

*INVESTIGATION OF THE COMPRESSIBILITY OF FIVE IONIC COMPOUNDS AT PRESSURES UP TO 5 Mbar*

S. B. KORMER, M. V. SINITSYN, A. I. FUNTIKOV, V. D. URLIN, and A. V. BLINOV

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The dynamic compression of five ionic crystals (LiF, NaCl, KCl, KBr and CsBr) of normal and reduced initial density was investigated. The highest pressure attained was 5 Mbar and the maximum compression ratio 3.4. The experimental data for some crystals could be described by an equation of state which allowed for the temperature dependence of the specific heat and for the thermal excitation of electrons. Data were obtained on the anomalous behavior of NaCl, KCl, KBr, and LiF under shock compression. For the first three crystals, density jumps were detected in the liquid phase. It is suggested that this was due to a change in the coordination number occurring during a time comparable with the time for the propagation of a shock wave along a sample.

## INTRODUCTION

UNTIL recently, the only experimental data on the behavior of ionic crystals at high pressures were those obtained by static methods. Moreover, even in Bridgman's work<sup>[1,2]</sup>, the maximum pressures achieved did not exceed 100 kbar ( $\approx 100\,000$  atm).

The development of dynamic methods<sup>[3,4]</sup> made it possible to extend considerably the range of investigated pressures, but most of the early work was concerned with metals. Ionic compounds have attracted the attention of investigators<sup>[5,6]</sup> because of the possibilities of interpreting the experimental data by means of well-developed theoretical models, and of measuring not only the kinematic parameters of shock waves, but also temperature<sup>[7]</sup> (owing to the transparency of the majority of ionic crystals), which is a very important thermodynamic parameter representing the state of the substance.

The present paper reports the results of investigations of the dynamic compression of five ionic crystals—LiF, NaCl, KCl, KBr, and CsBr—of normal ( $\rho_0$ ) and reduced ( $\rho_{00}$ ) initial density over a wide range of pressures, densities, and temperatures. LiF had the widest energy gap and the highest lattice specific heat, and CsBr had the lowest values of these two parameters. By studying samples of various degrees of porosity  $m = \rho_0/\rho_{00}$ , it was possible to realize high-temperature states ( $\approx 5-6$  eV) at relatively low compressions. This enabled the authors to obtain information on the thermodynamic properties of ionic compounds basically under conditions of the

liquid state, and to estimate the role of thermally excited electrons. The maximum pressures attained were 5 Mbar ( $\approx 5 \times 10^6$  atm). The highest ever compression ratios for solids  $\sigma = \rho/\rho_0 = 3.4$  ( $\rho_0$  and  $\rho$  are the normal and instantaneous densities) were recorded at the maximum pressures.

The results obtained for LiF, NaCl, and CsBr could be described by an equation of state which allowed for the change in the lattice specific heat at high pressures, in the same way as has been done for metals in<sup>[8]</sup>, as well as for the contribution of the thermal excitation of electrons, accompanied by transitions to the conduction band. The latter was most important for CsBr crystals, whose forbidden band width was  $w = 6$  eV, and least important for LiF, for which  $w = 11.5$  eV.

The dynamic adiabats of NaCl, KCl, KBr, and LiF exhibited density jumps of about 4–9%. This jump was clearest in the adiabat of dense NaCl ( $\Delta\rho/\rho_0 = 9\%$ ). In the first three crystals, anomalies appeared in the liquid phase region. To explain these, it was assumed that the liquid phase region of these crystals at  $\rho > \rho_0$  was represented by an effective coordination number larger

Table I

U, km/sec	D, km/sec	U, km/sec	D, km/sec	U, km/sec	D, km/sec
0.5	5.95	4.0	10.70	7.5	15.08
1.0	6.70	4.5	11.35	8.0	15.68
1.5	7.40	5.0	11.97	8.5	16.29
2.0	8.07	5.5	12.60	9.0	16.91
2.5	8.75	6.0	13.23	9.5	17.52
3.0	9.42	6.5	13.85	10.0	18.10
3.5	10.07	7.0	14.46	10.5	18.70

than the number for the initial crystal state and propagation of a shock wave across the sample.  
 that the time for the establishment of the new The phase transition of the first kind in the shock-  
 coordination was comparable with the time for the wave front was considered in the light of Zel'do-

