REVIEWS OF TOPICAL PROBLEMS

Contents

PACS numbers: 61.50.Ah, 62.50. + p, 61.66. - f, 71.15.Mb

Non-simple behavior of simple metals at high pressure

E G Maksimov, M V Magnitskaya, V E Fortov

DOI:	10.10	070/PU	2005v048	n08ABE	EH002315
------	-------	--------	----------	--------	----------

1. 2.	Instead of an introduction, or what simple metals are The study of alkali metals at high pressure	761 762
	2.1 Heavy alkali metals; 2.2 Light alkali metals; 2.3 First-principles calculations. Calculation of thermodynamic	
	functions; 2.4 Experimental methods of static and dynamic compression; 2.5 The crystal structure and the electrical	
	resistance of lithium at high pressure	
3.	The effect of pressure on the properties of alkali-earth metals	770
	3.1 High-pressure phases and the metal-semiconductor transition in heavy alkali-earth metals; 3.2 The study of the	
	properties of calcium at high pressure	
4.	Conclusion	779
	References	779

<u>Abstract.</u> Experimental and theoretical high-pressure research on simple metals is reviewed. It is shown that simple metals undergo transition sequences from close-packed highly-symmetric to less-symmetric and often less closely packed structures as pressure is varied over a wide range. A number of theoretical perspectives concerning the nature of this behavior are reviewed with a focus on the electrophysical properties of lithium and calcium at high pressure. Static and shock-wave compression data on Li and Ca are presented.

1. Instead of an introduction, or what simple metals are

Most physicists not directly involved in high-pressure research, when asked how substances behave under high compression, are most likely to say that they transform into phases that are more and more closely packed, and, specifically, insulators under pressure finally transform into metals. And metals, as textbooks on solid state physics tell us (e.g., see Ref. [1]), tend to crystallize in such structures in which the atoms are closely packed, and the most 'popular' are three highly symmetric structures, face-centered cubic

E G Maksimov P N Lebedev Physics Institute, Russian Academy of Sciences, Leninskii prosp. 53, 119991 Moscow, Russian Federation Tel. (7-095) 135 75 11. Fax (7-095) 135 85 33 E-mail: maksimov@lpi.ru M V Magnitskaya L F Vereshchagin Institute for High Pressure Physics, Russian Academy of Sciences, 142190 Troitsk, Moscow Region, Russian Federation Tel. (7-095) 334 07 34. E-mail: mvm@hppi.troitsk.ru V E Fortov Institute for High Energy Density, Russian Academy of Sciences, Izhorskaya ul. 13/19, 127412 Moscow, Russian Federation Tel. (7-095) 485 79 88. E-mail: fortov@ihed.ras.ru Received 14 December 2004 Uspekhi Fizicheskikh Nauk 175 (8) 793-813 (2005) Translated by E Yankovsky; edited by M V Magnitskaya

(fcc), body-centered cubic (bcc), and hexagonal close-packed (hcp), in which most metals crystallize at atmospheric pressure. As for insulator-metal transitions, today we know a lot about them from experiments. These data suggest that, when subjected to high pressure, many insulators and semiconductors transform into metals. For instance, for a long time it has been known that group-IV semiconductors, which crystallize in a cubic non-close-packed, or open, diamond structure (silicon, germanium, and gray tin) under fairly moderate pressures ($p \sim 11.7, 10.6, \text{ and } 0.5 \text{ GPa for Si}$, Ge, and α -Sn, respectively) transform into a less symmetric tetragonal structure of the white-tin (β -Sn) type and become metals [2]. In addition to covalent group-IV semiconductors, as increasingly higher pressures are reached owing to the advances in experimental techniques, many classical insulators, e.g., inert gases (Xe), molecular crystals (I₂), group-VIa semiconductors (S, Se, Te), and some others, are found to transform to the metallic state (e.g., see the reviews [3, 4]). Interestingly, some of these 'new metals' also exhibit a transition into the superconducting state.

In the early years of theoretical solid-state physics, Wigner and Huntington showed [5] that the pressure-induced transition of non-metallic molecular hydrogen to the atomic metallic state is possible. The authors used elementary, and therefore very approximate, methods of calculations, with the result that a very rough estimate was obtained [5] for the pressure of the insulator-metal transition in hydrogen. However, although the pressures at which such a transition should have happened (even according to much more accurate estimates) have long been reached, hydrogen 'stubbornly refuses' to transform into the metallic state at fairly low temperatures, where it is sure to be solid, despite all the efforts of experimenters. Instead, it forms exotic crystal structures, remaining an insulator and retaining its quasimolecular structure (e.g., see the review [6]). Unfortunately, the 'unwillingness' of hydrogen to become a metal denies us of the opportunity to obtain not merely high- T_c superconductor (as Ashcroft assumed [7]), but, so to say, 'heat-resistant' superconductor, since, according to the latest estimates [8], the superconducting transition temperature in it could be as high as 600 K.

As for simple (nontransition) metals (this review deals mainly with the simplest of such metals, s-elements of the first and second groups of the Periodic Table), it would seem that all basic questions concerning their behavior, including behavior under pressure, have been fully answered already in the period of the rapid development of pseudopotential theory (see Refs [9, 10]). Within this theory, due to the orthogonality of the wave functions of valence sp-electrons of simple metals to the wave functions of the ion core, the Coulomb electron-ion interaction is replaced with a much weaker pseudopotential. Moreover, it was assumed that in calculating the majority of physical properties of alkali metals we can always limit ourselves to second-order perturbation theory in the pseudopotential. When calculating the cohesive energies and phonon spectra of solids, such an approach is equivalent to assuming the point ions are submerged in a sea of the homogeneous gas of interacting electrons. It can be shown that in second-order perturbation theory the given problem is reduced to solving the problem of the behavior of neutral atoms with pair interparticle interaction.

Pseudopotential theory was used to calculate the phonon spectra of alkali metals, with the results demonstrating good agreement with the experimental data (see the collection of three articles by Heine, Cohen, and Weaire [10] and the literature cited therein). Also calculated were the total energies for simple structures, and it was found that for Li and Na the most energetically favorable structure is the hcp lattice [10].

At low temperatures these two metals do indeed have a rhombohedral structure, denoted 9R, which is close to the hcp structure, but at high temperatures their structure becomes bcc. According to the same calculations, such a rhombohedral structure must also be the ground state of potassium, rubidium, and cesium, which at low temperatures retain their bcc structure, however. Note that the difference in the total energies of these structures proved to be so small ($\sim 1 \text{ mRy} \approx 160 \text{ K}$) that at that time the discrepancy between theory and experiment seemed insignificant.

But the above approach contained a certain ambiguity, which amounted to the fact that the possibility of formulating pseudopotential theory for calculations of the lattice properties in terms of pair interaction leads to a contradiction in lattice dynamics theory. In a system with a pair potential, the Cauchy relations for elastic moduli must hold. However, Brovman et al. [11] found that for the Cauchy relations to be valid, in calculating the phonon spectra one must use not only second-order perturbation theory, but also third- and fourthorder perturbation terms in the pseudopotential. A detailed discussion of these aspects can be found in the review in Ref. [12].

Generally speaking, it could be understood as early as the 1970s that the problem of structural transformations in simple metals is actually more complicated than it would seem from the viewpoint of second-order perturbation theory in pseudopotential approach. It was then that Kagan's group studied in detail (see Ref. [13]) the properties of the hypothetical metallic phase of hydrogen, including the case of high pressure. The researchers used perturbation-theory techniques up to the fourth order in the electron-proton interaction. They found that simple highly symmetric structures in the metallic phase of hydrogen are dynamically unstable up to very high pressures of about 20 Mbar. At lower pressures, complex anisotropic structures have minimal energy. This enabled the researchers to assume that metallic hydrogen under ultrahigh pressures may be liquid, even at T = 0. Recently, their results (see Ref. [13]) were corroborated by *ab initio* density functional calculations [8]. In recent years, these studies have gained importance because of advances in experimental research into the crystal structure of simple metals at high pressure.

2. The study of alkali metals at high pressure

Alkali metals are simple s-metals, which under normal pressure are described fairly well by the model of quasifree electrons with a nearly parabolic dispersion law. Their Fermi surfaces differ very little from a sphere, and many of their properties can be calculated with good accuracy by perturbation techniques up to the second order in the weak pseudopotential. It would seem that, as pressure grows, they should continue being 'good' metals, while their crystal structure, which already under normal pressure is highly symmetric, should not change significantly upon compression.

The experimental situation is much more interesting, however. As high-pressure techniques were developed, i.e., as diamond anvil cells used for static compression appeared and as powerful synchrotron X-ray sources and refined methods of processing X-ray patterns were developed [3, 14, 15], it was found that in the pressure range to 200 GPa all alkali metals experience a series of structural transformations, with the emerging high-pressure phases often being less symmetric and having a less close packing than the phases that exist at ambient pressure. Modern dynamic (shock-wave) methods of quasi-isentropic compression (e.g., see Ref. [16]) have made it possible to arrive at new results that also corroborate the existence of phase transitions in alkali metals at such pressures. These data will be described in greater detail in Section 2.5.

In recent years, a number of review articles [15, 17-19] have been published in which the results of experimental research of structural transformations in alkali metals at high pressure are discussed in detail. For this reason, we will not describe the experimental details; instead we will focus on the most important points.

Table 1 lists the known data on sequences of structural phase transitions for some s- and p-elements and the pressures at which the transition to a particular structure occurs. The table was compiled from the data in Refs [2-4,15, 17-22]. Most of these results were obtained at room temperature. The first column lists the structures at normal pressure. Most structures are abbreviated in the traditional manner. Notation of type 'Cs-III', 'Ba-IV', etc. in quotation marks refer to complex structure types discussed below. (In the text we use symbols of type Cs-III without quotation marks to denote the sequential numbers of high-pressure phases.) The question marks in some places indicate structures that have yet to be solved. Table 1 illustrates the homological behavior of elements when within one group the sequences of high-pressure phases often coincide. For heavier elements, the transitions to similar structures happen at lower pressures, although there are exceptions to this rule. In those cases where experimental data exist, we see that the structural sequences end with the highly symmetric phases returning. Obviously, at some very high pressures all the other elements will finally transform into simple close-

Li, bcc Na, bcc K, bcc Rb, bcc Cs, bcc	(7.5) fcc (65) fcc (11.6) fcc (7.0) fcc (2.3) fcc	(38) rhombohedral (103) cI16 (23) 'K-III' (14) ? (4.2) 'Cs-III'	(42) cI16 (17) 'Rb-IV' (4.4) bct	(20) bet (12) oC16	(48) oC16 (72) dhep	
Be, hcp Mg, hcp Ca, fcc Sr, fcc Ba, bcc	(52) bcc (19.5) bcc (3.5) bcc (5.5) hcp	(32) sc (24) orthorhombic (13) 'Ba-IV'	(35) ? (45) dhcp	(46) 'Ba-IV'		
Si, diamond Ge, diamond Sn, diamond P, orthorhombic	(11.7) β-Sn (10.6) β-Sn (0.5) β-Sn (4.5) rhombohedral (25) so	 (13.2) orthorhombic (75) orthorhombic (15) bct (10) sc (48) 'Ba IV' 	(15.6) sh (85) sh (44) bcc (137) sh (97) bcc	(42) oC16 (102) oC16 (>120) hcp (262) bcc	(42) dhep (170) hep	(78) fcc
Sb, rhombohedral Bi, rhombohedral	(23) sc (6.4) sc (2.5) monoclinic	(46) Ba-IV (8.6) 'Ba-IV' (2.7) 'Ba-IV'	(97) bee (28) bee (4) oC16	(8.8) bcc		

Table 1. The structural sequences for s- and p-elements. The numbers in parentheses are the transition pressures in GPa.

packed structures (maybe with the exception of metallic hydrogen, which, as noted above, at ultrahigh pressures may be liquid at T = 0). Below we discuss in detail the structural sequences in alkali and alkali-earth elements.

Table 1 shows that under normal conditions ($p \approx 1$ bar and $T \approx 300$ K) all alkali metals crystallize into fcc structures. Here, we will not discuss the problem of the phase diagram of the light alkali metals Li and Na at $p \sim 1$ bar and low temperatures, where they transform into the rhombohedral phase 9R (a detailed bibliography on this topic can be found in Syassen's review [17]). In all alkali metals the first pressureinduced structural transition is the bcc-fcc transformation, which can be considered an entirely natural transition to a more closely packed structure under pressure. No further structural transitions follow this 'natural' pattern. Here, within the range of pressures reached in experiments, the very sequences of polymorphic transitions for light (Li and Na) and for heavy (K, Rb, Cs) alkali metals differ.

