Anomalies in elastic properties and features of electronic transitions in lanthanum and praseodymium at pressures up to 84 kbar

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The propagation velocities of longitudinal and transverse elastic waves in polycrystalline praseodymium have been measured by a pulsed ultrasonic method at pressures up to 84 kbar at room temperature. The density, elastic constants, and Debye temperature are calculated as functions of the pressure. The anomalies found in the pressure dependence of the sound velocities in praseodymium, as in lanthanum, which was studied previously {V. A. Goncharova and G. G. Pl'ina, Zh. Eksp. Teor. Fiz. **86**, 1708 (1984) [Sov. Phys. JETP **59**, 995 (1984)]}, reflect an additional anharmonicity of longitudinal and transverse acoustic phonons at two phase transitions which occur in the intervals 12–50 and 66–80 kbar. The experimental results on lanthanum and praseodymium are discussed on the basis of a pseudopotential method and in the Friedel model with 6*s*–5*d* electronic transitions. Estimates show that the observed anomalies in the elastic characteristic of both of these metals are caused by an accelerated 6*s*–5*d* "flow" of electrons. Similar anomalies should be observed in cesium II near the first-order isomorphic electronic 6*s*–5*d* transition at 42.2 kbar.

The family of lanthanides is a group of elements with completely filled outer 6*s* and 5*p* states, which screen 4*f* states which are localized within these outer states and which are progressively filled.

An empirical correlation between the crystal structure of the lanthanides and that part of the atomic volume which is occupied by the ion core was found[2] in 1975. The meaning of this correlation is that an increase in the relative volume of the ion core gives rise to a series of structures: hcp; a structure of the SM type; dhcp; and fcc. This series occurs in the trivalent lanthanides either as the pressure is raised or as the atomic number of the element decreases. Calculations[3] have shown that (1) the relative volume of the ion core is actually a measure of the filling of the *d* band and (2) it is the *d*-band contribution to the total energy which forces the lattice of trivalent lanthanides to undergo a change in crystal structure in the observed sequence as the number of *d* electrons increases from 1.5 to 2.5.

The reason for the decisive role played by the *d* electrons in the packing of the atoms is that the filled *d* states lie near the face of the Brillouin zone, while the filled *s* states (or *s-p* hybridized states) lie near the center of the zone and do not affect the crystal structure of the metal. Characteristically, the 4*d* transition element yttrium, which has no *f* electrons at all, also undergoes a change in atomic packing in the same sequence under pressure.[4]

Pressure increases the *d* nature of the conduction band of metals with vacant or partially filled *d* states, since upon compression the freer *s* states overlap the highly localized *d* states and increase in energy with respect to the latter states. As a result, a transition of electrons from the *s* band to the *d* band becomes favored from the energy standpoint. Recent calculations and experiments with shock waves have shown that this process stretches out along the pressure scale and "softens" the equation of state; i.e., the pressure and the bulk modulus increase with increasing compression slightly more slowly than they would in the absence of *s*–*d* transitions.[5]

An x-ray structural analysis confirms this sequence of crystal structures for several lanthanides,[6] which is determined by the filling of the *d* band. On the other hand, this method does not (for example) reveal a distorted fcc structure in lanthanum and praseodymium near 70 kbar. This phase was orginally discovered in lanthanum, praseodymium, and the 4*d*-transition element yttrium by a more sensitive energy-dispersion x-ray method.[4]

The ultransonic method which we have used permits a study of this transition in lanthanum[1] on the basis of anomalies in the compressibility and shear modulus. The results demonstrate again the high sensitivity of the ultrasonic method as a tool for studying phase transitions. Another advantage of the method is that it can continuously follow the changes in the compressibility of the substance as the pressure is being changed, both in regions in which the phases are stable and in the very course of a transition. The compressibility of a substance is extremely sensitive to the state of its electronic subsystem.