Table II

Substance	<i>m</i>	D, km/sec	U, km/sec	P, Mbar	$\sigma$	Screen material	U in screen, km/sec		
1	2	3	4	5	6	7	8		
LiF	1	8.94±0.06	2.87	0.68	1.47	Al	2.82		
		11.40±0.18	4.84	1.46	1.74	Fe	3.60		
		11.75±0.24	5.17	1.61	1.79	»	3.85		
		13.10±0.25	6.11	2.12	1.87	Al	6.03		
		18.30±0.26	10.01	4.85	2.21	»	9.95		
		11.70±0.25	6.19	1.239	1.37	Fe	4.13		
	1,55	4.52±0.02	2.40	0.138	1.025	Al	1.60		
	2,08	11.12±0.25	6.59	0.935	1.18	Fe	4.13		
3.00	10.57±0.23	7.03	0.655	0.994	»	4.13			
4.68	10.21±0.21	7.44	0.430	0.789	»	4.13			
NaCl	1	6.27±0.03	2.04	0.276	1.48	Al	1.72		
		10.39±0.17	5.19	1.17	2.00	Fe	3.60		
		10.75±0.24	5.55	1.29	2.07	»	3.85		
		11.61±0.14	5.95	1.49	2.05	»	4.16		
		12.14±0.17	6.52	1.71	2.16	»	4.56		
		11.84±0.16	6.80	1.74	2.35	Al	6.03		
		12.96±0.21	7.83	2.20	2.53	Fe	5.44		
		16.84±0.26	11.05	4.03	2.91	Al	9.95		
	1,514	4.95±0.03	2.29	0.162	1.228	Al	1.60		
		7.27±0.08	3.81	0.397	1.388	Fe	2.37		
		8.52±0.08	4.66	0.568	1.459	Al	3.54		
		9.06±0.19	4.97	0.645	1.465	Fe	3.15		
		9.93±0.11	5.66	0.804	1.536	»	3.60		
		10.19±0.17	6.00	0.874	1.600	Al	4.65		
		10.47±0.12	6.11	0.915	1.586	»	4.76		
		2,185	4.45±0.03	2.53	0.112	1.061	Al	1.60	
	6.68±0.05		4.06	0.268	1.167	Fe	2.37		
	8.33±0.09		5.12	0.424	1.188	Al	3.54		
	8.54±0.10		5.30	0.449	1.206	Fe	3.15		
	9.54±0.12		6.02	0.570	1.239	»	3.60		
	10.08±0.16		6.60	0.659	1.324	Al	4.65		
	10.49±0.09		6.70	0.695	1.265	»	4.76		
	KCl		1	5.62±0.05	2.17	0.24	1.63	Al	1.72
		9.76±0.12		5.35	1.04	2.21	Fe	3.60	
9.96±0.17		5.74		1.14	2.36	»	3.85		
10.67±0.13		6.16		1.31	2.37	»	4.16		
10.93±0.12		6.10		1.33	2.26	»	4.13		
11.43±0.15		6.71		1.53	2.42	»	4.56		
11.29±0.13		7.10		1.60	2.69	Al	6.03		
12.63±0.19		8.02		2.02	2.73	Fe	5.44		
1,41		16.69±0.14	11.38	3.79	3.14	Al	9.95		
		4.89±0.02	2.30	0.158	1.340	Al	1.60		
		10.34±0.20	6.56	0.958	1.940	Fe	4.13		
		2,51	4.23±0.03	2.66	0.089	1.072	Al	1.60	
			9.95±0.14	7.19	0.566	1.439	Fe	4.13	
			KBr	4.95±0.05	2.03	0.276	1.70	Al	1.72
				8.93±0.12	5.09	1.25	2.33	Fe	3.60
		9.65±0.10		5.83	1.55	2.53	»	4.13	
10.43±0.24	6.39	1.83		2.58	»	4.56			
10.33±0.18	6.57	1.87		2.75	Al	6.03			
12.92±0.17	8.80	3.13		3.12	Fe	6.33			
15.01±0.20	10.60	4.38		3.40	Al	9.95			
CsBr	1	3.17±0.01		0.75	0.11	1.31	Al	0.69	
		4.52±0.03	1.73	0.347	1.62	»	1.70		
		5.92±0.04	2.75	0.72	1.87	»	2.82		
		8.17±0.11	4.60	1.67	2.29	Fe	3.60		
		9.33±0.16	5.69	2.36	2.56	Al	6.03		
		13.19±0.16	9.29	5.45	3.38	»	9.95		
	1,51	3.90±0.02	1.99	0.228	1.352	Al	1.60		
		8.79±0.14	5.86	1.519	1.985	Fe	4.13		
		2,20	3.71±0.02	2.25	0.169	1.153	Al	1.60	
			8.77±0.11	6.33	1.122	1.631	Fe	4.13	

vich's theory<sup>[9]</sup> of the propagation of shock waves in the presence of relaxation effects. The work was carried out between 1957 and 1962.