2.1 Heavy alkali metals

Let us first discuss the transition in heavy alkali metals K, Rb, and Cs that are in the beginning of long periods of the Periodic Table, in which the d-shells of transition metals fill up. A special place in the structural sequences in these metals is occupied by the isostructural transition in fcc Cs at 4.2 GPa with an approximately 10% jump in volume (the Cs-II-Cs-III transition), first discovered by Bridgman [23] in the 1940s. An explanation of the nature of this transition, whose idea was first suggested by Fermi, was proposed by Sternheimer [24], who calculated the electronic structure of cesium in the approximation of a spherically symmetric Wigner-Seitz cell, i.e., actually in the 'compressed atom' model. On the basis of these calculations, Sternheimer concluded that, under compression corresponding to a pressure of approximately 4 GPa, the mutual arrangement of the s- and d-bands in Cs suddenly changes. In view of this, the s-band is depleted and the valence 6s-electron goes over to the 5d-shell, with the cesium becoming a transition metal, so to say. Since the radius of the 5d-orbital is much smaller than that of the 6s-orbital, the volume of metallic cesium suddenly decreases. (Note that an isostructural transition of this type can be initiated even in a simple model system with a stepwise pair potential when the interaction radius suddenly decreases.)

At that time it was assumed that under higher pressures both Rb and K would also undergo such transitions, which are related to changes in the electronic structure of the type $ns^1 \rightarrow (n-1)d^1$ (where *n* is the principal quantum number), but no isostructural transitions in these metals were ever discovered. What's more, subsequent ab initio, or firstprinciples, calculations of the electronic structure of Cs (e.g., see Ref. [25] and the literature cited therein) have shown that the picture of a sudden change in the electronic structure of Cs at certain pressure is to a certain extent an idealization. Actually, at pressures ranging from atmospheric to 11 GPa, the wave function of the cesium electron changes smoothly. More recent experimental studies (e.g., see Syassen's review [17]) have shown that the Cs-III phase exists only at high temperatures (> 200 K) but not at low temperatures. Most likely, as noted by Glötzel and McMahan [25], this means that the transition to the Cs-III phase is caused by effects related to the phonon contribution to the crystal's free energy. Of course, the effects proper may be caused by a change in the electronic structure, but in any case the existence of the hightemperature Cs-III phase is not a direct consequence of a sudden s-d transition. In addition, in recent experiments conducted by Schwarz [26] and McMahon et al. [27] it was shown that the Cs-II-Cs-III transition is not an isostructural one. X-ray diffraction analysis has shown that the structure of Cs-III can only approximately be considered a distorted fcc structure; actually it has orthorhombic symmetry and contains 84 (!) atoms in unit cell [27].

In alkali metals, the high pressure phases that appear after the fcc phase exhibit complicated crystal structures with a lower symmetry and a smaller number Z_{NN} of nearest neighbors than that in the fcc lattice. For instance, cesium under p = 4.4 GPa transforms into a body-centered tetragonal (bct) structure with four atoms per unit cell and a coordination number $Z_{NN} = 8$, which is known as Cs-IV. The structure can be imagined as consisting of layers of trigonal prisms, where in each subsequent layer the prisms are turned though an angle of 90° in relation to the previous layer. The Rb-V phase has a similar crystal structure under pressures ranging from 20 to 48 GPa. Interestingly, such a structure has not been detected in any other elementary substance. It can be considered similar to the structure of some metallic disilicides (the α -ThSi₂ structure type [28]). Here, the Cs atoms occupy the sublattice of cations (Th), while the locations of the anions



Figure 1. Crystal structure of the Rb-IV phase (view along the *c*-axis of the tetragonal framework). The square antiprisms form columns oriented parallel to the *c*-axis. Chains of Rb atoms are located in linear channels within the framework. The period in the chains is incommensurate with the frame period. (Taken from Ref. [17]).

(Si) remain vacant. The Cs-IV structure exhibits an interesting property (see Refs [29, 30]); namely, the electron density distribution in it has peaks at the interstitials corresponding to the positions of the Si atoms in ThSi_2 , as if electrons are trying to imitate the absent anions. The same similarities with structures of binary compounds are observed for many other high-pressure phases of alkali metals (for details see Refs [17– 19]).

One of the most exotic high-pressure phases of alkali metals is the Rb-IV phase, stable in the pressure range from 17 to 20 GPa (Fig. 1). It is a host – guest structure formed by a framework of columns of square antiprisms arranged parallel to the *c*-axis and located at the center and the corners of the unit cell (host structure). Along the faces of the cell channels are formed, and in these channels chains of Rb atoms forming tetragonal structures are located (guest structure). The atomic separations in the chains are incommensurate with framework period [32]. Apparently, to a certain extent the tetragonal K-III structure is similar to the structure of Rb-IV.

2.2 Light alkali metals

The high-pressure phases of the light alkali metals Li and Na, which we will examine in greater detail, proved to be no less complicated or exotic. Instead of unfilled d-states (the case of heavy alkali metals), in Li and Na above the Fermi level there are p-states, which means that when pressure is applied to light alkali metals, the situation is usually characterized in terms of electron s – p transitions. As with s – d transitions, we do not mean a sudden change in the mutual arrangement of the electronic bands at a certain pressure, but a gradual filling up of the p-band as the pressure grows at the expense of the s-band. As an example, Fig. 2 shows the dependence of the numbers of s- and p-electrons in lithium, N_s and N_p , on the relative volume V/V_0 (V_0 is the specific volume at p = 0), which we calculated for the fcc phase and the high-pressure cI16 phase of lithium, which we discuss in greater detail in



Figure 2. Variations in the numbers of s- and p-electrons in lithium upon compression.

Section 2.5. Upon compression, N_s monotonically decreases while N_p increases, with the ratio N_p/N_s in the cI16 phase increasing faster. Note that there is ambiguity in N_s and N_p , since their estimates depend on the geometry of the calculations. In the case at hand we used what is known as the atomic sphere approximation (for details see Section 3.2).

Several remarks concerning the relationship between s-d (or s-p) electronic transitions and structural sequences are in order. First, not in a single transition metal with d-electrons have crystalline phases similar to the complex high-pressure phases of alkali metals been observed. Second, Table 1 shows that such host-guest crystal structures have also been observed under pressure in elements of the fourth and fifth groups, although the electronic structure of the latter has little in common with the electronic structure of alkali metals. Such phases also exist in Bi-Pb and Bi-In alloys at normal pressure [33, 34]. Also, complex structures of the Cmca type, close to the orthorhombic structure of the Cs-V phase, are observed in solid molecular hydrogen (e.g., see Ref. [6]), in which there can be no s-p or s-d transitions. Moreover, as noted in the introduction, in the theoretical calculations of Kagan's group [13], the existence of highly anisotropic high-pressure phases for metallic hydrogen was also predicted. Since these calculations were done by perturbation techniques with the electron-proton coupling constant acting as the small parameter, it is more proper to speak of metallic hydrogen being closer (in this approximation) to a system of nearly free electrons than to transition metals. Nevertheless, anisotropic phases may exist in this case, too. The thing is that compression leads to a gradual change in the symmetry of the wave functions of the valence electrons due to the admixture of states with higher angular momenta, l = 1, 2, 3, etc., since these are less compressible than the spherical s-states. We will return to the discussion of the concept of an s-d transition in Section 3, where we discuss the high-pressure phases of alkali-earth elements, in which it also plays an important role, and will demonstrate, using the example of calcium, the results of numerical calculations of the electronic structure and behavior of the s- and d-bands.

In view of what has been said above, Degtyareva's attempt [34, 35] to describe the emergence of complex anisotropic structures in simple sp-metals by using the Hume-Rothery rule [36], which was initially formulated for

alloys of noble metals, appears to be very interesting. In the simplest approach, this rule amounts to the following. Let us take the Fermi sphere of free electrons for a certain alloy and build for it a large Brillouin zone. At a certain concentration of the alloy, when the Fermi sphere touches the faces of the Brillouin zone, structural transformation or ordering happens in the alloy. Clearly, in alkali metals with one atom per unit cell (as in the case of any odd number of atoms), the Fermi sphere cannot touch a face of the Brillouin zone, but this is quite possible in structures with an even number of atoms per unit cell. All the high-pressure phases in alkali metals discussed earlier have an even number of atoms per unit cell. Degtyareva [35] built a Brillouin zone for the orthorhombic structure oC16 (in another system of notations, Cmca) with 16 atoms per unit cell (Cs-V). Next, she showed that at the pressure at which the Cs-IV-Cs-V transition occurs the Fermi sphere may touch the faces of the Brillouin zone that correspond to the most intense diffraction peaks in the Cs-V phase. No specific calculations of the total energies of phases are given in Refs [34, 35].

Strong doubts have been repeatedly expressed in the literature of whether such a simple approach can lead to a quantitative description of structural transformations even in noble-metal alloys (e.g., see Ref. [37]). However, very recently calculations to verify and justify from first principles the Hume-Rothery rule as applied to the description of phase transformations were done for alkali metals under pressure [38] and for the sequences of complex structures in Cu-Zn and Cu-Al alloys [39]. In Section 3.2.2 we will continue the discussion of these works and, in general, will examine the microscopic mechanisms of structural transformations in simple metals. Now, however, we turn to the description of methods of *ab initio* calculations. We will also show that in most cases such calculations correctly describe the structural sequences for a large number of metals under pressure.

2.3 First-principles calculations.

Calculation of thermodynamic functions

Quantum mechanical first-principles calculations are done on the basis of the density functional theory (DFT) [40, 41]. Within this approach, the calculation of the physical properties of crystals is reduced to solving the three-dimensional Schrödinger-type equation for the electron wave functions $\psi_i(\mathbf{r})$, known as the Kohn–Sham equation:

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + V_{\text{eff}}(\mathbf{r})\right] \psi_j(\mathbf{r}) = \varepsilon_j \psi_j(\mathbf{r}) \,. \tag{1}$$

Thanks to translational symmetry, this equation can be solved for a single unit cell. The effective potential $V_{\text{eff}}(\mathbf{r})$ can be written as follows:

$$V_{\text{eff}}(\mathbf{r}) = \sum_{N} V_{N}(\mathbf{r} - \mathbf{R}_{n}) + e^{2} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r}' + V_{\text{xc}}\{n(\mathbf{r})\}, \, (2)$$

where V_N is the potential of the ion at point \mathbf{R}_N , $n(\mathbf{r})$ is the electron charge density, and

$$V_{\rm xc}\{n(\mathbf{r})\} = \frac{\delta E_{\rm xc}\{n(\mathbf{r})\}}{\delta n(\mathbf{r})}$$
(3)

is the exchange-correlation potential. Here, $E_{xc}\{n(\mathbf{r})\}$ is the exchange-correlation energy functional. The exact expression for this functional is unknown, and in most cases the local

density approximation (LDA) is used to calculate it:

$$E_{\rm xc}\{n(\mathbf{r})\} = \int n(\mathbf{r}) \,\varepsilon_{\rm xc}(n(\mathbf{r})) \,\mathrm{d}\mathbf{r}\,, \qquad (4)$$

where for $\varepsilon_{xc}(n(\mathbf{r}))$ at each point **r** one uses the well-known value for a homogeneous electron gas. This approximation produces results that agree very well with the experimental data, especially in the case of metals. Sometimes it is necessary to employ more intricate approaches, which allow, in particular, for the dependence of the exchange-correlation energy not only on the local density proper, but also on the gradients of this density. In the latter case one usually speaks of the generalized gradient approximation (GGA). Details can be found in Kohn's Nobel Lecture [41].

The following procedure is used in LDA to calculate the total energy of crystal. First, the Kohn–Sham equation (1) is solved self-consistently. For this a probe wave function $\psi_k(\mathbf{r})$ is expanded in a certain set of basis functions $\phi_{ki}(\mathbf{r})$,

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{i} c_{i} \phi_{\mathbf{k}i}(\mathbf{r}) , \qquad (5)$$

and the coefficients c_i of the basis functions $\phi_{\mathbf{k}i}$ are determined by the Rayleigh-Ritz variational principle. In this case, the solutions $\psi_{\mathbf{k}j}(\mathbf{r})$ are periodic Bloch functions depending on the quasimomentum \mathbf{k} and the band index *j*. Then we calculate the electron charge density

$$n(\mathbf{r}) = \sum_{\mathbf{k},j} \psi_{\mathbf{k}j}^*(\mathbf{r}) \,\psi_{\mathbf{k}j}(\mathbf{r}) \tag{6}$$

and the total energy

$$E_{\text{tot}}\{n(\mathbf{r})\} = T_0\{n(\mathbf{r})\} + \frac{e^2}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}' + \int n(\mathbf{r}) \, V_{\text{ext}}(\mathbf{r}) \, \mathrm{d}\mathbf{r} + E_{\text{xc}}\{n(\mathbf{r})\} + \frac{e^2}{2} \sum_{N,N'} \frac{Z_N Z_{N'}}{|\mathbf{R}_N - \mathbf{R}_{N'}|} \,. \tag{7}$$

Here, $T_0\{n(\mathbf{r})\}$ is the kinetic energy of a system of noninteracting electrons with the same charge density as that of the electrons in the crystal; the second and third terms on the right-hand side of equation (7) describe, respectively, the electron-electron and electron-ion interactions; V_{ext} is the external potential generated by the ion system [the first term on the right-hand side of equation (2)]; $E_{\text{xc}}\{n(\mathbf{r})\}$ is defined in (4); and, finally, the last term on the right-hand side of equation (7) describes the Coulomb ion-ion interaction (Z_N is the ion charge).