Our purposes in the present study were to determine the particular features of the changes in the elastic properties (compressibility, shear modulus, and Debye temperature) of praseodymium at the known dhcp-fcc structural transition and at the phase transition involving a distortion of the hcp lattice near 70 kbar and to identify the nature of the latter transition on the basis of the observed features in praseodymium and in lanthanum, which we studied previously.[1]

It is customary to assume that the conduction band of lanthanum is formed by two 6*s* electrons and a single 5*d* electron, while the trivalent state of praseodymium involves two 6*s* electrons and one (of the three) 4*f* electrons.

At both ordinary and high pressures, these two metals

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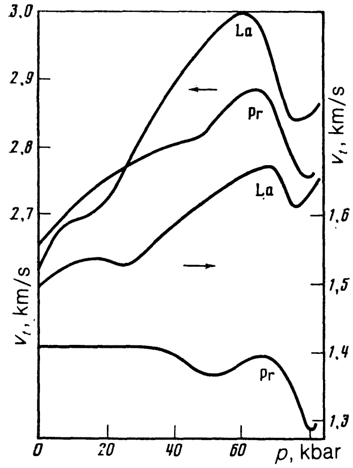

FIG. 1 Pressure dependence of the propagation velocities of longitudinal (v_l) and transverse (v_t) ultrasonic waves in polycrystalline lanthanum and praseodymium.

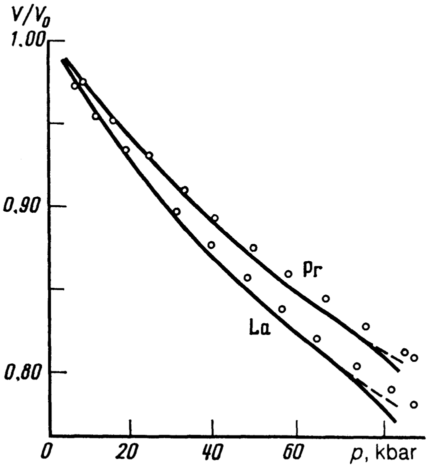

FIG. 3. Pressure dependence of the reduced volume V/V_0 for polycrystalline lanthanum and praseodymium. Solid lines—Data from the present study; ○—values calculated from Eq. (2) (the equation of state for lanthanum and praseodymium at $T = 0$); dashed lines-extrapolation of the normal dependence $V/V_0(p)$.

exhibit similarities in physical properties over a broad temperature range. For example, they have anomalously low melting and Debye temperatures and high electronic specific heats. At pressures up to 100 kbar they exhibit an identical allotropy,[7] and their electrical resistivities have a similar pressure dependence.[8,9]

The praseodymium samples used in the present experiments are 99.76% pure. The experimental procedure is described in Ref. 1.

From the experimental data on praseodymium, we calculated 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) up to 84 kbar. Shown for comparison in the same figures is the corresponding behavior for lanthanum.

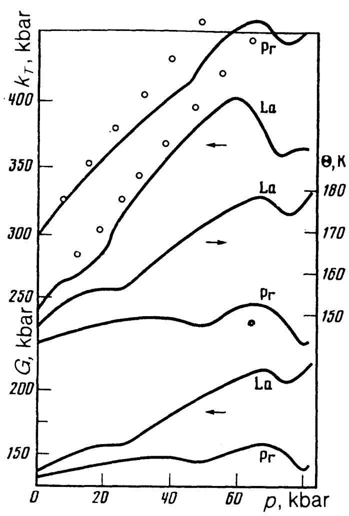

FIG. 2. Pressure dependence of the bulk modulus K_T, the shear modulus G, and the Debye temperature Θ for polycrystalline lanthanum and praseodymium. The circles are values of $K_T(p)$ calculated from (3).

Figure 1 shows the pressure dependence of the propagation velocities of longitudinal and transverse elastic waves, $v_l(p)$ and $v_t(p)$, respectively, in La and Pr. We can distinguish two regions in which the monotonic increase in the velocities is disrupted.