## 1. EXPERIMENTAL RESULTS

The shock wave parameters in the test substances were obtained by the reflection method.<sup>[3]</sup> The wave velocity  $D$  was found experimentally. The time intervals were measured by an electrical contact method<sup>[3]</sup> using rapid-response oscilloscopes type OK-21. The mass velocity  $U$  and the pressure  $P$  were found by means of a  $P-U$  diagram from known or experimentally determined parameters of a shock wave in a screen and known equations of state for iron<sup>[10,11]</sup> and aluminum, which were used as the screen materials.

Table I lists the parameters of the dynamic adiabat of aluminum ( $\rho_0 = 2.71 \text{ g/cm}^3$ ) which were assumed in the analysis of the experimental data. Additional measurements slightly refined these parameters compared with earlier work.<sup>[10,8]</sup>

The use of screens made of various materials and the use of a single explosive substance allowed one in addition to vary the pressure of a shock wave in the test substance. Samples of normal initial density were prepared directly from single crystals, and porous ones were made by pressing a fine powder. The dimensional requirements and the method of preparation of the samples were analogous to those described in<sup>[8]</sup>.

The value of the shock-wave velocity was de-

termined from a series of 5–8 tests, in each of which the time was recorded 3–6 times. From 15–50 measurements, we eliminated those values whose probability—found from the normal distribution—did not exceed  $1/2n$ , where  $n$  is the total number of measurements (the Chauvenet criterion<sup>[12]</sup>). In practice, the number of measurements rejected by the application of this criterion did not exceed 2% of the total. A check showed that the use of the criterion  $1/n$ , as employed in<sup>[2]</sup>, increased the accuracy of the results obtained but had practically no effect on the average value of the measured time.

The experimental results together with the parameters of the shock waves in the screens are listed in Table II and plotted in  $D-U$  coordinates in Fig. 1. Each experimental point in this figure gives the rms scatter. The figure also includes the data on the shock compression of NaCl, KCl, KBr, and LiF, obtained by Al'tshuler et al.<sup>[5,6]</sup>

It is evident from Fig. 1 that the experimental data for the CsBr crystal are well described by a single relationship between  $D$  and  $U$ . The  $D(U)$  plot has the form of a continuous curve concave toward the abscissa. This form of the  $D(U)$  curve is obviously governed by the influence of the thermal excitation of electrons. We shall show below that we can allow for the electron components, which are most important in the case of CsBr, and thereby account for this influence on the dynamic adiabat.

The experimental data for LiF, KCl, and KBr crystals at  $D \gtrsim 8 \text{ km/sec}$  can be equally well de-

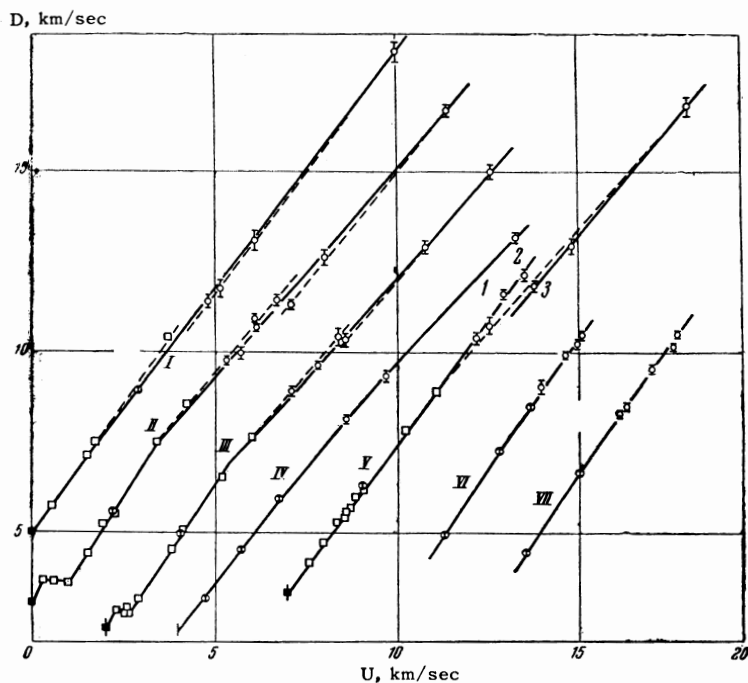


FIG. 1.  $D-U$  diagram: I) LiF; II) KCl; III) KBr ( $U + 2 \text{ km/sec}$ ); IV) CsBr ( $U + 4 \text{ km/sec}$ ); V) NaCl,  $m = 1$  ( $U + 7 \text{ km/sec}$ ); VI) NaCl,  $m = 1.514$  ( $U + 9 \text{ km/sec}$ ); VII) NaCl,  $m = 2.185$  ( $U + 11 \text{ km/sec}$ ). Experimental data:  $\circ$  — present work;  $\square$  — from<sup>[5,6]</sup>;  $\blacksquare$  — initial value  $U = 0$ .

scribed either by a single curve or by two straight lines with a discontinuity (Fig. 1). The latter means that in the investigated region of pressures there are phase transitions of the first kind.

