EQUATION OF STATE OF STATIC AND DYNAMIC COMPRESSION OF BARIUM CHALCOGENIDES

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The alkali-halide compounds and 16 crystals of chalcogenides of alkaline-earth metals (oxides, sulfides, selenides, tellurides) form a large group of ionic crystals which under normal conditions have a structure of the NaCl type. Analysis of the existing experimental data on the compression of ionic crystals shows that most of them undergo under pressure a first-order phase transition from a structure of the NaCl type (the B1 phase) to a structure of the CsCl type (B2 phase). Many theoretical works on the equations of state and phase transitions of ionic compounds are devoted to alkali-halide crystals. Similar theoretical calculations for chalcogenides have been performed only for oxides [1-3]. It is undoubtedly of interest to further study theoretically the equations of state of the static and dynamic compression of chalcogenides of alkaline-earth metals. This would enable establishing the general laws governing the behavior of chaocogenides and analyzing the specific features of their interparticle interactions at high pressure. In this paper the pressures of phase transitions of the type B1-B2, the equations of state of hydrostatic compression, and the shock adiabats of the barium chalcogenides BaS, BaSe, and BaTe in the B1 and B2 phases are calculated based on the binding energy function proposed in [1].

The shock adiabat $P_H(V)$ is calculated from the formula [4]

$$P_{\text{H}}(V)=\frac{P_{\text{x}}(V)+\gamma(V)\,[E_0-U(V)]/V}{1+\gamma(V)\,[V-V_0]/2V}, \qquad (1)$$

where U(V), $P_X(V)$ are the energy and pressure on the zero isotherm; $\gamma(V)$ is the Grüneisen constant; V_0, E_0 are the volume and internal energy of the free crystal. To calculate the pressures of phase transitions of barium chalcogenides from the NaCl structure to the CsCl structure it is necessary to determine the thermodynamic Gibbs potential Φ of both phases as a function of the pressure. At absolute zero temperature, and neglecting the energy of zero-point vibrations, the potential is given by

$$\Phi = U(V) + P_{\text{x}}(V)V. \qquad (2)$$

The dependence of the volume of the crystal on the pressure along the zero isotherm is determined by the equation

$$P_{\text{x}}(V) = -dU(V)/dV, \qquad (3)$$

which, together with (2), enables finding the pressure P_n and the jump in the volume $\Delta V = (V_1 - V_2)/V_0$ at the point of the phase transition (V_1 and V_2 are the volumes of the crystal at P_n in the phases B1 and B2, respectively).

According to [1], the binding energy function of the crystal, consisting of particles of different types and taking into account the pair and triple interactions, has the form

$$U=\frac{1}{2}\sum_{\substack{ll'\\kk'}}{}' \varphi_{kk'}\left(r^{ll'kk'}\right)+\frac{1}{6}\sum_{\substack{ll'l''\\kk'k''}}{}' \Psi_{kk'k''}\left(r^{ll'kk'}, r^{l''lk''k}, r^{l''l'k''k'}\right). \qquad (4)$$

Here $r^{\ell\ell'kk'}$ is the distance between particles of the type k and k' located in the unit cells ℓ and ℓ'; ϕ, Ψ are the potentials of the pair and three-particle interactions,

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respectively. The pair interactions are approximated by the Born–Mayer potentials

$$\varphi(r)=\frac{e_k e_{k'}}{r}+A_{kk'}\exp\left(-\frac{r}{\rho}\right)-\frac{c_{kk'}}{r^6}-\frac{d_{kk'}}{r^8},$$

where e_k, $e_{k'}$ are the charges of ions of the type k and k' (in what follows k = 1 and k = 2 denote the positive and negative ions, respectively); $c_{kk'}$, $d_{kk'}$ are the dipole–dipole and dipole–quadrupole interactions constants, whose values for barium chalcogenides are taken from [5]; and $A_{kk'}$, ρ are parameters. The three-body interactions were approximated by potentials of the form [1]