In a stable structure, we know that the ultrasonic should increase monotonically with the pressure, and its second derivative with respect to the pressure, $(\partial^2 v/\partial p^2)_T$, should be negative. The decrease in the transverse sound velocity v_t in the pressure intervals 18–23 kbar for La and 30–49 kbar for Pr (upon a sharp decrease in the signal amplitude) is evidence of an increase in the compliance of the lattice for shear strain and an increase in the anharmonicity of the atomic vibrations. When these vibrations reach a certain critical amplitude, the shear strain transforms the original dhcp lattice of the metal into an fcc lattice. The pressure at which this transition occurs is 23 ± 2 kbar for La and 50 ± 2 kbar for Pr in our measurements.

Measurements of the pressure dependence $v_t(p)$ have made it possible to evaluate the hysteresis of the dhcp-fcc transition in each of these metals: ~ 13 kbar for La and ~ 25 kbar for Pr. These results agree with the conclusions reached in Ref. 10. The significant hysteresis of the transitions in La and (especially) Pr is a consequence of a small difference in the specific volumes of the coexisting phases. In each case we were unable to detect an abrupt change in volume with a strain gauge, as in corresponding measurements for La (Ref. 11) and Pr (Ref. 12). After Bridgman determined[13] the magnitude of the abrupt change in volume ($\sim 0.26\%$) for this transition in La, he noted a pronounced hysteresis in the case of Pr, in measurements of the pressure dependence of the shear stress.[14] On the basis he concluded that this transition in Pr is a first-order phase transition.

There is no hysteresis loop on the pressure dependence of the longitudinal sound velocity, $v_1(p)$, for either of these metals. These curves typically have a rise in a region with $(\partial^2 v_l/\partial p^2)_T < 0$ before the transition, while near the transition there is a change in the sign of the second derivative, at a pressure ~ 12 kbar for La and at ~ 47 kbar for Pr. We believe that this stuctural feature may be due to some qualitative change in the electron spectrum of the metal, which stimulates dhcp-fcc transition.

The decrease in the transverse sound velocity found experimentally in lanthanum and praseodymium in the pressure intervals 18–23 and 30–49 kbar, on the one hand, and the pronounced hysteresis in this dependence, on the other, confirm that we are dealing with a first-order phase transition in each of these metals, which allows us to determine the parameters of this transition.

At pressures of 66–81 kbar for Pr, as at 62–77 kbar for La (Ref. 1), we observe softening of both longitudinal and transverse long-wave acoustic phonons, accompanied by the absorption of an ultrasonic signal (Fig. 1). The maximum decrease in the amplitude of both the longitudinal and transverse signals is noted near the minimum on the pressure depenence of the sound velocity. The anhysteric behavior of $v_l(p)$ and $v_t(p)$ is evidence that their structural features here are not due to a first-order phase transition.

The decrease in the longitudinal sound velocity with the pressure, in the intervals 62–76 and 66–81 kbar for the lanthanum and the praseodymium, respectively, causes a smooth decrease in the bulk modulus $K_T(p)$, by 9% and 4%, followed by an increase in this modulus (Fig. 2). The pressure dependence of the reduced volume, $V/V_0(p)$, has an inflection point at about 62 kbar for lanthanum and 66 kbar for praseodymium. This inflection point indicates an increase in the compressibility of these metals s they are compressed further (Fig. 3). The dashed lines in this figure are extrapolated regions of the normal dependence $V/V_0(p)$. The differences in the reduced volumes coresponding to the extrapolated and measured parts of the $V/V_0(p)$ curves at 80 kbar are ~0.006 for lanthanum and ~0.003 for praseodymium.

We attribute the observed decrease in the transverse sound velocity for both of these metals in the interval 66–80 kbar, accompanied by a significant attentuation of the ultrasonic signal, to the smooth distortion of the fcc lattices of lanthanum and praseodymium which was found[4] at a pressure ~ 70 kbar and classified as a second-order phase transition. However, despite the high sensitivity of the ultrasonic method, we have not been able to detect a jump of any sort in the change in the bulk modulus $K_T(p)$ at these pressures for either of the metals.