The experimental data for NaCl in the  $D-U$  coordinates, with  $m = 1$ , are grouped closely about two straight lines which do not intersect in the investigated region. If these data are approximated by a single straight line in the region  $D > 8$  km/sec, then at least two experimental points (1 and 2 in Fig. 1) are separated from the line by an amount twice or three times greater than the rms scatter.

It is noticeable that the experimental data for KCl and KBr at  $D < 10$  km/sec can be described by a  $D-U$  plot with a kink at mass velocities of  $U \approx 3.5$  km/sec. Such behavior of the  $D-U$  plot can be associated, as shown by analysis, with the melting of the substance in the shock wave front. However, a detailed consideration of this problem is outside the scope of the present communication.

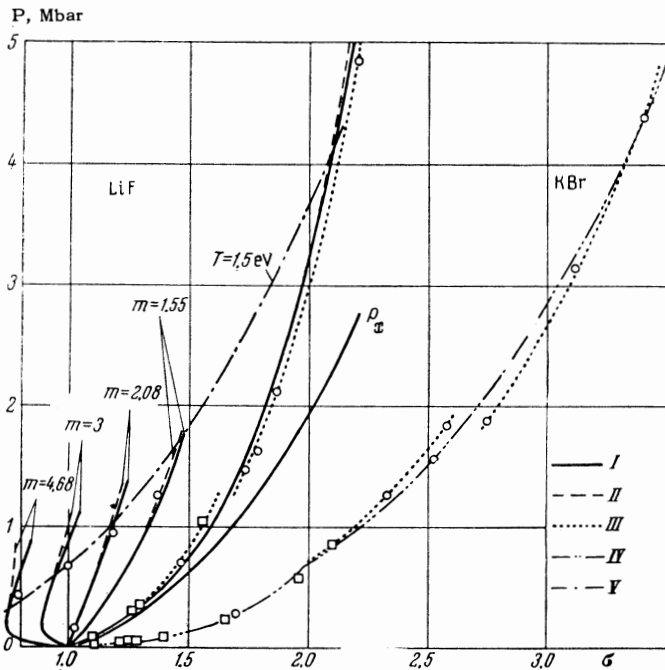


FIG. 2. Shock adiabats of LiF and KBr. Experimental data:  $\circ$  - present work;  $\square$  - from [6]. Calculated curves: I) with allowance for electrons; II) without allowance for electrons; III), IV) from the  $D-U$  relationship in Fig. 1; V) isotherm.

The highest compressibility (Figs. 2-4) was exhibited by the KBr crystal, the lowest by LiF. At the maximum pressure of  $\approx 4.5$  Mbar, the KBr crystal was compressed by a factor of 3.4. The kinks in the dynamic adiabats of KCl and KBr in  $P-\sigma$  coordinates represent the points of intersection of two linear regions of the  $D-U$  plots.

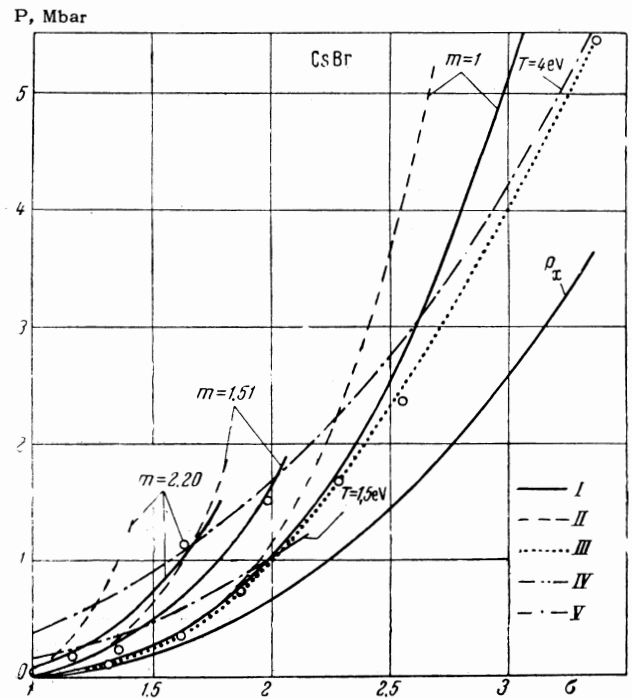


FIG. 3. Shock adiabats of CsBr. The notation is the same as in Fig. 2.