The calculations can be done for any crystal structure and any atomic separation, i.e., for any unit-cell volume. The pressure p corresponding to the given volume V,

$$p(V) = -\frac{\partial E_{\text{tot}}}{\partial V}, \qquad (8)$$

is usually determined via numerical differentiation of $E_{tot}(V)$. After this we can calculate the crystal's enthalpy

$$H = E_{\rm tot} + pV. \tag{9}$$

By comparing the enthalpies of different lattices at a given pressure we can determine the energetically favorable type of lattice at the given pressure (at T = 0). Actually, to calculate the phase diagram of a system at finite temperatures we must calculate not the enthalpy H, which describes the properties of a rigid lattice at T = 0, but the Gibbs free energy G [42], which, in addition to the energy of the static lattice, incorporates the contributions from electronic excitations and from lattice vibrations. When the temperature T is much lower than the characteristic electron energies E of about several electronvolts, all thermal effects associated with electronic excitations are small and can be ignored. At the same time, the contribution of lattice vibrations may prove significant in determining the phase diagram of the crystal, especially when the differences in the total energies of different phases are very small. This happens to be the case, say, for light alkali metals at low temperatures and pressures.

The Gibbs free energy G is equal to [43]

$$G = F + pV. \tag{10}$$

Here, F is the Helmholtz free energy,

$$F = E_{\text{tot}}(V) + F_{\text{ph}}(V, T), \qquad (11)$$

and the thermal (phonon) contribution to *F* can be written as follows:

$$F_{\rm ph}(V,T) = \frac{1}{2} \sum_{\mathbf{q},\lambda} \hbar \omega_{\mathbf{q}\lambda}(V) + k_{\rm B} T \sum_{\mathbf{q},\lambda} \ln \left[1 - \exp\left(-\frac{\hbar \omega_{\mathbf{q}\lambda}(V)}{k_{\rm B}T}\right) \right], \quad (12)$$

where **q** is the phonon wave vector and λ is the phonon mode index. The first term in this formula describes zero-point motion. The free energy of the phonon subsystem, $F_{\rm ph}$, in (12) is written in the 'quasiharmonic' approximation, in which the phonon frequencies $\omega_{q\lambda}$ depend on the volume V. Allowing for anharmonicity in this approximation is reduced to allowing for thermal expansion of the crystal at every temperature and then recalculating the phonon frequencies for the increased volume. The thermal expansion coefficient $\alpha(T)$ can be written as follows:

$$\alpha(T) = \frac{1}{3B} \sum_{\mathbf{q},\lambda} \gamma_{\lambda}(\mathbf{q}) c_{V\lambda}(\mathbf{q},T) , \qquad (13)$$

where *B* is the bulk modulus,

$$\gamma_{\lambda}(\mathbf{q}) = \frac{\mathrm{d}\ln\omega_{\mathbf{q}\lambda}(V)}{\mathrm{d}\ln V} \tag{14}$$

is the Grüneisen parameter for the λ th mode, and

$$c_{V\lambda}(\mathbf{q},T) = \frac{\omega_{\mathbf{q}\lambda}(V)}{V} \frac{\mathrm{d}}{\mathrm{d}T} \left[\exp\left(-\frac{\omega_{\mathbf{q}\lambda}(V)}{k_{\mathrm{B}}T}\right) - 1 \right]^{-1} \qquad (15)$$

is the contribution of the λ th mode to the lattice specific heat at constant volume V. Here, the crystal's total specific heat is

$$c_V(T) = \sum_{\mathbf{q},\lambda} c_{V\lambda}(\mathbf{q},T) \,. \tag{16}$$

Quong and Liu [44] showed that the use of the quasiharmonic approximation together with first-principles calculations of the free energy leads to an increase in the calculated lattice parameter for Li at room temperature by approximately 2%, which actually removes all discrepancy between theory and experiment. Furthermore, Liu et al. [45] showed that for lithium under normal conditions the bcc structure is the most energetically favorable one.

Several serious computational problems emerge when we carry out the above procedure, and the problems, basically, are related to solving the three-dimensional Kohn-Sham differential equation for crystals. Actually, this is a wellknown problem in solid-state physics when one has to deal with calculations of the electron band structure and the corresponding Bloch wave functions (e.g., see Ref. [46]). Many methods of solving this problem have been developed, and they differ mainly in the type of the basis functions ϕ_{ki} used to expand the wave function $\psi_{ki}(\mathbf{r})$. For instance, in the first-principles pseudopotential method (which, in contrast to the 'old' phenomenological pseudopotential method discussed earlier, uses no information from experiments), the basis functions are plane waves, exp (ikr). Among the most effective and fast methods we must mention the linear muffintin orbitals (LMTO) method [47]. A modification of this method, the full-potential linear muffin-tin orbitals (FP-LMTO) method, which incorporates the nonspherical crystal potential with the complete symmetry of the lattice [48] has been used in our calculations of lithium at high pressure, which we will describe in Section 2.5.

There is one more very important problem in the density functional method. The method was derived mathematically only to determine the energy and properties of the ground state of the electron system and static response functions (in particular, the electron contribution to the phonon spectra of crystals). The electron energy spectra $\varepsilon_i(\mathbf{k})$ determined by the Kohn-Sham equation (1) and the corresponding wave functions $\psi_{\mathbf{k}i}(\mathbf{r})$ are, in a sense, only auxiliary quantities that are needed in order to calculate the ground-state properties. By their very definition they do not necessarily coincide with the real electron excitation spectrum. On the other hand, to calculate the kinetic, optical, and other properties of crystals, we need to known the excitation spectrum. However, the large experience of specific calculations of metallic systems has shown that the electron spectrum obtained through the solution of equation (1) makes it possible to determine with good accuracy the optical spectra and the kinetic characteristics, including the electrical resistance [48].

2.4 Experimental methods of static and dynamic compression

In this section we briefly describe some of the modern experimental possibilities presented by high-pressure physics. In the late 1970s, the rapid development of diamond anvil high-pressure cells made it possible to achieve much higher pressures compared to the existing metal and hardalloy cells, although at the expense of the size of the samples being studied. Nevertheless, these techniques make it possible to investigate not only the crystal structure, but also many other properties, including optical spectra, electrical resistivity, and magnetic susceptibility. Usually, measurements in diamond anvil cells are done at relatively low temperatures, T < 500 K. It would be interesting, therefore, to conduct experiments in diamond anvils in a wider temperature range. Recently, there has been substantial progress in this field. Gregoryanz et al. [49] studied the phase diagram of hydrogen at $T \sim 1100$ K and pressures up to roughly 70 GPa and at $T\sim 650~{\rm K}$ and pressures up to roughly 150 GPa and established the melting curve of molecular hydrogen. At present, various groups of experimenters are working to further increase pressure and temperature simultaneously in diamond anvil cells.

The use of powerful shock waves to compress matter makes it possible to achieve much higher pressures than is possible in static compression. It is obvious, however, that the process heats the sample to very high temperatures, with the result that there is the danger of the sample melting. Naturally, for studying phase transitions in the solid state the effects of irreversible heating should be minimized, and this can be done via quasi-isentropic compression (i.e., with the entropy $S \approx \text{const.}$) For this reason, the compression of substances has been done through a sequence of direct and reflected shock waves, with the latter generated as a result of their reverberation in a plane geometry [50, 51]. Highexplosive generators of plane shock waves have been employed for this purpose. By using multi-step shock compression the heating of the samples is reduced tenfold, while the degree of compression of the samples is higher (by a factor of ten) than that in the direct shock wave. Recently, Loubeyre et al. [52] suggested combining the diamond anvils and shock wave methods. The essence of their suggestion is to pre-compress the sample in a diamond anvil cell up to pressures of about 1 GPa and additionally compress it by a laser-generated shock wave. This approach may prove to be very fruitful in high-pressure physics.

2.5 The crystal structure and the electrical resistance of lithium at high pressure

2.5.1 High-pressure phases of Li. We will now discuss in greater detail the high-pressure phases of lithium and their physical properties. Not so long ago the behavior of lithium under pressure attracted the interest of researchers, since Neaton and Ashcroft [53] expressed the idea that lithium under a pressure of about 100 GPa may transform into a crystalline low-symmetry phase with paired atoms, resembling one of the low-symmetry structures of solid molecular hydrogen. According to their calculations, lithium will be in the insulating (more exactly, semiconducting) state with a small band gap. This supposition was the more unexpected since, say, Cs remains a metal even in its anisotropic highpressure phases (earlier Wittig [54] found that in its Cs-V phase cesium even becomes a superconductor). Soon after that several anomalies in the behavior of lithium at high pressure, demonstrating at least a substantial worsening of lithium's metallic properties (Fig. 3) were discovered in shock-wave experiments [50, 51], which were later corroborated in independent experiments on a light-gas gun [55]. The behavior of lithium under pressures up to roughly 50 GPa has also been investigated under static compression in a diamond anvil cell [56]. By studying X-ray diffraction patterns it was found that at a pressure of about 42 GPa lithium transforms into a very unusual cubic structure cI16 with 16 atoms per unit cell (Fig. 4a), never before observed in elementary substances. Later, the cI16 phase was also discovered in experiments involving Na under 103 GPa [17]. The cI16 structure agrees fully with the structure of the compound CoU [18] and can be visualized as being a distorted bcc cell doubled along each of the axes x, y, and z. The displacements of atoms from their sites in an ideal bcc lattice are characterized by a quantity δ , which increases upon compression [56] (Fig. 4b).

Hanfland et al. [56] also did theoretical calculations of the total energies for a large number of crystalline phases of lithium for different compressions, including the semicon-



Figure 3. Dependence of electrical resistivity of lithium on density, obtained in shock-wave experiments. For each series of experiments the initial temperature and maximum pressure are given. The numbers at the points indicate the reference temperatures. (Taken from Ref. [51].)



Figure 4. (a) Cubic unit cell of the cI16 phase of lithium containing 16 atoms. (b) One-eighth of the unit cell represented as a distorted bcc cell. The signs '+' and '-' correspond to the displacements of atoms from the sites of an ideal bcc lattice up and down, respectively; the size of the displacement δ increases with pressure (taken from Ref. [18]).

ducting phase oC8 (proposed by Neaton and Ashcroft [53]). The researchers found that the cI16 phase has a broader stability range compared to all other studied structures and is the ground state of lithium up to pressures of about 165 GPa. The oC8 structure becomes energetically preferable only at pressures higher than 165 GPa. Recently, Rousseau et al. [57] once more calculated the phase diagram of lithium in the pressure range up to 140 GPa. In addition to finding the total energies, they also calculated the phonon frequencies for lithium under high compression. In particular, they found that up to roughly 140 GPa the oC8 phase is dynamically stable but is less energetically favorable than the cI16 phase. What is more, according to their calculations, at pressures higher than 88 GPa the most favorable structure was not the cI16 phase, as Hanfland et al. [56] maintained, but an orthorhombic structure with 24 atoms per unit cell, Cmca-24 (oC24). The transition to this new phase from the cI16 phase can be practically continuous, since there is a strain that transforms the cI16 structure at a certain value of $\delta (\geq 1/8)$ to the Cmca-24 structure. Note that under a pressure of roughly 165 GPa the calculated differences of the total energies for different crystalline phases of Li are very small.

2.5.2 Electrical resistivity of shock-compressed lithium.

Recently, measurements have been carried out [50, 51] of the electrical resistivity of shock-compressed lithium up to 210 GPa (see Fig. 3). Figure 3 clearly shows that the resistivity ρ of lithium under pressures ranging from 30 to 150 GPa increases by a factor of approximately 20 from values typical of metals, but in the interval from 160 to 210 GPa returns to its initial values. To interpret the experimental data presented in Fig. 3, we calculated the resistivity of lithium up to compressions of approximately $0.25V_0$ ($p \sim 165$ GPa) by the FP-LMTO method. The results of these calculations are briefly discussed in Ref. [51]. There, we calculated the total energy of the fcc and cI16 phases of lithium, and the cI16 phase proved to be stable with respect to the fcc phase in the pressure range from 50 to 165 GPa, which corroborates the results of the calculations done by Hanfland et al. [56]. The cI16 structure has a highly nontrivial electron spectrum (Fig. 5b), which is closer to the spectrum of semimetals than to that of simple metals. Note that for the same compression ($V \approx 0.3V_0$) the spectrum of fcc Li is close in shape to the parabolic law of dispersion of quasifree electrons (Fig. 5a).