DISCUSSION OF RESULTS

At the equilibrium volume ($p = 0$), metals with a relatively high binding energy are known to have a relatively low compressibility. However, the increase caused in this energy during compression by electronic transitions leads to an anomalous increase in the compressibility. We can show that the anomalous behavior which is observed for the elastic characteristics of lanthanum and praseodymium in the pressure interval 62–80 kbar can be explained by the pseudopotential method[15] with 6s–5d electronic transitions.

We write the total energy of the metal per unit volume of the deformed object as follows, where we are taking into account terms of zeroth and first orders in the pseudopotential of the vacant core[16]:

$$E=E_0+Ar_c^2/x-B/x^{1/3}, \tag{1}$$

where E_0 is the energy of the interacting electron gas, the second term is the energy of the repulsion of the vacant cores, the third term is the electrostatic energy of the ion lattice, $x = V/V_0$ is the relative compression, V_0 is the equilibrium volume at $p = 0$, and r_c is the radius of the vacant core, determined for metals with unfilled f shells from the ionization potentials of the atoms.[16]

Using the condition $p(1) = 0$, using $K_0 = xd^2E/dx^2|_{x=1}$, and ignoring the first term in (1), since an estimate shows that its contribution to the pressure and the bulk modulus is small in comparison with that of the second term for La and Pr, we find

$$p/K_0={}^3/_2[x^{-2}-x^{-4/3}], \tag{2}$$

$$K_T={}^3/_2K_0[2x^{-2}-{}^4/_3x^{-4/3}], \tag{3}$$

where K_0 is the bulk modulus at $T = 0$.

Expression (2) is the equation of state for La and Pr at $T = 0$. Since we have $(\partial K_T/\partial T)_p = K_T^2(\partial\alpha/\partial p)_T \sim -\alpha K_T$, however, ($\alpha$ is the bulk thermal expansion coefficient), the difference between the bulk modulus at room temperature, K_{T_0}, and that at zero temperature, K_0, is a few percent for La and Pr. The increment in the pressure due to $T \neq 0$ is on the order of $\alpha K_0 T$, or ~ 1 kbar at $T = 300$ K. This result means that expression (2) can also be used at $T \neq 0$, if we replace K_0 by K_{T0}.

The circles in Fig. 3 show function (2) for both of these metals. The agreement with experiment is satisfactory up to about 60 kbar; at higher pressures the discrepancy between the calculated and experimental data increases.

The results calculated on the function $K_T(p)$ from (3) also agree rather well with the experimental curve in the initial stage of the compression (Fig. 2). With increasing pressure, the calculated function $K_T(p)$ deviates significantly from the experimental behavior and does not describe the observed anomalies for either lanthanum or praseodymium. The reason for this striking discrepancy between the theoretical and experimental results on $K_T(p)$ is that expressions (2) and (3) ignore the role played by the transition of electrons from the 6s state to the 5d state with increasing compression.

The physical reason for the anomalous increase in the compressibility of La and Pr under pressure is that the coupling of the conduction electrons with the nucleus increases as these electrons acquire a more pronounced d nature. This result works in a self-consistent way to cause less effective repulsion of valence electrons from the electrons of the inner shells of the ions. In other words, valence electrons with different values of the orbital angular momentum l "feel" their own potential (1), with the corresponding value of r_c: With increasing l, the core radius r_c decreases.

Since the width of the d band is smaller than that of the s band, the effective mass of the electrons of the d band, m_d, is larger than that of the s electrons, m_s. Consequently, the effective mass of the conduction electrons increases in *s–d* transitions; this increase is superimposed on a general decrease, caused by the band broadening as the lattice atoms move closer together as a result of the pressure. However, it is this increase in the effective mass which is responsible for the anomalies in the pressure dependence of the compressibility.