For KCl and KBr, the experimental data, as for  $D-U$  coordinates, are given in two alternative ways. For LiF, only one variant with a density jump is shown in order not to complicate the figure. As mentioned earlier, the density jump is clearest in NaCl with  $m = 1$ , where it reaches  $\approx 9\%$ . A possible explanation of the density jumps under shock compression will be given below. The figures mentioned above also include the experimental data for LiF, NaCl, and CsBr of various degrees of porosity. They will be used to find the equation of state for these crystals.

## 2. EQUATION OF STATE AND ITS PARAMETERS FOR LiF, CsBr, and NaCl

The LiF and CsBr crystals occupy the extreme ends of the alkali-halide series of compounds. The former has the maximum lattice specific heat and maximum forbidden band width between the filled band and the conduction band. For CsBr, these parameters are lowest. NaCl occupies an intermediate position (cf. Table III). Therefore a study of these three compounds gives us a sufficiently complete representation of the equation of state for ionic crystals.

Preliminary estimates show that use of the Mie-Grüneisen equation of state for ionic crystals is invalid at temperatures above several thousands of degrees. First, it is necessary to allow for the change in the lattice specific heat, in the same way

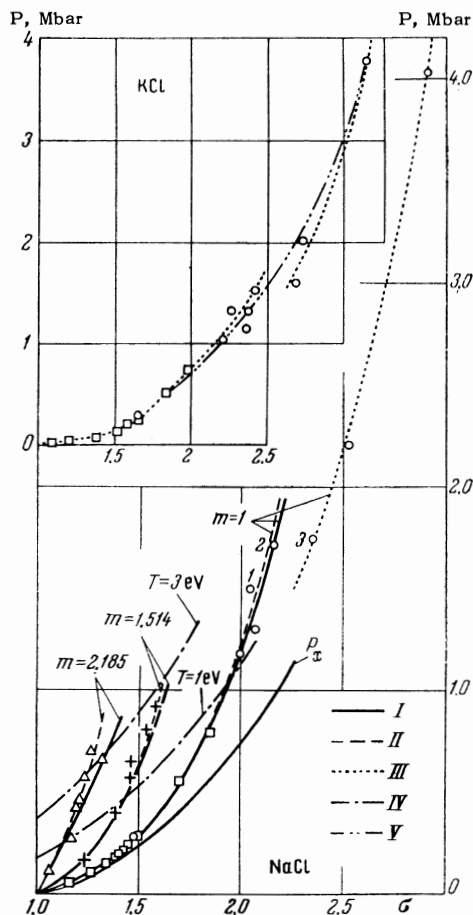


FIG. 4. Shock adiabats of NaCl and KCl. The notation is the same as in Fig. 2. + denotes  $m = 1.514$ ;  $\Delta$  denotes  $m = 2.185$ .

as has been done for metals.<sup>[8]</sup> Second, beginning with temperatures of the order of  $10^4$  °K, the contribution of the thermal excitation of electrons, associated with electron transitions to the conduction band, becomes important. In the first approximation, this electron contribution can be allowed for using the free-electron theory (cf., for example, <sup>[13]</sup>). With these modifications, the total free energy of an ionic crystal may be written in the form

$$F = E_x(\rho) + 6RT \ln \left[ \frac{\theta(\rho)}{T} (1+z)^{1/2} - \frac{4RT}{\rho} \left( \frac{2\pi m^* kT}{h^2} \right)^{3/2} e^{-w/2kT} \right], \quad (1)$$

$$\theta(\rho) = \text{const} \cdot \rho^{1/3} \left( \frac{dP_x}{d\rho} - n \frac{2P_x}{3\rho} \right)^{1/2}, \quad (2)$$

Table III

	LiF	NaCl	KCl	KBr	CsBr
$\rho_0$ , g/cm <sup>3</sup>	2.65	2.165	1.992	2.752	4.45
$6R$ , J.g <sup>-1</sup> .deg <sup>-1</sup>	1.923	0.8535	0.6693	0.4194	0.2355
$w_0$ , eV	11.5	7.7	7.5	6.6	6

$$z = lRT \left[ \frac{dP_x}{d\rho} - n \frac{2P_x}{3\rho} \right]^{-1}, \quad (3)$$

$$P_x = \rho^2 \frac{dE_x}{d\rho} = \sum a_i \delta^{i/3+1}, \quad \delta = \frac{\rho}{\rho_K}. \quad (4)$$

