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THE DYNAMIC COMPRESSIBILITY, EQUATION OF STATE, AND ELECTRICAL CONDUCTIVITY OF SODIUM CHLORIDE AT HIGH PRESSURES

L. V. AL'TSHULER, L. V. KULESHOVA, and M. N. PAVLOVSKIĬ

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Results are presented of an experimental investigation of the compressibility and electrical conductivity of shock-compressed single crystals of sodium chloride in the pressure range from 50 to 800 thousand atmospheres. The equation of state for sodium chloride in the high pressure region is deduced from these data. It is shown that in the compression range investigated, the interaction potential between ions can be satisfactorily described by a formula with an exponential term for the repulsive forces. The method for measuring the electrical conductivity is described. The dependence of electrical conductivity on temperature under shock compression conditions is derived and the activation energy is deduced. It is shown that a sharp increase in conductivity takes place behind the shock wave front. Just as under normal conditions, the conductivity is of an ionic nature.

INTRODUCTION

THE classical theory of ionic lattices was developed by Born and Madelung, who expressed the repulsive forces potential by a power term of the form br^{-n}. Later investigators tried to bring the classical theory into as close agreement as possible with the laws of quantum mechanics, representing[1] the repulsive potential as an exponential $Be^{-r/\rho}$. The parameters n and ρ in these expressions are determined from the experimental values of the compressibility. The validity of the formulae is usually established by comparing the calculated and experimental values for the lattice energy. However, this criterion is not unambiguous since the binding energy is weakly dependent on these parameters under normal conditions.

The most direct evidence about the law of ionic interaction can be obtained by measuring the pressure obtaining when the interatomic distance is reduced. Bridgman's measurements of the isothermal compressibility of rock salt[2] are of special interest in this respect. At a pressure of 100×10^3 atm the density was found to increase 1.27 times.

In the present work the compressibility and the equation of state of sodium chloride were investigated over a considerably greater range of pressure and density, obtained by using intense shock waves.

We also carried out a series of determinations of the electrical conductivity of sodium chloride. A sharp increase in conductivity for a number of solid dielectrics during the passage of shock waves was first found by Brish, Tarasov and Tsukerman[3] in 1950. A short note was published by Alder and Christian[4] in 1956 concerning the electrical conductivity of ionic and molecular crystals under dynamic loading. Unfortunately, the quantitative characteristics of the shock waves were not given and the relation between conductivity and the pressure and temperature was not determined.

We give below the results of a complex determination of the dynamic and electrical properties of sodium chloride, from which the conductivity can be related to the parameters of the shock compression and the equation of state derived for pressures up to 800×10^3 atm.

1. THE DYNAMIC COMPRESSIBILITY AND EQUATION OF STATE OF SODIUM CHLORIDE

Pure single crystals of sodium chloride, with density 2.16 gm/cm^3 were used for the investigations. The reflection method[5] was applied for measuring the dynamic compressibility behind the front of a plane shock wave. Several series of experiments were made, differing in the power of the explosive charge and also in the thickness of the copper, aluminium and iron barrier plates. The wave velocities were measured over reference bases of 4 — 8 mm. Time intervals were determined by the electrical contact method,[5] using high speed oscillographs of the OK-21 type. The time intervals were measured to an accuracy of 5×10^{-9} sec, and the wave velocities were accurate to ± 1.0%.

TABLE I

Point No.	D, km/sec	U, km/sec	P_H 10^{10} bars	v_0/v	δ	Plate material	U_p, km/sec
1	4,16	0.59	5.3	1.16	1.14	Copper	0.37
2	4,73	0,98	10.0	1.26	1.24	Aluminum	0.70
3	5,29	1.33	15,2	1.34	1,32	Aluminum	1.10
4	5.41	1.55	18,2	1.39	1.36	Iron	1.03
5	5,59	1.59	19,3	1.40	1.37	Aluminum	1,32
6	5.66	1.71	20,9	1.43	1.40	Aluminum	1,42
7	5,96	1,85	23.6	1.45	1,42	Aluminum	1.54
8	6,18	2.07	27.6	1.50	1.47	Aluminum	1.74
9	7.85	3.24	54.7	1,70	1.67	Aluminum	2.80
10	8,91	4.10	79.0	1.85	1.82	Iron	2.80