The electron density of states N(E) for the cI16 structure, calculated as an integral over the Brillouin zone,

$$N(E) = \frac{2}{(2\pi)^3} \sum_{\mathbf{k},j} \delta(E_{\mathbf{k}j} - E), \qquad (17)$$

is depicted in Figs 6a-c for successive compressions to $V/V_0 = 0.5$, 0.4, and 0.3, respectively. The density of states at $V/V_0 = 0.4$ (Fig. 6b) coincides almost perfectly with the diagram given in Ref. [56], which suggests that the two results are in good agreement. Figure 6d shows the behavior under compression of the density of states at the Fermi level, N(0), for the fcc and cI16 phases of Li. Clearly, N(0) in the cI16 phase is much smaller than in the fcc phase, and very rapidly decreases as the pressure rises. All this means that lithium in the cI16 phase becomes worse and worse as a metal as the pressure grows. Note, however, that up to the highest pressures studied so far in this case, $p \sim 165$ GPa, lithium does not transform into an insulator or semiconductor.

From the theory of metals (e.g., see Ref. [1]) it follows that the electrical resistivity of a metal as a function of pressure and temperature can be written as follows:

$$\rho(T,p) = \frac{4\pi}{\left[\omega_{\rm pl}(p)\right]^2} \frac{1}{\tau(T,p)} \,. \tag{18}$$



Figure 5. Electronic band structure of lithium compressed to $V = 0.3V_0$ in the fcc (a) and cl16 (b) phases. The horizontal line indicates the position of the Fermi level $E_{\rm F}$.

Here, τ is the electron lifetime, which depends on, among other things, temperature and pressure, and ω_{pl} is the electron plasma frequency, which can be calculated by the formula

$$\omega_{\rm pl}^2 = \frac{4\pi e^2}{3V} \sum_{\mathbf{k},j} |\mathbf{v}_{\mathbf{k}j}|^2 \,\delta(E_{\mathbf{k}j} - E_{\rm F})\,,\tag{19}$$

where $E_{\rm F}$ is the Fermi energy and

$$\mathbf{v}_{\mathbf{k}j} = \frac{1}{\hbar} \frac{\mathrm{d}E_{\mathbf{k}j}}{\mathrm{d}\mathbf{k}}$$

is the velocity of an electron in state $\psi_{\mathbf{k}j}$.

In the model of nearly free electrons, the plasma frequency is expressed in terms of the electronic density n_{el} by the Drude formula

$$\omega_{\rm pl}^2 = \frac{4\pi n_{\rm el} e^2}{m} = \frac{4\pi e^2}{m} \frac{Z}{V},$$
(20)

where V is the atomic volume and Z is the valence. This implies that as pressure grows, ω_{pl} increases as follows:

$$\omega_{\rm pl}(V) = \omega_{\rm pl}(0) \sqrt{\frac{V_0}{V}}.$$
(21)

Here, V_0 and $\omega_{\rm pl}(0)$ are, respectively, the atomic volume and plasma frequency at p = 0. If we think of lithium as a metal with nearly free electrons, then, according to (20), $\omega_{\rm pl}(0)$ should be equal to 8.04 eV. However, our calculations of the behavior of $\omega_{\rm pl}$ under pressure using formula (19) and their comparison with the values calculated by formulas (20) and



Figure 6. (a – c) Density of states in the cI16 phase of lithium at compressions to 0.5, 0.4, and $0.3V_0$, respectively; energy is measured from the Fermi level; solid curves represent the total density of states, and the dot–dash and dashed curves represent the partial s- and p-contributions, respectively. (d) Densities of states at the Fermi level for the fcc and cI16 phases of Li as functions of compression V/V_0 .



Figure 7. Dependence of $\omega_{\rm pl}$ on compression for the fcc and cI16 phases of lithium. The dashed curve represents the dependence for free electrons.

(21) show that even in the fcc phase lithium is not a metal with nearly free electrons (Fig. 7).

First, the value of $\omega_{pl}(0)$ for the fcc phase is smaller than in the free electron model and amounts to 6.73 eV. Second, as Fig. 7 shows, although ω_{pl} in the fcc phase increases with pressure, it does this much more slowly than formula (21) would suggest. In the cI16 phase the plasma frequency drops as the pressure grows, despite the fact that V decreases. The thing is that the summation in (19) for the cI16 phase is over a complex Fermi surface, which in no respect resembles the sphere of nearly free electrons, but, as in the case of semimetals, consists of several small surfaces containing a very small number of carriers (cf. the electron spectrum in Fig. 5b). Upon compression, the total area of all these surfaces for c116 Li decreases faster than does the volume V. This alone should lead, in accordance with formula (18), to a significant increase in the electrical resistivity of c116 Li with pressure.

In their experiments on measuring the resistivity of lithium up to 30-40 GPa, Lin and Dunn and Shimizu et al. [58] recorded a significant increase in ρ beginning at approximately 10 GPa, i.e., still in the fcc phase. This shows that, apparently, the relaxation time τ also changes with pressure. According to Matthiessen's rule, we can write

$$\frac{1}{\tau(T, p)} = \frac{1}{\tau_{\rm imp}(p)} + \frac{1}{\tau_{\rm ph}(T, p)}, \qquad (22)$$

where the electron lifetime due to the scattering on impurities and lattice defects is denoted by τ_{imp} , and the lifetime due to electron – phonon scattering by τ_{ph} . Of course, where there are many impurities and lattice defects, Matthiessen's rule may break down. However, the experimental data [58] show that, in addition to the absolute increase in the resistance of lithium with pressure, the resistance increases substantially with temperature, even at ~ 20-30 GPa. This means that not only an increase in the number of defects, especially dislocations, with pressure contributes substantially to resistance, but so does the increase in the relaxation rate due to electron scattering by phonons.

The relaxation rate $1/\tau_{\rm ph}(T, p)$ for $T \ge 0.3\Theta_{\rm D}$, where $\Theta_{\rm D} = 400$ K is the Debye temperature of lithium, can be



Figure 8. Electrical resistivity of lithium as a function of density at different temperatures. First-principles calculation.

expressed as follows:

$$\frac{1}{\tau_{\rm ph}(T,\,p)} = 2\pi\lambda(p)T.$$
(23)

Here, $\lambda(p)$ is the electron – phonon coupling constant, which can be written in the form

$$\lambda \approx \frac{\eta}{M\langle \omega^2 \rangle} \,, \tag{24}$$

where $\langle \omega^2 \rangle$ is the mean square of the phonon frequencies and η is the Hopfield parameter, which can be expressed in terms of matrix element of the electron – phonon interaction.

Figure 8 shows the dependence of the phonon part of the electrical resistivity of lithium on the density *n* and temperature, calculated by the formula

$$\rho_{\rm ph}(T,n) \sim \frac{\lambda(n)T}{\left[\omega_{\rm pl}(n)\right]^2} \,. \tag{25}$$

Here, we have used the functions $\omega_{\rm pl}(V)$ for the fcc and cI16 phases shown in Fig. 7. To estimate the dependence of λ on density, we used the results of Christensen and Novikov [59], who numerically analyzed the behavior of λ for fcc Li at compressions up to $V = 0.4V_0$. They found that λ at such compressions increases more than sixfold, from 0.4 to 2.55. Since from our calculations it follows that $1/\omega_{\rm pl}^2$ for fcc Li decreases slightly with increasing pressure (see Fig. 7), the overall increase in $\rho_{\rm ph}$ in the fcc phase due to electron–phonon scattering amounts to a factor of 3.6.

In experiments involving shock compression of lithium [50, 51, 55], the researchers observed a rapid increase in resistivity under compressions to about $0.4V_0$ (see Fig. 3), which apparently, in accordance with the experimental data of Hanfland et al. [56], corresponds to the transition of Li into the c116 phase. This assumption is corroborated by the theoretical results in Refs [51, 56, 59]. Estimates made by Christensen and Novikov [59] show that in c116 Li the value of λ is unlikely to vary noticeably with pressure and remains practically the same as in the fcc phase, i.e., about 2.55. However, in c116 Li, the value of $1/\omega_{pl}^2$ changes very perceptibly, which in turn leads to a very significant increase in electrical resistivity.

There are two more possible reasons for the increase in ρ of cI16 Li, observed in shock-wave experiments [50, 51, 55]. One reason is the increase in temperature that happens as the shock-wave compression grows; the other reason is the scattering on defects, whose role increases substantially as the number of carriers, i.e., the density of conduction electrons in the cI16 phase, drops. The subsequent decrease in ρ observed in shock-wave experiments cannot be explained if one considers only the crystalline phases of lithium. Apparently, the main role in this phenomenon is played by the destruction of the complex anisotropic crystal structures and the transition of lithium, caused by the increase in temperature in such shock compressions, into the liquid state, where the behavior of its electrons more resembles that of a homogeneous electron gas (of nearly free electrons).

3. The effect of pressure on the properties of alkali-earth metals

3.1 High-pressure phases and the metal-semiconductor transition in heavy alkali-earth metals

While the simplicity of alkali metals for a long time produced no serious doubts in the mind of physicists, the same cannot be said about some s-elements of the second group, precisely, about the heavy alkali-earth metals Ca, Sr, and Ba. The behavior of the light alkali-earth metals Mg and Be differs substantially from that of heavy alkali-earth metals, and we will not discuss the properties of Mg and Be in this review. Under normal conditions, heavy alkali-earth metals crystallize into highly symmetric close-packed structures with one atom per unit cell (see Table 1). In accordance with the simple single-particle model used to describe electronic structures, the two valence electrons may completely fill up the first Brillouin zone, which means that crystals of the bivalent alkali-earth elements could be insulators. However, it is a well-known fact that at atmospheric pressure they are metals.

We performed the *ab initio* density-functional calculations of calcium's properties by the full-potential linear augmented plane wave (FP-LAPW) method as implemented in the Wien2k program package [60]. In this method (e.g., see Ref. [46]), the electron wave functions $\psi_{\mathbf{k}}(\mathbf{r})$ are expanded on the basis of augmented plane waves, $\phi_{\mathbf{k}}$, linearized in energy. Near an atom, $\phi_{\mathbf{k}}(\mathbf{r})$ is a linear combination of the radial functions $u_l(r, E)$ multiplied by the spherical harmonics $Y_{lm}(\hat{\mathbf{r}})$, where *l* and *m* are quantum numbers. In interstitials the expansion is in plane waves, exp (ikr).

Figures 9a and b show the results of our calculations of the electronic band structure for fcc Ca under normal and high pressures. Clearly, at normal pressure, the larger number of filled electronic states below $E_{\rm F}$, as should be the case in all simple metals, correspond to the model of nearly free electrons with the parabolic dispersion law $\varepsilon_k \approx k^2/2m$. This band may be approximately considered as derived from the filled s-states of Ca atoms. The bands above $E_{\rm F}$ appear to a great extent because of the overlap of the atomic wave d-functions. In the larger part of the Brillouin zone these unfilled states are above the s-states, but along some directions the upper and lower bands overlap. It is because of this overlap that the crystals of alkali-earth elements are metals. In this sense, it would be more natural to call them semimetals, since they contain charge carriers of both signs, electrons and holes, and the number of such carriers is the same. One should bear in mind, however, that the total



Figure 9. Electronic band structure of calcium; the dashed curve indicates the position of the Fermi level. (a) Metallic fcc phase, $V = V_0$; (b) semiconducting fcc phase, $V = 0.6V_0$; (c) metallic bcc phase, $V = 0.55V_0$; and (d) semiconducting sc phase (unstable; see main text), $V = 0.53V_0$.

number of carries in alkali-earth metals in normal conditions is much higher than in such classical semimetals as bismuth.

In the 1960s, alkali-earth metals attracted much attention from physicists, both theoreticians and experimenters. In 1963, Stager and Drickamer [61] detected a peak in the electrical resistivity ρ of Ca at pressures of about 30– 40 GPa.¹ Moreover, they concluded from the temperature dependence of ρ that Ca in this pressure range behaves like a semiconductor or a semimetal with a very low carrier concentration. Actually, they observed a negative temperature coefficient of resistance $d\rho/dT$ in the temperature interval from 77 to 300 K. Soon after that, theoretical calculations of the electronic structure [62–64] showed that as the pressure to which fcc Ca is subjected grows, the number of carriers tend to decrease and even a small energy gap may appear in the electron spectrum.

