Elastic behavior of ytterbium at a semimetal-semiconductor-semimetal transition under pressure

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Pressure-induced interband $sp \leftrightarrow d$ transitions in strontium and ytterbium change both the type of conductivity and the crystal structure (fcc–bcc–hcp). To determine the effect of the band motion on the phonon spectrum, the elastic properties, the melting curve, and the equation of state of ytterbium under pressure, the propagation of velocities of longitudinal and transverse electric waves in polycrystalline ytterbium under pressures of up to 8.2 GPa and room temperature were measured by the pulsed ultrasonic method. The pressure dependence of the density and the elastic constants for the fcc and bcc phases of ytterbium were calculated. The first observations of anomalous pressure-induced changes of the measured sound speeds, the bulk elastic, and the shear moduli at semimetal-semiconductor-semimetal transitions were made in ytterbium and in the previously investigated strontium [V. A. Goncharova, G. G. Il'ina, and F. F. Voronov Fiz. Tverd. Tela (Leningrad) **24**, 1849 (1982)]. A comparative analysis of the pressure dependence of the elastic characteristics of ytterbium and strontium is made, and it is shown that the observed pressure-induced changes can be explained on the basis of the nonlinear dynamics of $d \leftrightarrow s$ electronic transitions. The character of the pressure-induced change of the shear modulus made it possible to predict the form of the melting curves of the bcc phases of ytterbium and strontium. © *1995 American Institute of Physics.*

1. INTRODUCTION

It has recently been found that taking into account the contribution of the d band, lying adjacent to the Fermi level, is very fruitful for explaining the observed change in the crystal atomic packing, both as a function of the atomic number and under pressure.[1] Analysis of the crystal structure in a series of transition metals (examples are Y, Zr...) gives a convincing picture of the dependence of the atomic packing motif on the occupancy of the d states. Moreover, there exists an entire series of nontransition metals, such as rare earths, heavy alkali metals (Rb, Cs), and alkaline-earth metals (Ca, Sr), whose d bands under ordinary conditions lie near the Fermi level. As the pressure increases, the d states, as a rule, become preferred; this results in the transfer of s and p electrons in them. As a result, these metals acquire the properties of transition metals under pressure.

Since its $4f$ shell is completely filled, ytterbium is divalent and acts more like a heavy alkaline-earth metal. Under ordinary conditions ytterbium is an fcc semimetal as a result of the partial overlapping of the $sp-d$ bands.[2] Under pressure this overlapping decreases and the d band is emptied, and at pressures near 1.3 GPa it becomes a semiconductor.[2] Further compression intensifies the d-character of the conduction of electrons of ytterbium; at 4 GPa this results in a first-order phase transition with the atomic packing changing from fcc to bcc.[3] Pressure-induced stabilization of the more open (from the standpoint of hard-sphere packing) bcc structure in both ytterbium and its electronic analogs calcium[4] and strontium[2] can be explained by a transition of the valence electrons to deeper-lying d levels; this transition creates the prerequisites for the interatomic spacing to decrease and the number of nearest neighbors to decrease to eight in the present case.

These features of the pressure-induced band motion in ytterbium under pressures of up to 4 GPa have also been observed in strontium.[2] Under higher pressures the bcc ytterbium, in contrast to bcc strontium, transforms, according to Ref. 5, into a state of variable valence as a result of gradual delocalization of one $4f$ electron and its transfer into the d band.

Therefore, in the case of both ytterbium and the previously investigated strontium it is possible to observe both the intensification and attenuation of the d character of the conduction electrons right up to formation of an energy gap. A study of how these processes influence the change in the phonon spectrum of the metal is not only of interest in itself, but it also makes it possible to understand more deeply the dynamics of $sp \leftrightarrow d$ electronic transitions.

We recently conducted an ultrasonic investigation of lanthanum and praseodymium—metals with a partially filled d band—and we observed the pressure-induced anomalies of the propagation velocities of elastic waves and compressibility, which were explained by the acceleration of the $sp \leftrightarrow d$ electron transfer process.[6,7] In Ref. 8 we employed the same method to investigate strontium, but the pressure-induced changes which we found in the elastic properties of strontium were not analyzed within the model of interband transitions.[1] In this connection, and also because of the striking similarities between the phase diagrams of Sr and Yb,[9,10] in the present paper we shall compare the observed effects in these semimetals and we shall try to explain them.