Here,  $E_x$  is the elastic compression energy,  $k$  and  $h$  are, respectively, Boltzmann's and Planck's constants,  $m^*(\rho) = (m_e^* m_h^*)^{1/2}$  is the geometrical mean of the effective electron and hole masses,  $w(\rho)$  is the width of the energy gap between the filled band and the conduction band,  $R$  is the gas constant,  $l$  is an empirical constant,  $\rho_K$  is the density at  $T = 0^\circ\text{K}$ . In deducing Eqs. (2) and (3), we used Dugdale and Macdonald's theory of small oscillations for  $n = 1$  in the case of NaCl and CsBr, and the theory of Slater and Landau with  $n = 0$  for LiF.<sup>[6] 1)</sup>

The values of  $w$  and  $m^*$  should, in principle, vary with density because both these quantities are associated with the widths of the energy bands. The determination of the functions  $w(\rho)$  and  $m^*(\rho)$  involves complex quantum-mechanical calculations. In the present work, we have assumed for our rough calculations that

$$w = w_0 \delta^\Gamma \quad (5)$$

$$m^* = m_0 \delta^{2/3+\Gamma}, \quad (6)$$

where  $m_0$  is the free-electron mass,  $w_0$  is the forbidden band width under normal conditions,  $\Gamma$  is an empirical constant found from the condition of best description of the dynamic adiabats at high temperatures.

The equation of state in the form (1) describes the dynamic adiabats of LiF, NaCl, and CsBr crystals. The need to allow for the transition of a substance from the effectively liquid to effectively gaseous state by the introduction of the parameter  $l$ <sup>[8]</sup> follows most clearly from the analysis of the experimental data on the shock compression of porous LiF. Here, the role of electrons is small because of the wide forbidden band and, if we use the equation of state in the Mie-Grüneisen form, i.e., if we ignore the electron contribution and assume that in Eq. (1)  $l = 0$ , then the calculated adiabat of porous LiF with  $m = 2.08$  follows the ordinate axis, in disagreement with experiment (Fig. 2).

For CsBr, the experimental data lie in such a region of densities and temperatures that we must allow for the role of thermally excited electrons.

The empirical constants  $l$  and  $\Gamma$  were selected

<sup>1)</sup>If the Dugdale-Macdonald theory is used to describe LiF it is impossible to obtain agreement with the initial value of the Grüneisen coefficient.

Table IV

	$l$	$\Gamma$	$\rho_K, \text{ g/cm}^3$	$a_1, \text{ Mbar}$	$a_2, \text{ Mbar}$	$a_3, \text{ Mbar}$	$a_4, \text{ Mbar}$	$a_5, \text{ Mbar}$
LiF	12	0	2.694	-0.428	0.438	-1.69	1.68	0
NaCl	9	0	2.218	-0.071	0.052	-0.693	0.712	0
CsBr	12	-0.5	4.583	-0.26	1.921	-4.392	3.431	-0.7

in the present work so as to fit as well as possible all the experimental data on shock compression. The values of these constants are listed in Table IV together with the coefficients of the shock compression curve (4), which were selected so that the following known properties were described correctly under normal conditions: the volume compressibility, the Grüneisen constant, the binding energy, and the dynamic adiabat of the dense substance. The form of the curve given in Eq. (4) was selected for reasons of mathematical convenience. The elastic compression curve found in this way for NaCl agreed with the curve in [6], described by the Born-Mayer potential, but for LiF it passed somewhat below the curve given in [6]. This was because in our case the  $P_x(\rho)$  dependence was found from the "softer" dynamic adiabat which described on the average all the experimental data (the continuous curve in Fig. 1). The calculated shock adiabats are shown in Figs. 2-4 by continuous curves. The dashed curves represent the adiabats calculated without allowance for electrons.

It is evident that in the investigated shock-compression region the electron contribution is relatively slight for LiF and NaCl and important for CsBr. For NaCl, we selected  $m_0^* = m_0/2$  in order to describe best the high-temperature data. The value of  $l$  was found from the low-temperature parts of the adiabats for the porous substance.<sup>2)</sup>

LiF and NaCl crystals could be described by assuming  $\Gamma = 0$ . Within the accepted theory of collective electrons, this indicates that the forbidden band width changes little with density. The experimental data for CsBr are not reproduced satisfactorily if it is assumed that  $\Gamma = 0$ ; it is necessary to take  $\Gamma = -1/2$ . This indicates, within the framework of the same theory, a considerable reduction of the energy gap with increase in density, which enhances even further the role of electrons in the equation of state of this compound. This explains the continuous reduction of the slope

of the  $D(U)$  curve of CsBr (Fig. 1). The  $D-U$  relationships for porous NaCl (cf. Fig. 1) are qualitatively similar since, in contrast to the dynamic adiabat of the dense NaCl, the role of the electron components is marked.