In the same period (1960s), the excitonic insulator model became very popular with theoreticians. In 1961, Mott [65] pointed out that semimetals with a low concentration n of electrons and holes ($na_B^3 < 1/4$, where a_B is the Bohr radius) cannot exist due to the formation in them of nonconducting states of bound electron-hole pairs, or excitons. Later, Keldysh and Kopaev [66] and Jérome, Rice, and Kohn [67] showed that even when $na_B^3 > 1/4$, there may be a transition of a semimetal to the insulator state, which became know as an excitonic insulator. However, for such a transition to happen at $na_B^3 > 1/4$, the spectrum of electronic excitations must exhibit specific properties. In this review there is no place for a discussion of all the details of the theory of excitonic insulators, all the more so since they have been described very well in the review articles [68, 69]. We only note

that the properties of an excitonic insulator do not differ in any way from those of an ordinary insulator. Perhaps, what is important is that this transition is largely determined by the correlation energy of the crystal's electrons. Among the large number of candidates for the role of excitonic insulators, Jérome, Rice, and Kohn [67] also mentioned alkali-earth metals, precisely for the reason that the results of their theoretical calculations demonstrated that even within the single-particle band approach an energy gap may appear.

All this prompted experimenters to study in detail the behavior of alkali-earth metals under pressure [70, 71]. McWhan et al. [70] measured the electrical resistivity of strontium and the bivalent rare-earth element ytterbium (which is close in its chemical properties to alkali-earth metals) in a temperature interval from 2 to 298 K at pressures up to 5 GPa. At $p \approx 2.5$ GPa and T = 4.2 K, they recorded a sudden jump in the value of ρ of Yb by a factor of approximately 6×10^4 . For Sr, at $p \approx 3.5$ GPa there was also a jump in ρ , but a much smaller one (the value increased only by a factor of 50). Both for Yb and Sr at T = 298 K the recorded variation of ρ was not so dramatic. A negative temperature coefficient of resistance was detected for ytterbium at 1 GPa and for strontium at3 GPa. Furthermore, in the temperature intervalfrom 100 to 300 K and at pressures $1.97 \le p \le 3.5$ GPa, ρ of Yb exhibited an exponential temperature dependence with a very low activation energy. The temperature dependence of ρ in Sr is not exponential, although its temperature coefficient of resistance is negative. All this prompted McWhan et al. [70] to suggest that, under pressure, Yb exhibits a transition from the metallic state to the semiconducting state, while Sr exhibits a transition from the metallic state to a semimetallic state with a small number of carriers. Another conclusion arrived at in Ref. [70] was that in neither Yb nor Sr had a transition to the excitonic insulator phase been detected.

¹ Most likely, these values of pressure are overstated, since the researchers used an old pressure scale. According to present views, the maximum in the electrical resistivity of Ca lies in the pressure range from 12 to 19 GPa.

Today, this seems only natural - nothing different could ever have been detected. According to the estimates made by these researchers, the binding energy of the excitons in these systems is very low, so that the emerging energy gaps must also be small. Actually, the researchers observed something very similar, especially if one bears in mind that when high pressure is applied, it produces many defects in the crystal and, accordingly, related electronic states in the energy gap. Of course, the presence of such states, especially with their number unknown, may lead to a sizable discrepancy between the properties of the real crystal and those of a pure semiconductor. Dunn and Bundy [71] studied the behavior of the electrical resistivity of calcium under pressure, but the results of their investigation will be discussed later, in Section 3.2, while here we will briefly discuss the experimental data and the results of theoretical calculations pertaining to the P vs. T phase diagram of alkali-earth metals.

Phase transitions in heavy alkali-earth metals at high pressure (see Table 1) have been thoroughly investigated by Olijnyk and Holzapfel [72], who studied the X-ray diffraction with allowance for dispersion in energy. They discovered structural transitions in Ca at 19.5, 32, and 42 GPa; however, further investigations [73] did not corroborate the transition at 42 GPa. In strontium, structural phase transitions were detected at 3.5, 24, 35, and 46 GPa, while in barium the phase transitions occurred at 5.5, 12.2, and 46 GPa. Here, the Ba-IV phase and the isostructural phase Sr-V have a very complex tetragonal structure. Like the host-guest structure of the Rb-IV phase, it is incommensurate (a similar structure type is that of CuAl₂ [18]), while the structure of the Sr-IV phase has yet to be solved. On the whole, the structural sequences in alkali-earth metals exhibit the same 'unorthodox' tendency also observed in alkali metals: as pressure is increased, transitions to less closely packed structures occur, with the symmetry of the lattice becoming lower. We will now examine this tendency using the phase diagram of calcium as an example. For calcium, all the known high-pressure phases have highly symmetric cubic structures which can be studied more easily from the theoretical viewpoint. Here, we would like to note that in the series of heavy alkali-earth metals there is partial similarity in relation to the fcc-bcc phase transition. According to the model of electron transfer from the s-band to the d-band, the pressure of the fcc-bcc transition is determined by a universal parameter, the number of valence d-electrons in the system, $N_{\rm d}$; under normal conditions, the heavy alkali-earth metals Ca, Sr, and Ba are, so to say, in different stages of a continuous electronic s-d transition [74]. Indeed, the number of d-electrons in the heaviest element, Ba, is higher than in Ca or Sr, with the result that the bcc structure in barium is realized already at atmospheric pressure. However, this simple model does not explain the entire sequence of transitions in alkali-earth metals.

3.2 The study of the properties of calcium at high pressure In normal conditions, calcium crystallizes into an fcc structure with the largest possible coordination number $Z_{\rm NN} = 12$ (packing index $\eta = 0.74$). At room temperature and a pressure of 19.5 GPa, calcium transforms into a bcc phase with $Z_{\rm NN} = 8$ and $\eta = 0.68$, while at 32 GPa it transforms into a less closely packed simple-cubic (sc) structure ($Z_{\rm NN} = 6$ and $\eta = 0.52$) [72]. After that, at least up to 80 GPa, experiments revealed no structural transformations in calcium [73, 75]. Earlier attempts [76] to calculate the phase diagram of calcium on the basis of phenomenological pseudopotential theory were not successful. In particular, these calculations suggested that at normal pressure the stable phase must be bcc. Actually, at p = 0, bcc Ca becomes stable at temperatures of about 700 K. More successful in this respect were the first-principles calculations by Skriver [74], Wentzcovitch and Krakauer [77], and Ahuja et al. [78], who used various modifications of the LMTO method [47]. For instance, already in the earlier work of Skriver [74] it was shown that the fcc-bcc transition in Ca must happen at ~ 21 GPa, which is slightly higher than the experimental value of 19.5 GPa. Later, Wentzcovitch and Krakauer [77] calculated that the transition occurs at a slightly lower pressure, p = 16 GPa, which is close to our result for Ca (17 GPa). Skriver [74] did not consider the possibility of a bcc-sc transition; instead he predicted a direct bcc-hcp transition at $p \sim 80$ GPa. In their theoretical paper, written after the experimental discovery of the bcc-sc transition, Ahuja et al. [78] calculated with reasonably high accuracy the pressures of the fcc-bcc (15 GPa) and bcc-sc (33 GPa) transitions. In addition, the researchers predicted an sc-hcp transition at $p \sim 120$ GPa.

3.2.1 The metal – semiconductor transition in Ca under pressure. We have done detailed calculations of the electronic band structure and related properties of calcium in a range of compressions corresponding to a variation of the specific volume from $1.1V_0$ to $0.3V_0$. The calculations were done for the fcc, bcc, and sc phases. Figure 10 shows the calculated differences of the total energies, $E_{\rm bcc} - E_{\rm fcc}$ and $E_{\rm sc} - E_{\rm fcc}$. Clearly, the total energy differences are very small and therefore the calculation of these differences requires special accuracy. This is also true of calculations of the total energies proper by formula (7), where very small differences of large quantities must be calculated exactly. The necessary accuracy is achieved by controlling the convergence in all *free* parameters of the calculation. We also calculated the



Figure 10. Calculated differences in the total energies of three phases of calcium as functions of the specific volume. Energy is measured from the energy of the fcc phase.



Figure 11. Density of states in the fcc (a) and sc (b) phases of calcium for different degrees of compression V/V_0 . Energy is measured from the Fermi level.

enthalpy (9) for these three phases and obtained the values of pressures of the fcc – bcc and bcc – sc transitions, which are in reasonable agreement with the results of the calculations done by Ahuja et al. [78] and the experimental data of Olijnyk and Holzapfel [72].

As noted above, even the simplest pseudopotential calculations [62, 63] show that as pressure grows, fcc Ca may transform into a semiconductor with a small energy gap. A similar result was obtained by Skriver [74], who used the LMTO method. Our calculations confirm that in the fcc Ca spectrum there is a very small ($\sim 0.1 \text{ eV}$) semiconductor gap; see Fig. 9b (as is known, in DFT the gap width is considerably understated [41]). Generally speaking, as noted in Section 2.3,



Figure 12. Densities of states at the Fermi level for the fcc, bcc, and sc phases of calcium as functions of relative volume V/V_0 .

the calculation of the energy gap in DFT is not rigorous, since DFT is intended only for calculations of ground-state properties. The properties of excited states, to which the gap width belongs, are calculated by employing approximations that go beyond DFT (for a more detailed discussion, see, for example, Ref. [41]).

Figure 11a shows the electron densities of states we calculated for fcc Ca at various compressions. Clearly, at normal pressure (i.e., at $V = V_0$), the density of states is that of an ordinary metal. At a compression up to approximately $V = 0.75V_0$, a gap appears in the electron spectrum (cf. Figs 9a and b), which under further compression widens, but then at approximately $V = 0.57V_0$ closes. Actually, the re-entrant metallic fcc phase of Ca is not realized, since somewhat earlier, at $V \approx 0.60 V_0$, there occurs the transition to the metallic bcc phase. Most likely, the real values of the gap in fcc Ca exceed the values obtained in our calculations, but they are sure to be very small [71]. No semiconducting state appears in the bcc structure, which is in full agreement with the shape of the electron spectrum in Fig. 9c. In sc Ca there is also a very narrow range of compressions, $V/V_0 = 0.53 - 0.55$ (Figs 9d and 11b), where a very narrow gap exists; most likely, this the region of 'pseudogap' behavior. However, no semiconducting state of calcium is realized in the sc structure, since in the indicated range of compressions the bcc phase is the ground state, while the sc phase becomes stable only at $V/V_0 \approx 0.45$. Nevertheless, immediately after the bcc-sc transition, calcium is a 'worse' metal than in the bcc phase. This becomes clear if we look at Fig. 12, which depicts the volume dependence of the density of states at the Fermi level in the fcc, bcc, and sc phases.

Figure 13 shows the results of measurements of the electrical resistance of Ca under pressure [71]. In the 12–19-GPa range there is a maximum in the resistance (Fig. 13b), and within this range the temperature coefficient of resistance is negative (Fig. 13a). In accordance with the results of experimental studies of transitions in Ca done by Olijnyk and Holzapfel [72], Skriver's theoretical calculations [74], and our calculations, the semiconducting state in fcc Ca exists up to the point where calcium transforms into the metallic bcc phase. Dunn and Bundy [71] related the subsequent increase in resistance, which begins at $\sim 23-25$ GPa, to the transition of Ca into a new unknown phase. However, later studies of the crystal structure of Ca [72, 73] clearly showed that there is



Figure 13. Electrical resistance of calcium as a function of temperature, R(T), at different pressures (a) and as a function of pressure, R(p), at different temperatures (b). The isotherms R(p) are built from the data on R(T) measurements shown in (a). (Taken from Ref. [71].)

no structural transition at these pressures. The increase in resistance observed by Dunn and Bundy [71] is, most likely, related to the increase in the number of defects in samples because of the increasing non-hydrostatic conditions near the highest pressure reached in these experiments. There is one more reason why resistance could increase at pressures higher than 23 GPa, and that is an increase in the electron-phonon coupling constant λ . Figure 13a shows that the temperature coefficient of resistance is positive for pressures higher than 23 GPa and increases with pressure still further. Bearing in mind that, according to formula (25), $d\rho/dT \sim \lambda$, the abovementioned increase in the temperature coefficient of resistance is an indication that the electron-phonon coupling constant grows with pressure. Unfortunately, the experimental data provided by Stager and Drickamer [61] and Dunn and Bundy [71] do not allow one to determine the semiconducting gap in fcc Ca, in contrast to the data on Yb [79] (mentioned above), where there is a range of pressures within which the observed dependence $\rho(T)$ is exponential.