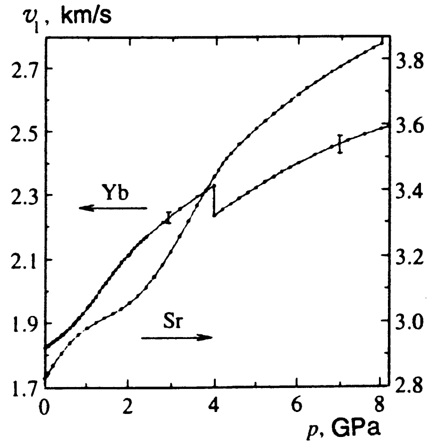

FIG. 1. Pressure dependence of the propagation velocity v_l of longitudinal sound in ytterbium and strontium.

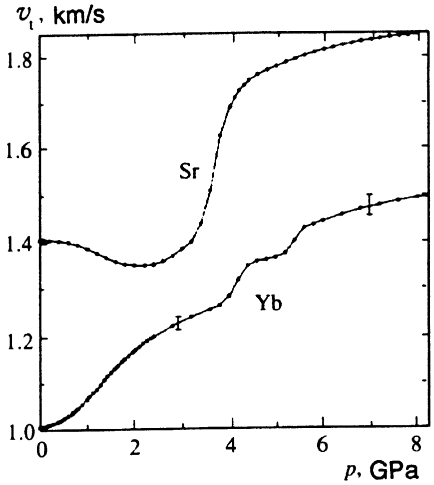

FIG. 2. Pressure dependence of the propagation velocity v_t of transverse sound in ytterbium and strontium.

2. EXPERIMENTAL PART

The propagation velocities of longitudinal and transverse sound in 99.6% pure polycrystalline ytterbium were measured by the pulsed ultrasound method[11] at frequencies of 3–5 MGz at room temperature and pressures of up to 8 GPa. The samples were prepared in the form of a cylinder 18 mm in diameter and 5–7 mm high as well as in the form of a ~3 mm high conical slice with an average diameter ~13 mm. The faces were parallel to within 0.001 mm.

The initial density of the ytterbium samples was $\rho_0=6.96\pm0.03$ g/cm^{3}and the initial propagation velocities of longitudinal elastic waves were $v_{l0}=1.816\pm0.006$ km/s and of transverse elastic waves $v_{t0}=1.003\pm0.005$ km/s were determined at atmospheric pressure and room temperature by the method of hydrostatic weighing.

The ytterbium samples were subjected to quasihydrostatic compression in high-pressure chambers of the piston-cylinder type (from 0 to 2.5 GPa)[12] and of the "toroid" type (from 2.5 to 8 GPa).[13,14] Benzene and indium served as the pressure-transmitting medium. In the course of the experiments the changes $\Delta t_t(p)$ and $\Delta t_l(p)$ in the transit times of longitudinal and transverse elastic waves, respectively, were determined by the pulsed ultrasonic method.[11] A single reading of the time was made with an accuracy of 1–2 ns. A quartz piezoelectric transducer was placed outside the high-pressure zone. Special experiments were performed in order to make corrections to the changes in the transit length and time of elastic waves in the sound guides. Corrections to the pressure-induced changes in the length and density of a sample were calculated on the basis of the experimental dependence of the transit times of $t_l(p)$ and $t_t(p)$ of longitudinal and transverse elastic waves, respectively, in accordance with the procedure of Ref. 15.

The pressure dependence of the density $\rho(p)$, the propagation velocities of longitudinal elastic waves $v_l(p)$ (Fig. 1) and transverse elastic waves $v_t(p)$ (Fig. 2), the bulk modulus $K_T(p)$ (Fig. 3), the shear modulus $G(p)$ (Fig. 4), the Debye temperature $\Theta(p)$, and the normalized volume V/V_0 as a function of the reduced pressure p/K_{T0}, where K_{T0} is the isothermal bulk modulus under normal conditions (Fig. 5) were determined by analyzing the experimental results for the fcc phase of ytterbium with increasing pressure from 0 to 4 GPa. The same figures display for comparison the corresponding behavior obtained in Ref. 8 for strontium.

To calculate the elastic properties of the high-pressure phase of bcc ytterbium, it is necessary to estimate its density at the transition pressure, taking into account the volume jump $\Delta V/V_0=0.032$, accompanying this transformation.[3] The elastic characteristics of bcc ytterbium and strontium in the pressure range 4–8.2 GPa are presented in the same figures as for the fcc phases of these semimetals.