$$\Psi_{kk'k''}=B_{kk'k''}\exp\left(-\frac{r^{ll'kk'}+r^{l''lk''k}+r^{l''l'k''k'}}{3\rho}\right)$$

where $B_{kk'k''}$ are parameters. When summing the potentials ϕ over the crystal lattice, because of the sharp drop in the repulsive energy accompanying an increase in the distance between the ions, the interactions of nearest neighbors were included in the corresponding terms in (4). For the same reason, when summing the three-body interactions the triplets, forming a configuration consisting of an equilateral right triangle for the phase B1 and an equilateral triangle for the phase B2, were taken into account. The two sides of the triangles are equal to the shortest distance between the ions in the corresponding phase. Taking this into account, the three unknown parameters of the model of the binding forces A_{12}, ρ, $(B_{112}+B_{221})/2$ were determined by using the experimental characteristics of the free barium chalcogenides: the binding energy, the lattice constants, and the modulus of hydrostatic compression [6, 7]. Table 1 shows the parameters of the model of the binding forces, and also the transition pressure and the volume jump, calculated at absolute zero temperature. The computed equations of state of hydrostatic compression as a function of the relative compression V/V_0 together with the available experimental data (○ [6], • [8]; 1) BaTe, 2) BaSe, 3) BaS) are shown in Fig. 1. As is evident from Table 1 and Fig. 1, the proposed model of the binding forces enables describing, in good agreement with experiment, like in the case of oxides [1], the behavior of BaS and BaSe at low and high pressures. In barium telluride our calculation predicts a phase transition of the type B1-B2 at a pressure of P_n = 5.2 GPa; the volume jumps equals 12.2%.

To calculate the shock adiabats, the Grüneisen constants $\gamma(V)$ were calculated using the formula of Zubarev and Vashchenko [9]. Figure 2 shows the pressure dependence of the Grüneisen constants (BaS (1), BaTe (2), and BaSe (3)). For all crystals studied the values of γ decrease as the pressure increases in both phases, with the exception of the phase-transition point, where they increase in a jump-like manner. We do not know of any experimental data on $\gamma(V)$ for barium chalcogenides. We point out that an analogous behavior of γ under pressure was established experimentally for a number of alkali-halide crystals [10]. Figure 3 shows the obtained shock adiabats 1) BaS, 2) BaSe, 3) BaTe in the B1 and B2 phases. There are no experimental data in the literature on the shock compression of barium chalcogenides. The good agreement between experiment and the computed values of $P_X(V)$ and also the results obtained previously for oxides [1] suggests that the shock adiabats obtained in this work correctly describe the actual behavior of barium chalcogenides under shock compression.

The shock adiabats of the crystals studied enabled calculating the ratio of the velocity of the shock wave D to the mass velocity of the material u. The relations

TABLE 1

Crystal	10^{-16} J		$10^{11}\rho$, M	P_n, GPa		ΔV,%	
	A_{12}	$-(B_{112}+B_{221})/2$		calcution	experiment	calcution	experiment
BaS	5,158	0,5208	3,895	6,4	6,5	13,3	13,7
BaSe	4,723	0,2032	4,074	5,5	6,0	13,5	13,9
BaTe	4,545	0,0750	4,288	5,2	—	12,2	—