3.2.2 The microscopic nature of structural transformations in

Ca. As with alkali metals, the calculations for calcium done by Skriver [74] and Ahuja et al. [78] show that the arrangement of its energy bands changes continuously. Figure 14a shows the arrangement of the unhybridized bands that originate from the atomic 3p-, 3d-, and 4s-states of calcium as calculated by Ahuja et al. [78] in accordance with the Wigner–Seitz rule.² Clearly, as the sample is compressed, all the bands gradually broaden, the bottom of the 3d-bands drops in relation to the Fermi energy $E_{\rm F}$ and the 4s-band, and the entire 4s-band moves above $E_{\rm F}$ when $V/V_0 \sim 0.2$.

Calculations have shown that already at normal pressure the d-band of pretransition element Ca contains a substantial number of electrons. According to our estimates, under threefold compression to $V \approx 0.3 V_0$, the electronic configuration in Ca changes from $4(sp)^{1.48}3d^{0.52}$ to 4(sp)^{0.64}3d^{1.36}. Thus, almost 0.9 of an electron gets redistributed from the sp-band to the d-band. This estimate was done in the atomic sphere approximation (ASA), in which the polyhedral unit cell is replaced by an equally large Wigner-Seitz sphere and the crystal potential is assumed to be spherically symmetric. Figure 14b shows the results of our calculation of the number of sp- and d-electrons in Ca as a function of compression. In this case $N_{\rm sp}$ and $N_{\rm d}$ were estimated in a more realistic approximation, with allowance for the true shape of the cell and the crystal potential. Here, the MT-geometry is used, in which there is an intersphere region of a complicated shape, and in this region it is difficult to represent the wave function as a linear combination of 'quasiatomic' s-, p-, and d-states. In the case at hand, the redistribution of charge takes place with the active participation of this interstitial region, with the result that the total number of valence electrons of Ca, $N_{sp} + N_d$, is smaller than 2 and changes under compression. Moreover, since there is a certain ambiguity in the definitions of $N_{\rm sp}$ and $N_{\rm d}$, they may be weakly dependent on the selected radius of the spheres surrounding the atoms, the number of reciprocal lattice vectors taken into account, and some other free parameters used in the calculation. However, it must be noted that when the accuracy of calculations is high (and takes up a lot of computer time), the observed characteristics of substances, such as the total energy or the equation of state, should not depend on these free parameters.

Thus, there is no way in which one can rigorously determine the number of valence p- or d-electrons in the

² According to the Wigner–Seitz rule, the top of a band (antibonding state) is defined as the energy $E = E_{top}$ at which the function $u_l(r, E)$ at $r = r_{WS}$ is zero, while the bottom of a band E_{bot} (bonding state) corresponds to the zero of the radial derivative $u'_l(r = r_{WS}, E)$. Here, $u_l(r, E)$ is the solution of the radial Schrödinger equation, r_{WS} is the radius of the Wigner–Seitz sphere, and $l = s, p, d, \dots$.



Figure 14. (a) Positions of the 3p-, 3d-, and 4s-bands in calcium in relation to the Fermi level for different compressions V/V_0 (taken from Ref. [78]). (b) The number of sp- and d-electrons in calcium as a function of compression (calculations done in the present work). The dotted curve shows the results of calculations in the atomic sphere approximation (ASA).

system and relate them uniquely to the crystal structure. To obtain a correct sequence of phases that appear under pressure by theoretical means, we must carry out exact calculations of the total energies of the various crystal structures. Qualitatively, however, such a 'quasiatomic' picture of the transformation of the electronic states in alkali and alkali-earth metals under pressure proves to be useful. Indeed, atoms with valence electrons primarily of the s-type can be pictured as spheres for which close packing into highly symmetric, isotropic structures seems only natural. Under compression, when the contributions of d- and p-components in the wave function increase, the tendency toward anisotropy, caused by an increase in the directionality of the bonds, becomes more and more evident, with the result that there is a redistribution of electron charge from the nucleus to the periphery, since p- and d-states, in contrast to s-states, contribute nothing to the change density on the nucleus. This last fact was used by Takemura et al. [29] to account for the stabilization of the Cs-IV structure mentioned in Section 2.1, a structure in which the electronic density has maxima in the interstitials, which correspond to the positions of negative ions. A similar description of the stabilization of the Cs-IV structure has been recently proposed in Ref. [30]. The researchers did first-principle calculations in the tight-binding method to build Wannier functions and found that at pressures corresponding to the transition to the Cs-IV phase these functions resemble atomic d-orbitals much more than they do spherically symmetric s-orbitals. As for calcium, we note that because of the directionality of the d-wave functions their overlap integrals are large, with the result that the d-band in the sc structure proves to be almost twice as wide as that in the bcc structure, which facilitates stabilization of the sc phase at appropriate compressions. However, we note once more that the reasoning concerning the role of s-d and s-p transitions in the structural transformations of simple metals is, basically, of a qualitative nature: it more likely provides an easy-to-grasp picture useful for understanding the results of first-principles calculations.

Concluding this section, we turn once more to the problem of an alternative explanation of the sequence of structural transformations in simple metals and, in particular, in lithium, an explanation based on the Hume-Rothery rule. As noted earlier, attempts of this kind have recently been made by Degtyareva [35] and Ackland and Macleod [38]. In particular, Ackland and Macleod [38] discussed the possibility of using the Hume-Rothery rule to explain the structural transformations in a large number of simple metals, including Li, Na, K, Rb, Cs, Ca, Sr, and Ba. In addition, the researchers actually performed extensive density-functional calculations for the cI16 phase of lithium using a first-principles pseudopotential method. They found that the region of stability of the cI16 phase that emerged from their calculations was in good agreement with the Hume-Rothery rule. In the cI16 structure there appears a Bragg plane (211), for which the reciprocal lattice vector is close in length to the Fermi momentum of free electrons with a density corresponding to the electronic density in cI16 Li. Actually, Ackland and Macleod's results [38] cannot serve as proof that the Hume-Rothery rule can be used to describe all structural transformations in simple metals. These results, as well as the reasoning concerning s-d and s-p transitions, can only illustrate that in this specific case the Hume-Rothery rule qualitatively explains the nature of the stability of the cI16 phase. For instance, it is quite clear that the existence in calcium of an sc structure does not fit into the Hume-Rothery rule. It is also clear that any attempt to calculate the total energy of crystal structures with allowance, in the spirit of the Hume-Rothery rule, for the interaction of electrons only with Bragg planes whose reciprocal lattice vectors G are close in size to the Fermi momentum of free electrons with an appropriate charge density is doomed to failure. As is known, in the calculations that use a first-principles pseudopotential, achieving convergence requires using a very large number of plane waves (or corresponding to them reciprocal lattice vectors G) and not a small number of vectors G whose size is close to $k_{\rm F}$.

3.2.3 The thermodynamic and electrophysical properties of Ca. By numerically calculating the partial derivative of the total energy [see Eqn (8)] we arrived at an equation of state for calcium at T = 0, i.e., the relation between pressure and specific volume, p(V). Figure 15 shows the calculated functions p(V) for the fcc, bcc, and sc phases of calcium. It



Figure 15. Equation of state for calcium, p(V). Curves with symbols represent the experimental results, and dashed, dotted, and dash-dot curves represent the results of our calculations for the fcc, bcc, and sc phases of calcium, respectively. The results of static experiments in diamond anvil cells (DAC) are marked by lozenges (estimates made from the data given in the main text of paper [72]), while the results of shockwave (SW) experiments are marked by circles [81] and asterisks [82]. Vertical arrows indicate the fcc-bcc and bcc-sc transitions, while the slanted arrow indicates a kink in the Hugoniot adiabat obtained in processing the data in Ref. [80].

also shows the experimental p(V) curves obtained in static experiments [72] and under shock compression [79–81]. Clearly, under low compression, the data of shock-wave experiments agree fairly well with the static data and the results of our calculations. However, beginning with $V/V_0 \approx 0.45$ the pressure begins to rise very rapidly,which was interpreted by Bakanova and Dudoladov [79] and Al'tshuler et al. [80] as a kink in the Hugoniot curve related to a structural transition to a *less* compressible phase due to an s-d electron transition.

As the data of static experiments [72] and the results of theoretical calculations show, at pressures that approximately coincide with the assumed kink, at room temperature there is a transition from the bcc structure to the sc structure, i.e., on the contrary, to a *more* compressible phase with a smaller number of nearest neighbors, Z_{NN} . Furthermore, as mentioned earlier, there are no abrupt s-d electron transitions in calcium. The thing is, most likely, that under high compression and upon transforming into the more open sc structure with an 8% decrease in volume, the temperature in the shock wave rises substantially. Thus, we can assume that the kink on the p(V) curve reported in Refs [79, 80] is caused not by an electron transition but by a polymorphic bcc-sc transformation.

Recently, the electrical resistivity of shock-compressed calcium and its melt has been measured in the high-pressure (10-50 GPa) and high-temperature (800-1600 K) regions [82]. The researchers used the method of multi-step shock compression, briefly described in Section 2.4. The obtained experimental time profiles of pressure p(t) and electrical resistance R(t) for calcium are shown in Fig. 16. They also calculated the thermodynamic characteristics of calcium with the use of equations (10)-(12) for the thermodynamic potential and did first-principles calculations of the total energy $E_{\text{tot}}(V)$ for the three crystalline phases of Ca using formula (7). Since at present there are no detailed calculations of the phonon spectra of calcium, to calculate the thermal



Figure 16. Time profiles of pressure p(t) (solid curves) and electrical resistance R(t) (dashed curves) for multi-step shock compression of a calcium sample: (a) shock-compressed solid Ca, and (b) calcium that melted as a result of shock compression. Vertical arrows indicate the moments t_1 , t_2 , and t_3 of jumps in the measured quantities caused by successive shock waves and moments t_r when the electrical resistance begins to gradually increase. The slanted arrows indicate the moments at which a decrease in pressure caused by the arrival of the rarefaction wave from the back surface of the impactor begins. (Taken from Ref. [82]).

contribution $F_{\rm ph}(V,T)$ the authors used a semiempirical expression within the Einstein model. This expression can be written as follows [83, 84]:

$$F_{\rm ph}(V,T) = E_{\rm tot}(V) + + 3R \left\{ \frac{\Theta_{\rm D}}{2} + T \ln \left[1 - \exp \left(-\frac{\Theta_{\rm D}}{T} \right) \right] \right\} - a_{\rm s}RT + E_{\rm m}.$$
(26)

Here, the notation is quite common. The adjustable parameter a_s is zero for the solid state and finite for the melt. The parameter $E_{\rm m}$ sets the reference point for the total energy $E_{tot}(V)$ of each phase and is used to remove small inaccuracies in determining the pressures of the structural transitions, discrepancies that emerged both in our first-principles calculations and in the works of Skriver [74], Wentzcovitch and Krakauer [77], and Ahuja et al. [78]. Such discrepancies may be related to the use of approximate expressions for the exchange-correlation potential or to the fact that the fccbcc transition is close to a semiconductor-metal transition. As noted above, the calculations of such transitions in DFT must be highly accurate. Detailed descriptions of the method of calculating the thermal contribution to the free energy and of building the $\Theta_{\rm D}(V)$ function can be found in Refs [83, 84]. Here, the adjustable parameters (other than $E_{\rm m}$) in (26) were determined from the Hugoniots obtained in Refs [79-81].

The extraction of the Hugoniot adiabats for different phases of calcium from the experimental data in Refs [80, 81]



Figure 17. Hugoniot adiabat (HA) of calcium in D, u coordinates. The dots represent the experimental data taken from Refs [80, 81]; the solid line represents the results of calculations in Ref. [82]: segment *1*, HA for the fcc phase; *2*, HA for a mixture of fcc and bcc phases; *3*, HA for the bcc phase built on the basis of first-principles calculations of $E_{tot}(V)$; *4*, HA of a mixture of the bcc phase and Ca melt; and *5*, HA of Ca melt. (Taken from Ref. [82]).

was done on the assumption that for small (compared to $p = -\partial E_{tot}/\partial V$) thermal pressures the location of the calculated Hugoniot in the *D*, *u* plane, where *D* is the shock wave velocity and *u* is the mass velocity, is for all practical purposes independent of the constant term E_m in (26). It was found that in this approximation it is possible to calculate the Hugoniot for bcc Ca by using only the total energy of this phase, which we calculated from first principles, and the expression (26) with the functions $\Theta_D(V)$ and $E_{tot}(V)$ in the form proposed by Molodets [83]. The results of these calculations are depicted in Fig. 17 by the segment 3.