The linear increase in the propagation velocity of longitudinal elastic waves $v_l(p)$ in ytterbium at ~0.4 GPa (Fig. 1) is replaced by anomalous growth, and it is only at pressures of ~1.3 GPa (semimetal-semiconductor phase transition) that the pressure dependence $v_l(p)$ acquires the normal form $(d^2v_l/dp^2|_T<0)$ and remains so right up to the fcc-bcc tran-

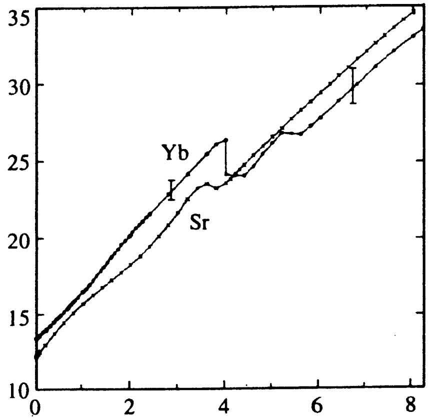

FIG. 3. Pressure dependence of the bulk modulus K_T of ytterbium and strontium.

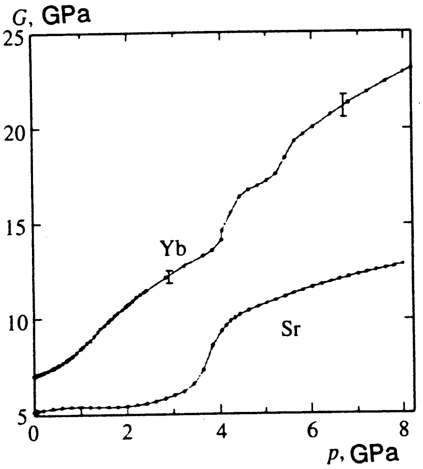

FIG. 4. Pressure dependence of the shear modulus G of ytterbium and strontium.

sition at 4.0 GPa. This phase transition is accompanied by a discontinuous decrease in the velocity v_l by approximately 4%. In bcc ytterbium the propagation velocity of longitudinal waves increases without any anomalies up to a pressure of 8.2 GPa.

When fcc strontium undergoes a small compression, in contrast to ytterbium, a normal increase of the velocity v_l is observed up to ~1.8 GPa, and as the pressure increases up to ~3 GPa, when strontium becomes a semiconductor, the increase accelerates.[2] Under further compression up to 8 GPa, the pressure dependence $v_l(p)$ becomes normal, and the fcc–bcc phase transition does not destroy its monotonicity, evidently, because the volume change at the phase transition in Sr is quite small.[8]

The pressure dependences $v_t(p)$, $K_T(p)$, and $G(p)$ displayed in Figs. 2, 3, and 4 will be examined in detail in the next section when we discuss the results.

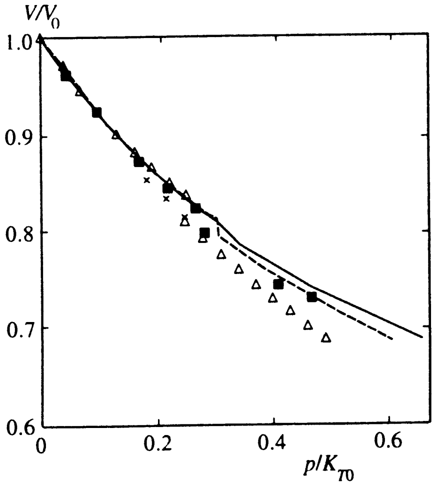

FIG. 5. Reduced volume V/V_0 versus the normalized pressure p/K_{T0} for ytterbium (dashed line) and strontium (solid line). The dots are the results of x-ray and piezometric investigations: △—Ref. 16, ■—Ref. 17, ×—Ref.18.

Figure 5 displays the normalized volume V/V_0 versus the reduced pressure p/K_{T0} for both phases of ytterbium (dashed line) and strontium (solid line). In spite of the nontrivial character of the pressure dependences of the bulk elastic modulus K_T for ytterbium and strontium (Fig. 3), V/V_0 as a function of p/K_{T0} for the fcc phase of these semimetals can be approximated by a common continuous curve, which fits well the data from x-ray[16,17] and strain gauge[18] investigations of ytterbium. Murnagan's equation describes this curve well. For the bcc phases of ytterbium and strontium the pressure dependence $V/V_0(p/K_{T0})$ differs, for all practical purposes, only because different authors obtained different volume jumps at the fcc–bcc phase transition.[5]

3. DISCUSSION AND CONCLUSIONS

We now make a comparative analysis of the pressure dependence of the elastic characteristics of ytterbium and strontium, and we shall show that the observed features of the changes in the propagation velocities of elastic waves, the bulk modulus K_T, and the shear modulus G can be explained on the basis of the nonlinear $sp \leftrightarrow d$ dynamics of electrons of these metals.