Let us use the relationship between the width of the *d* band, W_d, and the radius of an atomic sphere, *r*, and between the width and the radius of a *d* state, r_d, which has been found for transition metals[16]:

$$W_d=6.83\hbar^2 r_d^3/m_s r^5, \quad W_d\approx 12.4\hbar^2/m_d r^2.$$

We thus find

$$r_d\approx (m_s/m_d)^{1/3} r. \tag{4}$$

We assume that a function of the type (4) also holds for the lanthanides with some effective radius r_{sd}, i.e., for a state which incorporates the 6*s*–5*d* transitions of electrons under pressure:

$$r_{sd}=(m_s/m_d^*(x))^{1/3} r, \tag{4a}$$

where

$$m_d^*|_{x=1}=m_s.$$

Since the enhancement in the *d* nature of the conduction electrons increases the ionization potential *U*, which is inversely proportional to r_c, we can write

$$U\sim\frac{Ze^2}{r_c'}\sim\frac{Ze^2}{r_c}\left[\frac{m_d^*(x)}{m_s}\right]^{1/3},$$

i.e.,

$$r_c'=[m_s/m_d^*(x)]^{1/3} r_c. \tag{4b}$$

Taking into account the enhancement of the pseudopotential during *s–d* electron transitions, and using (4a) and (4b), we can replace (1) by

$$E=E_e+\left[\frac{m_s}{m_d^*(x)}\right]^{2/3}\frac{Ar_c^2}{x}-\left[\frac{m_d^*(x)}{m_s}\right]^{1/3}\frac{B}{x^{1/3}}. \tag{5}$$

Using the initial conditions

$$p(1)=0, \quad K_{T0}=x\frac{d^2E}{dx^2}\bigg|_{x=1}, \quad m_d^*|_{x=1}=m_s,$$
$$\frac{dm_d^*}{dx}\bigg|_{x=1}=0, \quad \frac{d^2m_d^*}{dx^2}\bigg|_{x=1}=0,$$

we find

$$p=\frac{3}{2}K_{T0}\left[x^{-2}y^{-2/3}-x^{-4/3}y^{1/3}+\frac{dy}{dx}\left(\frac{2}{3}y^{-5/3}x^{-1}+y^{-2/3}x^{-1/3}\right)\right], \tag{6}$$

$$\begin{aligned}K_T=\frac{3}{2}K_{T0}\bigg[&2y^{-1/3}x^{-2}-\frac{4}{3}y^{1/3}x^{-4/3}\\&+\frac{dy}{dx}\left(\frac{2}{3}y^{-4/3}x^{-1}+\frac{2}{3}y^{-2/3}x^{-1/3}\right)\\-\frac{d^2y}{dx^2}&\left(\frac{1}{3}y^{-4/3}+y^{-2/3}x^{2/3}\right)+\left(\frac{dy}{dx}\right)^2\left(\frac{4}{9}y^{-5/3}+\frac{2}{3}y^{-5/3}x^{2/3}\right)\bigg],\end{aligned} \tag{7}$$

where $y=m_d^*(x)/m$, and dy/dx is a measure of the rate of the *s–d* flow of electrons upon compressions.

Let us analyze expressions (6) and (7). It follows from (6) that there are two possibilities for a first-order phase transition: 1) Since we have $dy/dx<0$, a first-order phase transition is possible if there is an abrupt increase in $|dy/dx|$. In this case, the pressure dependence of the bulk modulus has no anomalies in the region before the transition. 2) A first-order phase transition is possible if, under compression, d^2y/dx^2 increases nonlinearly and without bound, so that the structure may become labile ($dp/dx>0$). In this case the bulk modulus should undergo an anomalous decrease in the region before the transition, according to (7). It is probably this possibility which is realized in cesium II at 42.2 kbar, as we will discuss below.

An abrupt change in the second derivative d^2y/dx^2 leads to a second-order phase transition.