As Fig. 17 suggests, the straight line 3 coincides only with a fraction of the experimental data taken from Refs [80, 81]. Consequently, the other segments of the Hugoniot adiabat belong to other phases of calcium and their mixtures: I, fcc phase; 2, a mixture of fcc and bcc phases; 4, a mixture of the bcc phase and Ca melt; and 5, Ca melt. In the final analysis, this separation made it possible to build the thermodynamic potentials of the above phases, to calculate the equilibrium lines, and to identify in detail the thermodynamic states of calcium in an experiment in which the electrical resistance of calcium was measured at high pressures and temperatures.

Figure 18 shows the phase diagram and thermodynamic states of calcium under multi-step shock compression. Calculations of the fcc-bcc equilibrium line with allowance for temperature (segment 2) have shown that there is not one thermodynamic state realized in the experiment that lands in the stability region of the fcc phase. The thermodynamic state in the first shock wave is located, most likely, in the stability region of the bcc phase. This state is depicted in Fig. 18 by a black square, while the respective temperature and reciprocal specific volume 1/V calculated for this state are listed in Table 2, taken from Ref. [82].

A much more complicated situation arises in the identification of the thermodynamic state in the second shock wave. As Fig. 18 shows, the value of the pressure measured in the experiment, p = 28 GPa, is to the left of the bcc-sc equilibrium line (the dotted line 4), i.e., in the stability region of the bcc phase. We immediately note that on this equilibrium curve taken from Ref. [72] there is only one experimental point, which corresponds to room temperature and a



Figure 18. Phase diagram and thermodynamics states of calcium subjected to multi-step shock compression. \triangle and \times represent the experimental data for the fcc-bcc equilibrium line and for the melting curve of the bcc phase, respectively [89]; + represents the experimental data for the melting curve of calcium [75]; and \diamond marks the pressures of phase transitions in Ca at room temperature [72]. Solid line I, the Hugoniot adiabat calculated in Ref. [82] for the case of single-shock compression of monolithic Ca; 2, results of calculations of a segment of the fcc-bcc equilibrium line; 3. results of calculations of a segment of the bcc-melt equilibrium line: dashed curve, results of calculations of the adiabat of multi-step shock compression; dotted line 4, the bcc−sc equilibrium line [75]; ■, thermodynamic state of bcc Ca in the first shock wave; ■, thermodynamic state near the bcc-sc equilibrium line, for which the crystalline phase has not been uniquely determined (see main text); □, estimate of thermodynamic states in the sc phase; and ●, thermodynamic state of the Ca melt in the first shock wave. (Taken from Ref. [82]).

Table 2. Electrical resistivity $\rho(p, T)$ of different phases of calcium at high pressure *p* and temperatures *T*.

Phase of Ca	$ ho, \mu\Omega \ { m cm}$ (±5%)	p, GPa (±8%)	<i>Т</i> , К	1/V, g cm ⁻³
bcc	12.0	14	810	2.346
	14.5	18	1325	2.476
bcc, sc (?)	21.7	28	1080	2.821
sc	16.6	36	1165	
	17.8*	41*	1210*	
Melt	11.8	32	1580	3.057

1. In calculations of $\rho(p, T)$ for sc Ca, the variation in the specific volume V in the bcc-sc phase transition was not taken into account.

2. Asterisks mark the values of ρ , p, and T that refer to the moment t_r at which resistivity begins to gradually increase.

3. The question mark indicates the state in the bcc-sc transition region for which the crystalline phase has not been uniquely defined (see main text).

pressure of 32 GPa [72, 73]. Due to the scantiness of thermophysical data, at present it is difficult to calculate this equilibrium curve using Molodets's approach [83], as we did in Ref. [82] in the case of the fcc – bcc transition. What is clear, however, is that since the sc phase is less closely packed than the bcc phase, the equilibrium curve may, as the temperature increases, slant to the left, i.e., to the region of lower pressures. Such behavior is clearly evident from the equilibrium line 2 that we calculated. Of course, the slant to the left on the bcc–sc line may prove to be much smaller than on the fcc–bcc line. Bearing in mind the aforesaid and the existing

experimental inaccuracies in determining the pressure, we cannot be certain that the thermodynamic state in the second shock wave is in the stability region of the bcc phase.

As for the thermodynamic state of calcium in the third shock wave, the corresponding pressure of 36 GPa indicates that this state is in the stability region of the sc phase. To estimate the temperature in the second and third shock waves, we used the free energy of the bcc phase [82]. Of course, in such a calculation the kink in the Hugoniot adiabat on the bcc-sc equilibrium line, which is determined by the transition heat of this polymorphic transformation, is not taken into account. Let us assume that the overstatement of the temperature resulting from such an approximation is no smaller than the change in temperature in the segment where the Hugoniot coincides with the fcc-bcc equilibrium line, which is roughly 150 K (see Fig. 18). The thermodynamic states found by such a method with an error in temperature of roughly 150 K are listed in Table 2 and depicted in Fig. 18. The state in the second shock wave is marked by a gray square and that for the sc phase by white squares.

Now let us go back to discussing the behavior of electrical resistance under compression. The typical experimental step-wise time profiles of the electrical resistance R(t)of calcium obtained in the experiments [82] were of two types. Figure 16a shows the first type, whose characteristic feature is the nonmonotonic increase in resistance with pressure. The first sudden jump in R at time t_1 corresponds to the jump in pressure in the first shock wave. The second sudden jump in R at time t_2 occurs in the second shock wave. There is nothing remarkable in the increase of the sample's resistance caused by a shock wave: such a wave initiates a rise in temperature and increases the number of various defects in the sample. However, at time t_3 the sample's electrical resistance suddenly drops. Such behavior of R in the third shock wave is clearly remarkable. The measured values of electrical resistance did not allow us, due to the small number of experimental points, to carry out a detailed quantitative analysis of the dependence of R on temperature and pressure. However, combining the results of theoretical calculations with the experimental data for calcium under static compression (at T = 300 K) and on heating up to about the melting point (at $p \approx 0$), we were able to develop scenarios [82] that explain the experimental results.

Table 2 lists, in addition to the thermodynamic characteristics, the measured values of the electrical resistivity $\rho(T, p)$ for all the thermodynamic states being discussed. It also lists the data on $\rho(T, p)$ for the bcc phase, obtained in a separate experiment at p = 18 GPa in a single shock wave. An approximation of the three values of ρ at p = 14, 28, and 18 GPa by the linear function

$$\rho(T, p) = A(T - T_0) + B(p - p_0) + C$$
(27)

yields

$$A = -6.20 \times 10^{-10} \ \Omega \ \text{cm K}^{-1} ,$$

$$B = 7.05 \times 10^{-7} \ \Omega \ \text{cm GPa}^{-1} ,$$

$$C = 2.17 \times 10^{-5} \ \Omega \ \text{cm} .$$

Due to the ambiguity in the results of measurements and the small number of experimental points, we cannot state with confidence that $\rho(T, p)$ is described by linear function (27). However, despite the large errors, we can definitely say that for calcium the value of the temperature coefficient of resistance

$$\sigma = \frac{1}{\rho} \frac{\partial \rho}{\partial T} = \frac{A}{\rho}$$

at $T \sim 1000$ K is several orders of magnitude smaller than in normal conditions. This fact does not come as a surprise. The thing is that, in contrast to most simple metals, alkali-earth metals in the melted state have a temperature coefficient of resistance that is nearly zero or even negative [85]. Bearing in mind that in a shock wave the crystal not only gets heated but becomes disordered, small values of the temperature coefficient of resistance in shock-compressed calcium at high temperatures is quite permissible. Many transition metals in an amorphous or disordered state also have small or even negative temperature coefficients of resistance at high temperatures [86]. Our first-principles calculations of the electronic structure of Ca at high pressures show, as do the earlier calculations of Skriver [74] and Ahuja et al. [78], that in the investigated pressure range d-electrons play an important role in calcium and that the properties of calcium in these conditions are close to those of transition metals.

As noted above, in the oscillograms in Fig. 16a the electrical resistance R of a calcium sample varies nonmonotonically with increasing pressure: the jump in pressure in the third shock wave at time t_3 is accompanied by a sudden drop in R rather than by an increase. If we assume that the thermodynamic state of calcium in the second shock wave corresponds to the bcc phase and the one in the third shock wave corresponds to the sc phase, it becomes very difficult to explain the sudden drop in resistance in the third shock wave. Earlier, we remarked that at a pressure above the fcc-bcctransition pressure, calcium in the sc phase is a worse metal than in the bcc phase. But if we assume that the thermodynamic state of calcium in the second shock wave is also an sc phase, the subsequent drop in electrical resistance in the third shock wave finds a simple and natural explanation. What we mean is that the metallic properties of calcium in the sc phase improve with increasing pressure (see Fig. 12), leading to a decrease in resistance in the third shock wave. The existing ambiguities in the calculated values of temperature and the experimental errors in measuring pressure and the bcc-sc phase boundary proper allow for such a possibility.

The experimental profiles of the electrical resistance R(t) of the second type are shown in Fig. 16b. What sets these profiles apart from those of the first type is that here resistance varies monotonically with pressure. Our calculations (see Ref. [82]) show that in the given case the thermodynamic state of calcium behind the front of the first shock wave corresponds to the melt of this metal. The obtained value of the electrical resistivity ρ of the Ca melt in the first shock wave at time t_1 is presented in Table 2 together with the calculated temperature. The thermodynamic state of the melt is marked in Fig. 18 by a black circle. No calculations of the thermodynamic state of calcium in the second and subsequent shock waves for the case corresponding to Fig. 16b were done.

Note the specific feature of the thermophysical properties of the melt of calcium. As Fig. 17 shows, the Hugoniot adiabat (HA) for Ca melt (segment 5) is located to the right of the HA for bcc Ca (segment 3). This fact is an indication that as calcium melts in the shock wave, its specific volume decreases. This experimental fact agrees with the negative slope of the calculated equilibrium line 3 in Fig. 18, which means that within the given range of pressures and temperature the melt of calcium is more dense than the crystal proper.

We also note that, according to the calculations [82], the sudden increase in the slope of the HA at $u \sim 3-4$ km s⁻¹ (see Fig. 17) is a consequence of the kink in the HA as the adiabat intersects the equilibrium line and the melt curve (curves 2 and 3, respectively, in Fig. 18) and not the result of an electron transition, as assumed by Bakanova and Dudoladov [79] and Al'tshuler et al. [80].

4. Conclusion

In our review we limited ourselves to a discussion of a very small area of recent high-pressure research. We covered the structural and electrical properties of alkali and alkali-earth metals somewhat more thoroughly. However, even this was enough to see the progress in high-pressure physics in the last few years, which was caused by developing experimental techniques and by raising the accuracy of theoretical calculations. Let us briefly summarize our discussion.

First, at high pressures alkali and alkali-earth metals, which in normal conditions behave as systems with nearly free electrons and crystallize in highly symmetric close-packed lattices, often demonstrate polymorphic transitions into exotic structures, many of which have never before been observed. Second, as pressure grows, these metals may transform into semimetallic phases with a small number of charge carriers or even into narrow-gap semiconductors. Third, modern *ab initio* density-functional calculations make it possible to predict and with good accuracy establish the limits of existence of new crystalline phases in the given metals. These calculations show, in particular, that simple models of the respective structural transformations, models related to s-p and s-d electronic transitions or the Hume-Rothery rule, cannot guarantee sufficient accuracy in determining the structural sequences and the exact boundaries in the phase diagram.

Note that the problem of predicting high-pressure phases is a difficult one. In the above-described methods, the search for stable high-pressure phases is done by looking through all possible crystal structures and comparing their total energies. However, as it became clear from experiments, even simple metals under high compressions may have such complex structures (e.g., the Rb-IV in Fig. 1) that it is hardly possible to suppose a priori that such structures exist, with the result that one is forced to calculate total energies for an extremely large number of different structures. In such cases, one can use, say, the method of *ab initio* molecular dynamics (the Car – Parrinello method [87]), in which the atoms 'themselves' seek the energy minimum in the process of computer simulation. However, the number of local minima that emerge in the process can be so large that even the power of modern computers may not be enough. The second difficulty in these predictions and even simply in calculations is related to the fact that differences in the enthalpies of many highpressure phases are very small and comparable to the thermal energy of the crystal. In our review we briefly described a way to calculate the free energy within the quasiharmonic approximation. Unfortunately, there are very few works in which this time-consuming procedure is consistently realized to the end within DFT. A detailed list of references to the literature in this field can be found in Katsnel'son and

Trefilov's monograph [88]. The paper by Liu et al. [45] is one example of calculations of this kind. The researchers calculated the free energy of lithium in the bcc, fcc, hcp, and 9R structures over the range of compressions $\pm 12\%$ by volume.