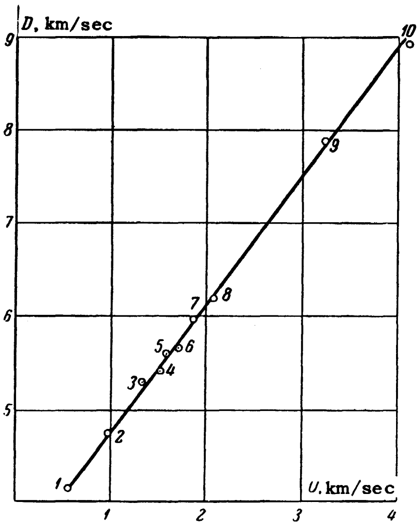
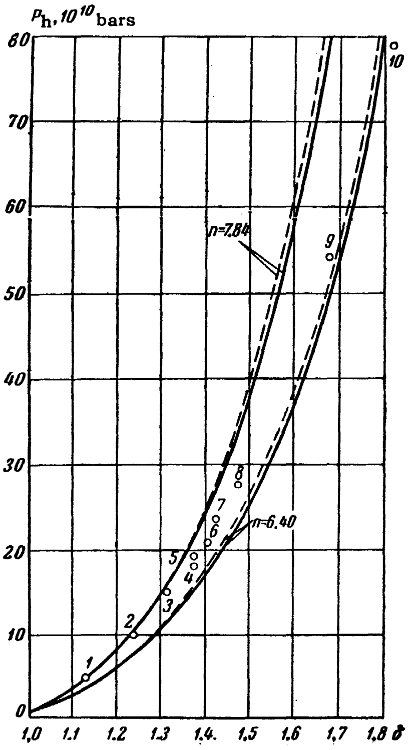


FIG. 1. D–U diagram of the shock adiabat of sodium chloride (the points are numbered to correspond to Table I).

Table I shows the parameters for the experimental points for the shock adiabats of sodium chloride. The wave, D, and mass, U, velocities of the shock waves are given for each point and also the shock compression pressure P_H, the relative compression v_0/v and $\delta = v_{0K}/v$ (where v, v_0 and v_{0K} are the corresponding specific volumes behind the shock front, in the initial state and for P = 0, T = 0°K). The mass velocities in the plates, U_p, are given in the last column. The parameters of the points were determined by using a P — U diagram. The D — U relation for copper, aluminum and iron, given previously[6] was used. In the first eight series of experiments the pressure in the specimens was produced by reflection of the detonation wave from the barrier plate, and in the final two by impact from aluminum and iron discs, driven by the explosion products.[6] The measurements cover the pressure range from 50×10^3 to 790×10^3 atm. At the highest pressure the density of the crystal is increased 1.85 times. The dynamic adiabatics of sodium chloride are shown graphically in D — U coordinates in Fig. 1 and in P — δ coordinates in Figs. 2 and 3.

We express the equation of state of sodium chloride by the Debye formula:

FIG. 2. Experimental data and calculated shock adiabats (with a power law for the repulsive forces): dashed curve is calculated according to Eq. (7a), the continuous curve according to (7b).



$$P = P_c + (\gamma/v)E_t, \tag{1}$$

where P is the pressure, P_c the pressure at absolute zero, v the specific volume, γ the Grüneisen constant, determining the ratio of thermal pressure to the thermal energy density and E_t is the thermal energy of the lattice.

On the assumption that the atoms of the lattice undergo harmonic oscillations, Slater[7] and Landau[8] derived the following relation for γ (v)

$$\gamma = -\frac{2}{3} - \frac{v}{2}\frac{d^2P_c/dv^2}{dP_c/dv}. \tag{2a}$$

There is another expression for γ (v), derived by Dugdale and MacDonald[9] from the theory of finite deformations:

$$\gamma = -\frac{1}{3} - \frac{v}{2}\frac{d^2(P_c v^{2/3})/dv^2}{d(P_c v^{2/3})/dv}. \tag{2b}$$