Figure 3 displays the pressure dependence of the bulk modulus K_T for both phases of ytterbium and strontium. The linear increase of this modulus for fcc ytterbium up to ~0.8 GPa is replaced by an anomalous increase, so that the derivative $d^2K_T/dp^2|_T$ becomes positive. The same feature of the pressure dependence $K_T(p)$ was noted in the investigation of strontium[8] and is clearly seen in Fig. 3 at pressures above ~2 GPa.

It is well known that the change in the bulk modulus K_T under pressure is determined by at least two factors: 1) Pressure-induced broadening of the bands reduces the growth of this modulus and 2) interband electronic transitions can give rise to compressibility anomalies. For example, an ultrasonic investigation of lanthanum and praseodymium under pressure revealed an anomalous increase of the compressibility (decrease of the modulus K_T).[6,7] These anomalies were explained on the basis of the empty-core pseudopotential model[19] by acceleration of the interband $s-d$ transitions. It should be noted that the pressures at which an anomalous increase of the bulk modulus was observed both for fcc Yb and fcc Sr correspond to the regions where they undergo a gradual transition to the semiconducting state.[2] In the light of modern ideas about the electronic structure of these metals, this is caused by a transition of the electrons from the d into the s state. It is therefore natural to analyze the expression (1) for the pressure-dependence of the bulk modulus K_T, as obtained in Ref. 6 on the basis of the empty-core pseudopotential model and successfully used to explain the anomalies in the pressure dependence of the bulk modulus $K_T(p)$ for lanthanum and praseodymium. This expression has the form

$$K_T = K_{T0}\Big[3x^{-2}y^{-2/3} - 2x^{-4/3}y^{1/3} + \frac{dy}{dx}(2y^{-5/3}x^{-1}$$

$$+ y^{-2/3}x^{-1/3}) + \left(\frac{dy}{dx}\right)^2\left(\frac{5}{3}y^{-8/3} + y^{-5/3}x^{2/3}\right)$$

$$
+\frac{d^2y}{dx^2}\left(y^{-5/3}+\frac{3}{2}x^{2/3}y^{-2/3}\right)\Bigg]. \tag{1}
$$

Here K_{T0} is the atmospheric-pressure isothermal bulk modulus at $T=0$; $x=V/V_0$ is the normalized volume; $y=m_{ds}(x)/m_d\leq 1$, since m_d and $m_{ds}(x)$ are, respectively, the effective mass of d-band electrons which are transferred under compression from the d into the s band.

We now construct a series expansion of $y=y(x)$ near $x=1$ as follows:

$$
y(x)=1+\left.\frac{dy}{dx}\right|_{x=1}(x-1)+\frac{1}{2}\left.\frac{d^2y}{dx^2}\right|_{x=1}(x-1)^2
+\frac{1}{6}\left.\frac{d^3y}{dx^3}\right|_{x=1}(x-1)^3+\frac{1}{24}\left.\frac{d^4y}{dx^4}\right|_{x=1}(x-1)^4.
$$

Since setting $dy/dx|_{x=1}=d^2y/dx^2|_{x=1}=d^3y/dx^3|_{x=2}=0$ (see Ref. 6), we obtain

$$
y=1-\alpha(x-1)^4. \tag{2}
$$

Here $\alpha=-1/24(d^4y/dx^4)|_{x=1}$.

Analysis of the expression (2) yields $dy/dx>0$, $d^2y/dx^2<0$, and $d^3y/dx^3>0$ for $x<1$. Substituting the expression (2) into Eq. (1), we easily find that the anomalous increase of the bulk modulus K_T under pressure ($d^2K_T/dp^2>0$) is determined by the term with the derivative d^2y/dx^2, which decreases nonlinearly as the electrons pass from the d into the s state. For $\alpha=1/2$ a result close to the experimental result is obtained. If the dynamics of the $d\rightarrow s$ transition of the electrons is linear, the bulk modulus $K_T(p)$ must have a normal pressure dependence so that $d^2K_T/dp^2<0$.