It should be noted that we cannot expect complete agreement between the calculated and experimental adiabats because of the approximate nature of the assumptions made in the equation of state, as clearly indicated by the case of CsBr with  $m = 1$  (Fig. 3). This applies first to the electron components because of the indeterminacy in the dependence of the forbidden band width, as well as of the effective electron and hole masses, on density and temperature. In this respect, the calculated data for LiF and NaCl<sup>3)</sup>, in which the role of electrons is less, are more reliable. The equations of state discussed here do not allow for the possible melting of crystals under shock compression.

### 3. ANOMALOUS BEHAVIOR OF NaCl AND OTHER CRYSTALS UNDER SHOCK COMPRESSION

In connection with one of the possible explanations of the anomalous behavior of NaCl, we shall consider the propagation of a shock wave in a substance which undergoes a phase transition accompanied by a density increase. A similar problem was considered by Zel'dovich<sup>[9]</sup> for the propagation of shock waves in a gas with a delayed excitation of the internal degrees of freedom. The same problem in the case of polymorphic transitions is partly dealt with in the work of Duff and Minshall.<sup>[14]</sup>

Assume that a shock wave enters a sample of the investigated substance from a screen, which is in contact with the sample. Initially, we have an overstressed state of the first phase—the point 1 in the  $P-(\rho_0/\rho)$  diagram of Fig. 5. The shock wave velocity corresponding to this state is given by the slope of the straight line 0-1 in Fig. 5.

<sup>2)</sup>The adiabats for NaCl with  $m = 1.51$  and  $m = 2.18$ , calculated using the free volume theory [6] without allowance for electrons, are practically identical with the dashed lines in Fig. 4.

<sup>3)</sup>For NaCl, the equation of state was determined only in the region before the density jump. For the same reason, we did not consider here the equations of state of KCl and KBr which have undergone a polymorphic transition at 20 kbar.<sup>[6]</sup>

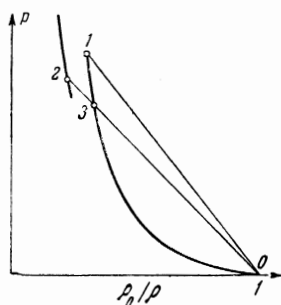


FIG. 5

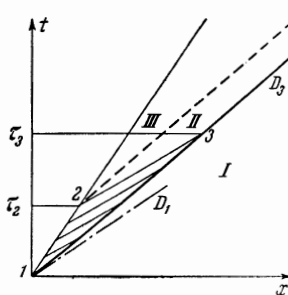


FIG. 6

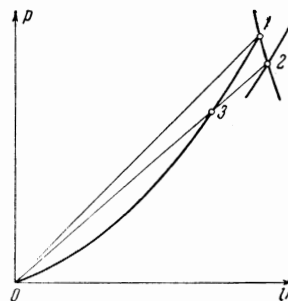


FIG. 7

In Fig. 6, the velocity is given by a tangent to the curve 1—3 at the point 1 (chain curve; the notation of all points in Figs. 5—7 is the same) in  $x-t$  coordinates. Simultaneously, a phase transition begins at the screen—sample boundary, and this transition ends after a time  $\tau_2$  (cf. Fig. 6). Then the state at the contact boundary varies along the 1—2 curve of the  $P-U$  diagram (Fig. 7). The pressure at the boundary decreases to the point 2, representing the state of the second phase. Then the velocity of the boundary will increase. Perturbations (thin lines in Fig. 6) will be propagated from the point where the phase transition has already occurred in the direction of the shock-wave front and these perturbations will overtake the front and reduce the pressure in it along the shock adiabat of the first phase from the point 1 to the point 3. Correspondingly, the velocity of the shock-wave front will decrease from the value  $D_1$  to the value  $D_3$ .

In the  $x-t$  diagram (Fig. 6), we can distinguish three zones. In the rest zone I, the substance is naturally in the first phase. In the shock-wave front, we have the states representing the dynamic adiabat of the first phase. In the zone II, there is a mixture of the two phases with a fraction of the second phase increasing away from the front. Finally, in the zone III, which extends to the interface with the screen, the substance is in the second phase.

If  $\tau$  is much greater than  $\tau_D$ , the time for the propagation of a shock wave along the measurement base, then the change in the velocity of the front is slight and we have the state representing the first phase. In the other extreme case, when  $\tau \ll \tau_D$ , the measured wave velocity represents the second phase of the substance. Finally, at relaxation times comparable with the time for the propagation of a shock wave along the test sample, the measured wave velocity represents, in the  $P-(\rho_0/\rho)$  field, an intermediate (two-phase) state of the substance.

