken off in the hole part of the Fermi surface. The anomalous increase in the electrical resistance of lanthanum at 60–80 kbar and 294 K is evidently caused by the same features of the density of states that are responsible for the nonlinear pressure dependence of T_c.

In summary, it follows from what we have said that the compressibility anomalies (see Fig. 2) and the pressure dependence of T_c and R (Ref. 1) suggest that the lanthanum transition at 62–76 kbar can be ascribed to an electronic transition of order $2\frac{1}{2}$. However, the final conclusion as to whether this transition is in fact an electronic–topological one can be drawn on the basis of direct measurements of the topology of the Fermi surface.

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