The observed anomalous increase of the pressure derivative dK_T/dp for Sr and Yb can also be obtained within a simple model of the total energy

$$
E_{\text{tot}}=Ax^{-n(x)}-Bx^{-1/3}. \tag{3}
$$

The first term in Eq. (3) determines the repulsion with a pressure-dependent parameter $n(x)$; the second term determines the Coulomb attraction. Then, the expressions for $p(x)$, $K_T(x)$, and $dK_T(x)/dp$ assume the form

$$
p(x)=\frac{3}{2}K_{T0}\left\{x^{-n(x)}\left[\frac{dn(x)}{dx}\ln x+\frac{n(x)}{x}\right]-x^{-4/3}\right\}, \tag{4}
$$

$$
\begin{aligned}
K_T(x)=\frac{3}{2}K_{T0}\Bigg\{x^{1-n(x)}\Bigg[\left(\frac{n(x)}{x}+\frac{dn(x)}{dx}\ln x\right)^2+\frac{n(x)}{x^2}\\
-\frac{d^2n(x)}{dx^2}\ln x-2\frac{dn(x)}{dx}\frac{1}{x}\Bigg]-\frac{4}{3}x^{-4/3}\Bigg\},
\end{aligned} \tag{5}
$$

$$
\begin{aligned}
x\frac{dK_T}{dx}=\frac{3}{2}K_{T0}\Bigg[x^{2-n(x)}\Bigg\{\left(\frac{1-n(x)}{x}-\frac{dn(x)}{dx}\ln x\right)\\
\times\Bigg[\left(\frac{n(x)}{x}+\frac{dn(x)}{dx}\right)^2+\frac{n(x)}{x^2}-\frac{d^2n(x)}{dx^2}\ln x\\
-2\frac{dn(x)}{dx}\frac{1}{x}\Bigg]+2\left(\frac{n(x)}{x}+\frac{dn(x)}{dx}\ln x\right)\\
\times\left(2\frac{dn(x)}{dx}\frac{1}{x}-\frac{n(x)}{x^2}+\frac{d^2n(x)}{dx^2}\ln x\right)\\
+3\frac{dn(x)}{dx}\frac{1}{x^2}-\frac{2n(x)}{x^3}-\frac{d^3n(x)}{dx^3}\\
\times\ln x-3\frac{dn^2(x)}{dx^2}\frac{1}{x}\Bigg\}+\frac{16}{9}x^{-4/3}\Bigg],
\end{aligned} \tag{6}
$$

$$
\frac{dK_T(x)}{dp}=-xK_T^{-1}(x)\frac{dK_T}{dx}. \tag{7}
$$

Suppose that at normal pressure ($x=1$) the substance under study is a metal, i.e., $n(1)=1$. Assume that under pressure the electron gas fills the valence band in an accelerated manner, so that $dn/dx|_{x=1}=0$ and $d^2n/dx^2|_{x=1}=0$. In accordance with these conditions, we define the repulsion parameter $n(x)$ by a nonlinear function of the form

$$
n=1+\beta(1-x)^3. \tag{8}
$$

Then, for example, for $\beta=1/3$, it follows from Eqs. (6)–(8) that if at atmospheric pressure $dK_T/dp|_{x=1}=3.3$ holds, then under compression we have $x=0.9$ (corresponding to a pressure of 1.3 GPa for Yb, when Yb becomes a semiconductor) $dK_T/dp|_{x=0.9}=3.9$. If, however, $\beta=1/2$ holds, then we have $dK_T/dp|_{x=1}=3.3$ and $dK_T/dp|_{x=0.9}=4.9$.

In summary, though the repulsion parameter is essentially equal to unity under compression $x=0.9$, according to Eq. (8), the accelerated increase of this parameter with increasing pressure results in the experimentally observed accelerated growth of the derivative dK_T/dp. This is illustrated well by the part of the domain of the function $K_T(p)$ (Fig. 3) from ~0.8 to ~1.3 GPa for ytterbium: The derivative dK_T/dp increases sharply from 1.8 at $p=0$ to 4.0 at 1.3 GPa, typical of semiconductor materials.[20,21]