We turn now to the features of the changes in dy/dx and d^2y/dx^2 as functions of the pressure for both metals. We will draw on our experimental behavior $V/V_0(p)$ and $K_T(p)$ and also expression (6) and (7). Calculations show that the decrease in the bulk modulus observed experimentally is due to a progressively increasing *s–d* "flow" of electrons in the interval 62–72 kbar for La and 66–76 kbar for Pr. The term containing d^2y/dx^2 in (7) is responsible for these anomalies. This term increases nonlinearly in those pressure intervals. Starting at 72 kbar for La, and at 76 kbar for Pr, the process of *s–d* electron transitions begins to slow down, with the result that the bulk modulus increases above 80 kbar. If the *s–d* transitions does not slow down, a first-order phase transition would have occurred. A possible reason for the decrease in the compliance of the lanthanum and praseodymium lattices with respect to compression above 80 kbar is an increase in the Fermi repulsion of electrons. Alternatively, it might be caused by subtler effects, stemming from the continuously varying curvature of the bottoms of the *s* and *d* bands in the course of the *s–d* flow of electrons.

It follows from the estimates above, in the model which we are using here, that the anomalies observed in the bulk modulus can be explained by a fairly small increase in the effective mass with increasing pressure: $dy/dp\approx 10^{-5}$ dbar^{-1}. The augmented plane wave method was used in Ref. 17 to calculate the band structure and the pressure dependence of the electron states of the *s*, *p*, *d*, and *f* bands of lanthanum; transitions of electrons to narrow *d* and *f* bands were taken into account. From the results of those calculations we find the rather rough estimate $dy/dp\sim 10^{-4}$ kbar^{-1}. Such a value of dy/dp should lead to a first-order electron transition in model (6),(7).

The maximum value of the derivative dy/dp which causes an increase in compressibility is, in order of magnitude, relatively insensitive to variations of the exponents in (4a) and (4b) over fairly wide ranges. This result is evidence that the estimates are of satisfactory reliability.

It can thus be concluded that the anomalies in the compressibility are determined by *s–d* transitions of electrons and are very sensitive to them. According to our estimates, and in agreement with Ref. 18, the topological transition in lanthanum for which calculations were carried out in Ref. 17 makes only a small contribution to the increase in the compressibility (within the experimental error).

We have been discussing the anomalies in the compressibility of lanthanum and praseodymium on the basis of a simplified single-band model or the pseudopotential of the vacant cores. The use of a two-parameter pseudopotential model (incorporating the finite well depth), however, should lead to the same results, since the well depth increases upon *s–d* transitions.

On the other hand, as Harrison has mentioned,[16] the vacant-core model is a rather crude approximation for the lanthanides, since the *d* band is partially filled in these metals. For this reason, it is worthwhile to evaluate the effect of the 6*s*–5*d* flow of electrons on the pressure dependence of the compressibility of La and Pr on the basis of the graphic Friedel model,[16,19] which explains the increase in the total binding energy and the decrease in the compressibility toward the middle of the series of transition metals.

Using the expression for the *d*-electron contribution to the binding energy,[16] we find the increments in the pressure and the bulk modulus due to the *s–d* transitions:

$$\delta p \approx \frac{1}{2}\frac{W_{d0}}{V_0 x^{5/3}}\left(1-\frac{n_d}{5}\right)\frac{dn_d}{dx}, \qquad (8)$$

$$\delta K_0 \approx \frac{5}{6}\frac{W_{d0}}{V_0 x^{5/3}}\left(1-\frac{n_d}{5}\right)\frac{dn_d}{dx}+\frac{W_{d0}}{10V_0 x^{4/3}}\left(\frac{dn_d}{dx}\right)^2 - \frac{W_{d0}}{2V_0 x^{4/3}}\left(1-\frac{n_d}{5}\right)\frac{d^2n_d}{dx^2}, \qquad (9)$$

where W_{d0} is the width of the deep end at $p=0$, n_d is the number of *d* electrons, and V_0 is the volume per atom at $p=0$.

Because of the relation $dn_d/dx<0$, the values of δp and δK_0 are negative; i.e., the compressibility increases during *s–d* transitions under pressure. Using the data from Ref. 17 ($W_{d0}\approx 8.5$ eV, $V_0=179.5$ Å^3, $n_d=1.54$, $dn_d/dp\approx 10^{-3}$ kbar^{-1}) and the values $K=358$ kbar and $x\approx 0.79$ from the present study, we find $\delta p=-17$ kbar for lanthanum from (8). This figure agrees fairly well with the experimental value (Fig. 3). It also follows from (9) that the term containing d^2n_d/dx^2, which increases nonlinearly, is responsible for the anomaly in the compressibility which is observed experimentally.