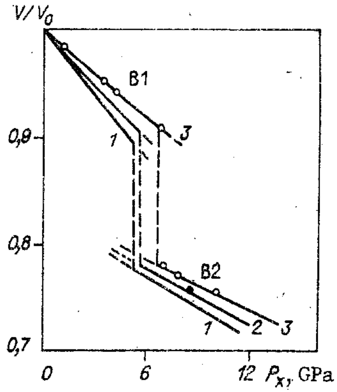

Fig. 1

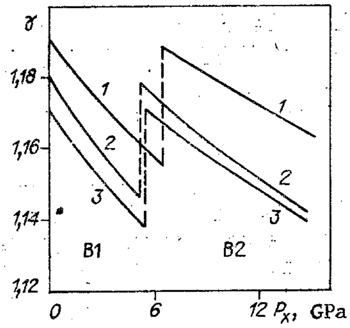

Fig. 2

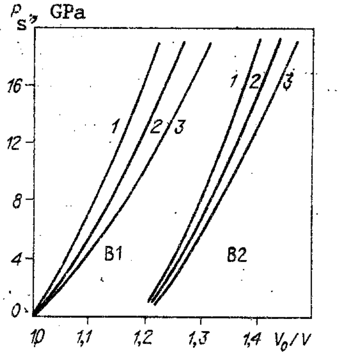

Fig. 3

TABLE 2

Crystal	B1 phase			B2 phase		
	a, km/sec	*b*	(km/sec)$^{-1}$	*a*, km/sec	*b*	*c*, (km/sec)$^{-1}$
BaS	3,789	1,005	0,017	1,178	2,882	—0,381
BaSe	3,050	1,291	0,006	1;362	2,211	—0,171
BaTe	2,709	1,300	0,000	1,004	2,755	—0,576

$$D(v) = v_0\sqrt{P_H(v)/(v_0 - v)},$$
$$u(v) = \sqrt{P_H(v)(v_0 - v)},$$

which follow from the conservation laws and in which $P_H(v)$ and v (the specific volume) are taken from our calculations, were used in the calculation. The relationship between D and u was interpolated by a function of the form $D = a + bu + cu^2$.

Table 2 presents the parameters a, b, and c, found from the computed velocities D and u by the method of least squares for the phases B1 and B2. As is evident from Table 2, the relationship between D and u for barium chalcogenides, unlike the oxides [1], can be interpolated in a wide range of velocities by a function of the form D = a + bu only for the phase B1.

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CRITICAL LOADING PARAMETERS FOR THE DEVELOPMENT OF ADIABATIC SHEAR IN TITANIUM

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An increase in deformation normally leads to metal strengthening, which is connected with a reduction in the travel of mobile dislocations and an increase in defect density with a fixed amount of strain. However, with explosive and high-velocity impact experiments under different loading schemes (always with the presence of a free surface) there is a change in deformation mechanism from uniformly distributed shear to clearly nonuniform shear with formation of "adiabatic shear bands." The intensity of plastic flow in the bands is much greater than in the basic material, which leads to additional warm-up of the deformed region, its weakening, and as a consequence to its more active deformation in the band. The governing role of adiabatic shear in processes of high-velocity punching, formation of spalling, high-speed cutting, and stamping, was demonstrated in [1-4].

In order to study the nature of adiabatic shear and a credible solution of applied problems it is very important to consider the question of critical parameters for high-velocity loading leading to a change in deformation mechanism. In the known works on adiabatic shear there is no systematic study of this type, which is connected with the complexity of the experiments. For this purpose there are a number of procedures: radial disintegration of a tube under the action of explosive loading from the direction of the internal surface [2] and shock loading in shear [4]. In the present work a simple procedure is suggested making it possible to change the loading parameters over wide ranges.

Shown in Fig. 1 is the scheme for carrying out the experiment. The plate of test material is thrown by a smooth-bore gun or by means of an explosive charge (at velocities greater than 1100 m/sec) at a massive substrate. The angle of impact prescribes the amount of shear deformation to $\tan\gamma$. With prescribed deformation time the process may be controlled by changing the flight velocity of the thrown plate. To a first approximation the impact velocity v is proportional to the shear deformation rate. In view of the importance of this question, a series of special experiments was carried out for measuring by means of a pulsed x-ray emitter the dimensions of the transition zone with different impact velocities. In order to avoid welding by explosion, in some of the experiments a thin fluoroplastic or polyethylene film was placed on the impact surface, and no marked effect of the film on deformation within the volume of the thrown plate was noted. Impact velocity and angle were controlled by means of the standard procedure of charged needles.

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