We now discuss the physical reason for this behavior. In a metal (semimetal) the valence electrons can be regarded as a free-electron gas. The static ionic potential of the lattice in the limit of small wave vectors is screened exponentially (Ref. 22, p. 34), as a result of which the Fourier transform of the potential is not singular in the long-wavelength limit. In a semiconductor, however, the electron gas entirely fills the valence band, separated by a gap from the conduction band, and does not completely screen the ions. For this case the dielectric theory of the covalent bond[22] postulates that to maintain the crystal as a whole electrically neutral, the negative charges of localized bonds, which are usually assumed to be concentrated on a line connecting the two nearest neighbors, must be introduced. The degree of bond localization is determined by the exponent n in the repulsion potential. The exponential screening of the ions at the transition from the semiconductor into the metallic state "softens" the repulsion, and the increasing bond localization in the reverse transition makes the repulsion "harder."

The increase in the derivative dK_T/dp for ytterbium at pressures above ~0.8 GPa means that the localized bonds are strengthened and, therefore, the repulsion becomes "harder;" this corresponds to a transition of ytterbium into the semiconductor state near 1.3 GPa. A direct proof of this transformation is provided by measurements of the temperature coefficient of the resistivity of ytterbium at different pressures.[2] It should be noted that we did not observe either a compressibility jump (Fig. 3) or a volume jump (Fig. 5) at a semimetal-semiconductor transition in ytterbium. At pressures above ~1.5 GPa, all the way to the start of the fcc-bcc phase transition, the pressure dependence $K_T(p)$ becomes normal.

In strontium, in contrast to ytterbium, the bulk modulus K_T increases normally with increasing pressure up to ~1.8 GPa: $d^2K_T/dp^2|_T<0$ (Ref. 8, Fig. 3). Further, for Sr the pressure dependence $K_T(p)$ under compression is reminiscent of the behavior of this modulus for Yb in the pressure range ~0.8–1.3 GPa. This is also evidently associated with the $d \rightarrow s$ transition of the electrons and the formation of a gap.[2]

We now consider the bcc phase. Calculations show[1] that the sequence fcc–bcc–hcp of crystal structures observed under pressure for a series of metals including ytterbium and strontium is due to the transition of electrons from the s into the d state when the metal is compressed. Indeed, the phase transition accompanied by a decrease of the packing density of the atoms with increasing pressure could be due to electrons flowing into deeper d orbitals. An increase in the d-electron density with increasing pressure, however, can result in an anomalous increase of the compressibility, as shown in Ref. 6. Therefore, the experimentally observed (Figs. 3 and 5) sharp increase of the compressibility at a fcc–bcc transition in ytterbium agrees with the electronic mechanism proposed in Ref. 1 for the fcc–bcc transition.

We now discuss the effect of compression on the change in the propagation velocity $v_t(p)$ of transverse elastic waves (Fig. 2) and the shear modulus $G(p)$ (Fig. 4) of ytterbium and strontium. One would expect that under pressure these elastic characteristics would decrease as the fcc–bcc structural phase transition is approached. As a rule, the softening of the shear acoustic long-wavelength modes is accompanied by a process which prepares the lattice for a phase transition (see, for example, Refs. 6, 7, and 21). Anomalies of this type in La and Pr were explained by the progressive increase of the pseudopotential and, correspondingly, the band energy of the crystal as a result of the $s \rightarrow d$ transitions,[6,7] which results in loosening up of the lattice by shear deformations and in a change of the lattice symmetry. In fcc ytterbium, however, we did not observe softening of the shear modes (Figs. 2 and 4). The shear modulus G of fcc strontium remained practically unchanged, and the propagation velocity v_t of transverse waves decreased in the pressure range $0.6<p<2$ GPa, i.e., long before the fcc–bcc phase transition. At pressures $p>2$ GPa, both the propagation velocity v_t of transverse waves (Fig. 2) and the shear modulus G (Fig. 4) exhibited accelerated growth. These elastic characteristics of fcc ytterbium changed similarly as the pressure increased from 0 to 1.3 GPa.

We note that the accelerated growth of the propagation velocity v_t of elastic waves and the shear modulus G in the fcc phases of ytterbium and strontium occurs in the same pressure ranges where the type of conductivity changes: a semimetal becomes a semiconductor. Since in strontium a gap appears only near 3 GPa,[2] at lower pressures (from 0 to ~2 GPa) interband transitions probably do not appreciably influence its phonon spectrum. For this reason, a decrease of the propagation velocity v_t of transverse waves with increasing pressure from ~0.6 to ~2 GPa, seemingly foreshadowing a fcc–bcc structural phase transition, is observed. At pressures $p>2$ GPa the intensifying process of d- to s-band electron transfer[2] decreases the pseudopotential and the band energy, as a result of which the tendency for the pretransitional softening of the transverse modes is suppressed and the propagation velocity v_t of transverse waves (Fig. 2) and the shear modulus G of strontium (Fig. 4) increase with an increasing derivative.