We thus see that estimates based on the pseudopotential model and on the Friedel model, incorporating the *d*-electron contribution to the binding energy, show that 6*s*–5*d* electron transitions are responsible for the observed anomalies in the compressibility of lanthanum and praseodymium.

Let us briefly discuss the reason for the anomalous behavior of the shear modulus of lanthanum and praseodymium under pressure near the polymorphic transition and in the interval 60–80 kbar.

The shear modulus, in contrast with the bulk modulus, is determined by structure-dependent terms in the expression for the energy. A significant contribution is made to the shear modulus of polyvalent metals by the band energy calculated in second-order perturbation theory in the pseudopotential.[16] Even a very slight increase in the band energy leads to a substantial decrease in the shear modulus in this case and thus to an instability of the lattice. Since the *s–d* flow of electrons under pressure increases the pseudopotential and thus the band energy, the shear modulus decreases.

We thus believe that the decrease in the shear modulus of La and Pr under pressure near the polymorphic dhcp-fcc transition and at ~70 kbar, where one observes distortion of the fcc structure of each of these metals, can also be attributed to 6*s*–5*d* electron transitions.

The anomalous change in slope on the $K_T(p)$ curves at the dhcp-fcc transition in each of these metals also reflects the *s–d* dynamics of the electron structure upon this transition.

Our conclusions agree with calculations[17] for lanthanum, which predict ranges in which the lattice is unstable within the intervals, 0–50 and 50–120 kbar. Our conclusions also agree with measurements of the pressure dependence of the electrical resistance, $R(p)$, of lanthanum[8] and praseodymium.[9] For each of these metals, an anomalous increase in $R(p)$ is found starting at about 60 kbar, with saturation above 80 kbar. The change in slope occurs at ~70 kbar for La and at ~75 kbar for Pr. The authors attribute those anomalies to a rapid increase in the contribution of soft phonons. Actually, the relative contribution to the change in the resistance as a function of the pressure during scattering of electrons by the vibrations of thermal phonons is[20]

$$\frac{d\rho}{\rho\, dp}\approx-\frac{2d\Theta}{\Theta\, dp}.$$

A decrease in the Debye temperature θ with the pressure leads to an increase in the amplitude of the vibrations and thus an increase in the resistance. According to our estimates, the value of $(d\rho/dp)/\rho$ from the data of Refs. 8 and 9 is about 0.004, on the average, for both lanthanum and praseodymium. According to our own data, the value of $(2/\Theta)(d\Theta/dp)$, for lanthanum and praseodymium are 0.002 and 0.004, respectively. The agreement between the results, at least in order of magnitude, is obvious. The increase in the resistance is therefore indeed a consequence of softening of phonons.

We note in conclusion that in cesium II, as mentioned above, the same factors should lead to a decrease in the bulk and shear moduli with the pressure near the isomorphic 6*s*–5*d* electron transition near 42 kbar (Ref. 12). The reason is that, in contrast with lanthanum and praseodymium, the progressive increase in the rate of *s–d* transitions in this case, as follows from (6), unrestrained by anything, leads to a labile lattice ($\partial p/\partial x>0$) and thus a first-order phase transition with a 9% jump in volume. It is easy to give a qualitative description of the tendency toward an abrupt electron transition. An increase in compression accelerates the *s–d* flow of electrons and promotes compressibility of the lattice, which in turn accelerates *s–d* transitions even further. A feedback loop arises wich is capable of causing an avalanche process, sharply decreasing the lattice constants. We should stress that it is the decrease in the bulk and shear moduli with pressure near the electron transition in cesium II which is the reason for the increase in the electrical resistance of this substance and also for the formation of a maximum on the melting curve.

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