The system (1), (2a) and (2b) is usually used to

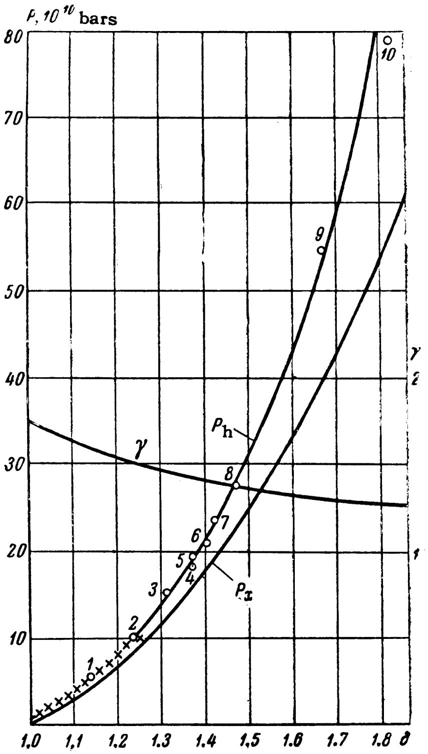


FIG. 3. The shock adiabat, the "cold" compression curve $P_c(\delta)$ and the function $\gamma(\delta)$ for sodium chloride, with ρ = 0.318 A. γ is calculated from equation (9b). o – experimental data, x – Bridgman's data on isothermal compression.

obtain the unknown functions $P_c(v)$ and $\gamma(v)$ from the data of dynamic experiments. For this purpose the pressure P_H and the internal energy

$$E_t = E_0 + \frac{1}{2} P_\Gamma (v_0 - v) - \int_v^{v_{0K}} P_c\, dv$$

of the states on the shock adiabat are substituted into (1) (E_0 is the energy of the initial state for $v = v_0$ and $T = 300°$ K). The equation then obtained

$$P_H = \left[P_c + \frac{\gamma}{v} E_0 - \frac{\gamma}{v} \int_v^{v_{0K}} P_c\, dv\right]\left[1 - \frac{\gamma}{2}\left(\frac{v_0}{v} - 1\right)\right]^{-1} \quad (3)$$

is solved together with (2a) or (2b). The value of v_{0K} can be determined easily from (3), since for $v = v_{0K}$

$$P_c = 0, \quad \gamma \approx \gamma_0 = \frac{\beta v_0}{K c_v}, \quad P_H \approx \frac{1}{K}\left(\frac{v_0}{v_{0K}} - 1\right).$$

β is the coefficient of volume expansion, K is the compressibility, and c is the specific heat. The values of the various parameters used in the calculations below are as follows:

$K = (4.24 \text{ to } 4.16) \cdot 10^{-12}\ \text{cm}^2/\text{dyne}$, $\beta = 1.15 \cdot 10^{-4}\ \text{deg}^{-1}$,
$\gamma_0 = 1.51$, $v_0 = 0.463\ \text{cm}^3/\text{g}$, $v_{0K} = 0.455\ \text{cm}^3/\text{g}$.

The unknown functions $P_c(v)$ and $\gamma(v)$ can also be determined by another method. We can use the analogous expression for $P_c(v)$ given by ionic lattice theory, which contains the undetermined parameter n or ρ. The system (2) and (3) is solved for P_H and γ with various values for the undetermined parameters which enter into the expression for P_c, and the variant is chosen which gives the best agreement with the experimental data on the dynamic compressibility.

As has been pointed out, there is no unique way of representing the repulsive force potential in an ionic crystal. We shall examine two expressions for the interaction energy:

$$E = -A\left[r_{0K}/r - n^{-1}(r_{0K}/r)^n\right], \quad (4)$$

$$E = -A\left[r_{0K}/r - (\rho/r_{0K}) \exp\{(r_{0K} - r)/\rho\}\right], \qquad A = N\alpha e^2/r_{0K}\mu. \quad (5)$$

N is Avogadro's number, μ the molecular weight, α the Madelung constant, e the electronic charge, r the interatomic distance and r_{0K} is the interatomic distance for P = 0 and T = 0° K; with v_{0K} = 0.455 cm^3/g, r_{0K} = 2.797 A.

We will first consider the representation of the potential in the form (4). The pressure is then

$$P_c = -\frac{dE}{dv} = \frac{A}{3v_{0K}}\left(\delta^{n/3+1} - \delta^{4/3}\right), \qquad \delta = \frac{v_{0K}}{v} = \left(\frac{r_{0K}}{r}\right)^3. \quad (6)$$

Substituting $P_c(v)$ in (2a) and (2b) leads to the following expressions for the Grüneisen constant:

$$\gamma = \frac{1}{6} \frac{(n+2)(n+3)\delta^{(n-1)/3} - 12}{(n+3)\delta^{(n-1)/3} - 4}, \quad (7a)$$

$$\gamma = \frac{1}{6} \frac{(n+1)(n+2)\delta^{(n-1)/3} - 6}{(n+1)\delta^{(n-1)/3} - 2}. \quad (7b)$$

The pressure on the Hugoniot adiabat is found from Eq. (3) using expression (7a) or (7b) for γ and (6) for P_c.