The present authors are grateful to V V Brazhkin, V F Degtyareva, M I Eremets, J J Kohanoff, I V Lomonosov, A M Molodets, and V I Postnov for the fruitful discussions and to O K Andersen, K Syassen, and J S Tse for supplying us with preprints of their articles and for useful discussions of problems covered in the review. The work was financially supported by the President's Program 'Leading Scientific Schools', the Russian Academy of Sciences Presidium Program 'Thermal Physics and Mechanics of Extreme-Energy Effects', the Russian Foundation for Basic Research (RFBR) (Grants Nos 03-02-16322, 04-02-16061, and 05-02-17359), and NWO-RFBR (Grant No. 047.016.005). M V M would like to express her gratitude for the support from the Royal Society and for the hospitality of the staff of Queen's University Belfast, where part of this work was done.

References

- Ashcroft N W, Mermin N D Solid State Physics (New York: Holt, Rinehart and Winston, 1976) [Translated into Russian (Moscow: Mir, 1979)]
- Tonkov E Yu Fazovye Diagrammy Elementov pri Vysokom Davlenii (Phase Diagrams of Elements under High Pressure) (Moscow: Nauka, 1979)
- 3. Jayaraman A Rev. Mod. Phys. 55 65 (1983)
- 4. Holzapfel W B Rep. Prog. Phys. 59 29 (1996)
- 5. Wigner E, Huntington H B J. Chem. Phys. 3 764 (1935)
- Maksimov E G, Shilov Yu I Usp. Fiz. Nauk 169 1223 (1999) [Phys. Usp. 42 1121 (1999)]
- 7. Ashcroft N W Phys. Rev. Lett. 21 1748 (1968)
- 8. Maksimov E G, Savrasov D Yu Solid State Commun. 119 569 (2001)
- Harrison W A Pseudopotentials in the Theory of Metals (New York: W.A. Benjamin, 1966) [Translated into Russian (Moscow: Mir, 1968)]
- Heine V "The pseudopotential concept" (p. 1), Cohen M L, Heine V "The fitting of pseudopotentials to experimental data and their subsequent application" (p. 38), Heine V, Weaire D "Pseudopotential theory of cohesion and structure" (p. 250), in *Solid State Physics: Advances and Applications* Vol. 24 (Eds H Ehrenreich, F Seitz, D Turnbull) (New York: Academic Press, 1970) [Translated into Russian: *Teoriya Psevdopotentsiala* (Pseudopotential Theory) (Moscow: Mir, 1973)]
- 11. Brovman E G, Kagan Yu M, Holas A *Fiz. Tverd. Tela* **10** 1001 (1969)
- Brovman E G, Kagan Yu M Usp. Fiz. Nauk 112 369 (1974) [Sov. Phys. Usp. 17 125 (1974)]
- Brovman E G, Kagan Yu, Holas A Zh. Eksp. Teor. Fiz. 61 2429 (1971); 62 1492 (1972) [Sov. Phys. JETP 34 1300 (1972); 35 783 (1972)]; Kagan Yu, Pushkarev V V, Holas A Zh. Eksp. Teor. Fiz. 73 967 (1977) [Sov. Phys. JETP 46 511 (1977)]
- 14. Eremets M I *High Pressure Experimental Methods* (Oxford: Oxford Univ. Press, 1996)
- 15. Tse J S Z. Kristallogr. 220 521 (2005)
- Nabatov S S et al. Pis'ma Zh. Eksp. Teor. Fiz. 29 407 (1979) [JETP Lett. 29 369 (1979)]
- Syassen K "Simple metals at high pressure", in *High Pressure Phenomena, Varenna, Italy, July 3–13, 2001* (Proc. of the Intern. School of Physics 'Enrico Fermi', Course 147, Eds R J Hemley et al.) (Amsterdam: IOS Press, 2002)
- Kolobyanina T N Usp. Fiz. Nauk 172 1361 (2002) [Phys. Usp. 45 1203 (2002)]
- 19. Schwarz U Z. Kristallogr. 219 376 (2004)
- Winzenick M, Vijayakumar V, Holzapfel W B Phys. Rev. B 50 12381 (1994)

- 21. Ostanin S et al. Phys. Rev. Lett. 91 087002 (2003)
- 22. Takemura K et al. *Phys. Rev. B* **62** R10603 (2000)
- 23. Bridgman P W Proc. Natl. Acad. Sci. USA 76 55 (1948)
- 24. Sternheimer R Phys. Rev. 78 235 (1950)
- 25. Glötzel D, McMahan A K Phys. Rev. B 20 3210 (1979)
- 26. Schwarz U et al. Phys. Rev. Lett. 81 2711 (1998)
- 27. McMahon M I, Nelmes R J, Rekhi S Phys. Rev. Lett. 87 255502 (2001)
- Wells A F Structural Inorganic Chemistry 5th ed. (Oxford: Clarendon Press, 1984) [Translated into Russian (Moscow: Mir, 1988)]
- 29. Takemura K et al. Phys. Rev. B 61 14399 (2000)
- 30. Zurek E, Jepsen O, Andersen O K, cond-mat/0504374
- 31. Schwarz U et al. *Phys. Rev. Lett.* **83** 4085 (1999)
- McMahon M I, Rekhi S, Nelmes R J Phys. Rev. Lett. 87 055501 (2001)
- Degtyareva V F, Ponyatovskii E G, Rastorguev L N *Fiz. Tverd. Tela* 17 439 (1975) [*Sov. Phys. Solid State* 17 274 (1975)]; Degtyareva V F, Ponyatovskii E G *Fiz. Tverd. Tela* 17 2413 (1975) [*Sov. Phys. Solid State* 17 1593 (1975)]
- 34. Degtyareva V F Phys. Rev. B 62 9 (2000)
- Degtyareva V F, in *High-Pressure Crystallography* (NATO Sci. Ser., Ser. II, Vol. 140, Eds A Katrusiak, P McMillan) (Dordrecht: Kluwer Acad. Publ., 2004) p. 447
- Hume-Rothery W *Electrons, Atoms, Metals and Alloys* 3rd ed. (New York: Dover Publ., 1963)
- Paxton A T, Methfessel M, Pettifor D G Proc. R. Soc. London Ser. A 453 1493 (1997)
- 38. Ackland G J, Macleod I R New J. Phys. 6 138 (2004)
- 39. Asahi R et al. *Phys. Rev. B* **71** 165103 (2005)
- Hohenberg P, Kohn W Phys. Rev. 136 B864 (1964); Kohn W, Sham L J Phys. Rev. 140 A1133 (1965)
- 41. Kohn W Rev. Mod. Phys. 71 1253 (1999); Usp. Fiz. Nauk 172 336 (2002)
- Landau L D, Lifshitz E M Statisticheskaya Fizika (Statistical Physics) Pt. 1 (Moscow: Nauka, 1976) [Translated into English (Oxford: Pergamon Press, 1980)]
- 43. Maradudin A A et al. *Theory of Lattice Dynamics in the Harmonic Approximation* 2nd ed. (New York: Academic Press, 1971)
- 44. Quong A A, Liu A Y Phys. Rev. B 56 7767 (1997)
- 45. Liu A Y et al. Phys. Rev. B 59 4028 (1999)
- Ziman J M "The calculation of Bloch functions", in *Solid State Physics* Vol. 26 (Eds H Ehrenreich, F Seitz, D Turnbull) (New York: Academic Press, 1971) [Translated into Russian (Moscow: Mir, 1973)
- 47. Andersen O K Phys. Rev. B 12 3060 (1975)
- Savrasov S Yu, Savrasov D Yu Phys. Rev. B 46 12181 (1992); Maksimov E G, Savrasov D Yu, Savrasov S Yu Usp. Fiz. Nauk 167 353 (1997) [Phys. Usp. 40 337 (1997)]
- 49. Gregoryanz E et al. Phys. Rev. Lett. 90 175701 (2003)
- Fortov V E et al. Pis'ma Zh. Eksp. Teor. Fiz. 70 620 (1999) [JETP Lett. 70 628 (1999)]
- 51. Fortov V E et al. J. Phys.: Condens. Matter 14 10809 (2002)
- 52. Loubeyre P et al. *High Pressure Res.* **24** 25 (2004)
- 53. Neaton J B, Ashcroft N W Nature 400 141 (1999)
- 54. Wittig J Phys. Rev. Lett. 24 812 (1970)
- 55. Bastea M, Bastea S Phys. Rev. B 65 193104 (2002)
- 56. Hanfland M et al. *Nature* **408** 174 (2000)
- 57. Rousseau R et al. Chem. Phys. Chem. (2005) (in print)
- Lin T H, Dunn K J Phys. Rev. B 33 807 (1986); Shimizu K, Ishikawa H, Amaya K J. Phys.: Condens. Matter 14 10433 (2002)
- 59. Christensen N E, Novikov D L Phys. Rev. Lett. 86 1861 (2001)
- Blaha P, Schwarz K, Madsen G K H, Kvasnicka D, Luitz J, WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (Vienna: Karlheinz Schwarz, Techn. Universität Wien, Austria, 2001)
- 61. Stager R A, Drickamer H G Phys. Rev. 131 2524 (1963)
- 62. Altmann S L, Cracknell A P Proc. Phys. Soc. London 84 761 (1964)
- 63. Vasvari B, Heine V Philos. Mag. 15 731 (1967)
- 64. Mickish D J, Kunz A B, Pantelides S T Phys. Rev. B 10 1369 (1974)
- 65. Mott N F Philos. Mag. 6 287 (1961)
- Keldysh L V, Kopaev Yu V Fiz. Tverd. Tela 6 2791 (1964) [Sov. Phys. Solid State 6 2219 (1965)]
- 67. Jérome D, Rice T M, Kohn W Phys. Rev. 158 462 (1967)

- Halperin B I, Rice T M, in *Solid State Phys.* Vol. 21 (Eds H Ehrenreich, F Seitz, D Turnbull) (New York: Academic Press, 1968) p. 115
- Kopaev Yu V Tr. Fiz. Inst. Akad. Nauk SSSR 86 3 (1975) [Proc. Lebedev Phys. Inst. 86 1 (1977)]
- 70. McWhan D B, Rice T M, Schmidt P H Phys. Rev. 177 1063 (1969)
- 71. Dunn K J, Bundy F P Phys. Rev. B 24 1643 (1981)
- 72. Olijnyk H, Holzapfel W B Phys. Lett. A 100 191 (1984)
- Winzenick N, Holzapfel W B, in High Pressure Science & Technology: Proc. of the Joint XV AIRAPT & XXXIII EHPRG Intern. Conf., Warsaw, Poland, Sept. 11-15, 1995 (Ed. W A Trzeciakowski) (Singapore: World Scientific, 1996)
- 74. Skriver H L Phys. Rev. Lett. 49 1768 (1982)
- 75. Errandonea D, Boehler R, Ross M Phys. Rev. B 65 012108 (2002)
- 76. Animalu A O E *Phys. Rev.* **161** 445 (1967)
- 77. Wentzcovitch R M, Krakauer H Phys. Rev. B 42 4563 (1990)
- 78. Ahuja R et al. Phys. Rev. Lett. 75 3473 (1995)
- 79. Bakanova A A, Dudoladov I P Pis'ma Zh. Eksp. Teor. Fiz. 5 322 (1967) [JETP Lett. 5 265 (1967)]
- Al'tshuler L V, Bakanova A A, Dudoladov I P Zh. Eksp. Teor. Fiz. 53 1967 (1967) [Sov. Phys. JETP 26 1115 (1968)]
- Marsh S P (Ed.) LASL Shock Hugoniot Data (Berkeley: Univ. of California Press, 1980)
- Fortov V E et al. Pis'ma Zh. Eksp. Teor. Fiz. 79 425 (2004) [JETP Lett. 79 346 (2004)]
- Molodets A M Fiz. Goren. Vzryva 34 (4) 94 (1998) [Combust. Explosion Shock Waves 34 453 (1998)]
- 84. Molodets A M, Molodets M A, Nabatov S S Khim. Fiz. 18 67 (1999)
- Regel' A R, Glazov V M Fizicheskie Svoistva Elektronnykh Rasplavov (Physical Properties of Electron Melts) (Moscow: Nauka, 1980)
- 86. Mooji J H Phys. Status Solidi B 17 521 (1973)
- 87. Car R, Parrinello M Phys. Rev. Lett. 55 2471 (1985)
- Katsnel'son M I, Trefilov A V Dinamika i Termodinamika Kristallicheskoi Reshetki (The Dynamics and Thermodynamics of the Crystal Lattice) (Moscow: IzdAT, 2002)
- Jayaraman A, Klement W (Jr), Kennedy G C Phys. Rev. 132 1620 (1963)