It must be pointed out that the discussion given above applies to the case when the phase transi-

tion does not give rise to a two-wave configuration.<sup>4)</sup>

It is known<sup>[1]</sup> that some ionic crystals with lattices different from that of CsCl (body-centered cubic) undergo a polymorphic transition on compression. Under static conditions, such transitions were observed experimentally by Bridgman in KCl and KBr at pressures of the order of 20 kbar. At similar pressures, the same transitions were found by the dynamic method of Al'tshuler et al.<sup>[6]</sup> This means that the relaxation time of these polymorphic transitions is shorter than the time for the propagation of a shock wave along a sample, i.e.,  $\tau \approx 10^{-7}$  sec.

Under static conditions, Evdokimova and Vereshchagin<sup>[15]</sup> found a polymorphic transition in NaCl at 18 kbar and normal temperature. An X-ray structure analysis of the compressed sample allowed them to find this transition in spite of the small amount (5—8%) of the newly formed phase. An interesting feature of the growth of the new phase was its sluggishness. However, at pressures up to 800 kbar, obtained by the dynamic method,<sup>[5]</sup> no polymorphic transition was found in NaCl. In our case, the anomalies in the shock adiabats were found at densities and pressures very different from those reported in<sup>[15]</sup>. Estimates carried out by a method proposed in<sup>[16]</sup> showed that the anomalies in the shock adiabats of NaCl, as well as of KCl and KBr, were observed in the liquid-phase region.

So far, we have not discussed the reason for these anomalies. Having only data on the density of the substance at a definite pressure and being unable to investigate experimentally the structure of the substance under dynamic compression conditions, we can only, strictly speaking, make some suggestions. Let us consider one of them.

Let us assume that the liquid phase of NaCl in the investigated range of pressures and densities

<sup>4)</sup>This case may be realized if the kinetics is such that a phase transition appears at pressures so high that  $P_s > P_e$  where  $P_e$  is the pressure at the equilibrium transition.

is represented by the equilibrium coordination number  $K$ , where  $6 < K < 8$ . A shock wave is propagated along the substance, whose initial coordination number is 6, and at first this wave melts the substance without altering the number of the nearest neighbors. During the relaxation time, the substance behind the shock wave front acquires an equilibrium coordination  $K$ . If this time is comparable with the time for the propagation of a shock wave along the sample, we obtain the picture described above. On increase of the shock-wave intensity, which increases the temperature, it is natural to expect that the relaxation time will decrease. These assumptions allow us to explain qualitatively the experimental data obtained for NaCl. Up to certain pressures ( $\approx 1.3$ – $1.7$  Mbar at  $m = 1$ ), nonequilibrium states with the coordination 6 are recorded but at higher pressures and temperatures we have the states with the coordination  $K$ . This explains the density jump.

From this point of view, we can also understand the possible anomalies in the shock adiabats of KCl and KBr, since in the initial state they also have the coordination number 6. We can analyze the results for KCl and KBr in a different way by assuming that in the liquid phase, in the region of pressures where density jumps are observed, there is a phase transition due to a change in the effective coordination number from  $K_1$  to  $K_2$ , where  $K_1 < K_2$ . This treatment does not require the assumption that the relaxation time for the change of the coordination number in the liquid phase of KCl and KBr is longer than that in the solid phase.

Estimates show that the anomaly in the shock adiabat of LiF is observed in the solid phase region, and it may be identified with a polymorphic transition to the CsCl-structure. However, the smallness of the effect, which is comparable with the experimental error, requires, as in the case of KCl and KBr crystals, more detailed and accurate studies using essentially different methods.

We have considered also another approach in which the anomalous behavior of NaCl, KCl and KBr is ascribed to the sudden "switching on" of the electron influence on the shock adiabat. Al'tshuler et al.<sup>[6]</sup> drew attention to the fact that when the forbidden band width between the filled band and the conduction band is reduced, a region with negative electron pressure will be reached. The influence of this effect could give rise to an inflection of the dynamic adiabat. However, calculations show that this cannot produce a change in the shock adiabat as sharp as that observed experimentally. A clear example of this is the

CsBr adiabat (cf. Fig. 3), for which the influence of the electron components is considerably greater than for the crystals referred to above, and in which this effect should appear more strongly than in others. It follows that the anomaly can hardly be explained in this way.

Note added in proof (August 29, 1964). After submitting the present paper for publication, we carried out a series of experiments in which the power of the explosive charge was reduced in the measuring device employed to obtain the point 3 on the dynamic adiabat of NaCl (Fig. 4). This did not change the wave velocity in NaCl but the velocity did decrease in control samples of Al, as expected, by 0.53 km/sec. The state of NaCl was found to lie in the region 1–2 of the curve in Fig. 4. The result obtained confirmed the anomalous behavior of NaCl under shock compression.

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177