In ytterbium the $d \rightarrow s$ transition of electrons starts practically at the onset of the pressure increase, so that $dG/dp|_{p=0} \sim 1.1$ and $dG/dp|_{p=1.2\,\mathrm{GPa}} \sim 1.9$, which results in a gap even at 1.3 GPa. As a result, both v_t and G of ytterbium exhibit accelerated growth as the pressure increases right up to 1.3 GPa. The reverse transition from the semiconducting into the semimetallic state in both ytterbium and strontium occurs simultaneously with a structural fcc–bcc phase transition.

As the type of bond changes, i.e., at the moment a gap appears under pressure, the Friedel oscillations vanish, and the observed anomalous increase of the pressure derivative dG/dp can be obtained for Sr and Yb by using a potential function of the form

$$\varphi(r)=Ar^{-n(r)}-Br^{-m}(n>m), \tag{9}$$

where the first term determines the repulsion with parameter n, which depends on the interionic distance r with $n(r_0)=n_0$, $n'(r_0)=0$, and $n''(r_0)=0$; r_0 is the equilibrium distance between the nearest ions. For $n_0=3$ and $m=1$, on the basis of the approach used in Ref. 23, we obtain for the fcc phase, summing over the lattice up to the sixth nearest neighbor inclusively,

$$\frac{dc_{44}}{dp}=-1+\frac{3.82x^{-7/3}-1.53x^{-5/3}}{3x^{-2}-2x^{-4/3}}, \quad \frac{1}{2}\frac{d(c_{11}-c_{12})}{dp}$$
$$=-1+\frac{3.2x^{-7/3}-1.495x^{-5/3}}{3x^{-2}-2x^{-4/3}}. \tag{10}$$

For $1 \geqslant x \geqslant 0.9$, the value $dG/dp \sim 1$, obtained as an average from Eq. (10), agrees fairly well with the data for Yb. At the same time, it follows from Eq. (10) that as compression increases, the derivative dG/dp decreases. Estimates show, however, that taking into account the weak nonlinear increase of the repulsion [of the type Eq. (8)], limited by the nearest neighbors, results in the observed anomalous increase of the derivative dG/dp under pressure.

As the pressure increases, the tendency for the shear modulus of the bcc phase of strontium to saturate becomes more noticeable (Fig. 4). This is connected, in our opinion, with the comparatively high degree of localization of its $4d$ electrons, which participate in $s \rightarrow d$ band motion. The increase of the pseudopotential and band energy at $s \rightarrow d$-transitions is larger in strontium than in ytterbium, where the less localized $5d$ electrons participate in this process. As indicated above, the increase in the pseudopotential and the band energy softens the shear modes and, hence, accelerates the saturation of the shear modulus prior to the subsequent bcc-hcp structural phase transition under pressure. Indeed, the bcc-hcp phase transition in strontium[4] occurs at ~18 GPa, while in ytterbium[5] it occurs at ~26 GPa. For the same reason, in accordance with Lindemann's criterion,[24] the melting curve of the bcc phase of strontium should also saturate more quickly. In the $p-T$ diagram this tendency can be observed even at ~3 GPa.[9]

It should be expected that as the bcc–hcp phase transition is approached the shear moduli of both strontium and ytterbium start to soften, as observed for bcc barium prior to its transition into the hcp phase at 5.6 GPa;[25] this is also caused by the $6s \rightarrow 5d$ electronic transitions. Recent calculations[26] have shown that the shear modulus c_{44} of the bcc phase of strontium must decrease rapidly as the bcc–hcp transformation is approached.

Softening of the shear modes in the phonon spectra of bcc strontium and ytterbium should give rise to an anomalous increase of the entropy of melting with increasing pressure; this will inevitably lead to the formation of a maximum on the melting curve.[27] The phase diagrams of strontium and ytterbium at high pressures must be similar to the phase diagram of barium:[28] peaks of the melting curves and a negative slope of the bcc–hcp transition line.

In conclusion, it is our present duty to thank V. K. Luĭkh for assisting in the experiments.

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