Different authors[10,11] give values between 7.84 and 9.1 for n. Figure 2 shows the dynamic adiabats calculated for two values of n for the two values of γ obtained from (7a) and (7b). The curves for n = 7.84 fit the initial part of the experimental adiabat satisfactorily and the curves for n = 6.4 fit the final part. The repulsive forces cannot be fitted throughout by using a power expression.

We now look at the representation of the lattice energy in the form (5). As before, we obtain an expression for the pressure

$$P_c = (A/3v_{0K})\left\{\delta^{2/3} \exp\left[(r_{0K}/\rho)(1 - \delta^{-1/3})\right] - \delta^{4/3}\right\} \quad (8)$$

and the two corresponding expressions for the Grüneisen constant:

$$\gamma = \frac{1}{6} \frac{\left[2\delta^{-2/3} + 2r_{0K}/\rho\delta + (r_{0K}/\rho)^2 \delta^{-4/3}\right] \exp\left[(r_{0K}/\rho)(1 - \delta^{-1/3})\right] - 12}{\left[2\delta^{-2/3} + r_{0K}/\rho\delta\right] \exp\left[(r_{0K}/\rho)(1 - \delta^{-1/3})\right] - 4}, \quad (9a)$$

$$\gamma = \frac{1}{6} \frac{(r_{0K}/\rho)^2 \delta^{-4/3} \exp\left[(r_{0K}/\rho)(1 - \delta^{-1/3})\right] - 6}{(r_{0K}/\delta\rho) \exp\left[(r_{0K}/\rho)(1 - \delta^{-1/3})\right] - 2}. \quad (9b)$$

The dynamic pressure is calculated by substituting (8) and (9) into (3).

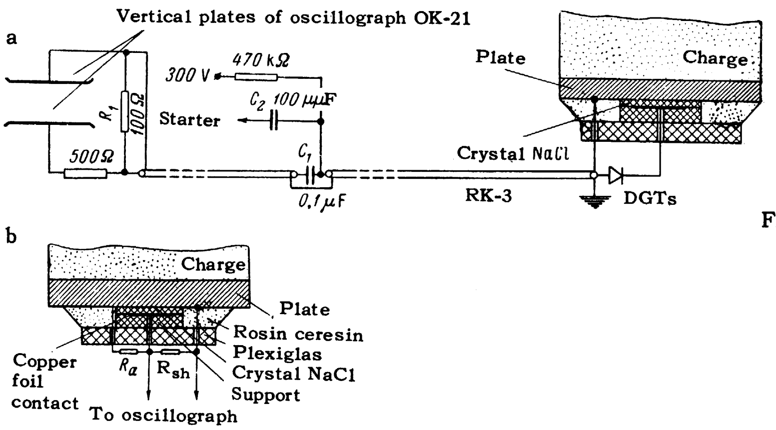


FIG. 4. Apparatus for measuring electrical conductivity.

The parameter ρ was determined earlier from the compressibility. With the value $\rho = 0.328$ A given by Born and Huang,[12] the calculated adiabat lies somewhat lower than the experimental. Davydov[13] previously used Eq. (8) with $\rho = 0.287$ A ($r_{0K}/\rho = 9.69$) to extrapolate Bridgman's data to a pressure of 2×10^6 atm. The value of ρ chosen by Davydov differs from the true in the opposite direction, in so far as the corresponding shock adiabat lies above the experimental.

We tried to obtain the best agreement between calculation and experiment by changing the parameter ρ. The closest agreement was reached with $\rho = 0.318$ A when γ is calculated according to Dugdale's formula (9b) (see Fig. 3). The calculated adiabat then agrees satisfactority with the experimental data over the whole pressure range from 50×10^3 to 800×10^3 atm. Slater's formula (9a) with $\rho = 0.324$ A gives only a slightly worse result, but preference must be given to Dugdale's formula since it gives for $v = v_0$ better agreement with the experimental values, as follows:

	γ_0	$K(v_0)$
Experimental data	1.51	$(4.24\div 4.16)\times 10^{-12}$ bar^{-1}
Calculated from formulae:		
Dugdale	1.75	4.32×10^{-12} bar^{-1}
Slater	2.02	4.45×10^{-12} bar^{-1}

The values of P_C, $E_C = \int_V^{V_{0K}} P_C dv$; γ, P_H and T are given as functions of δ in table 2.

The temperatures on the Hugoniot adiabat are calculated from the equation

$$T, ^\circ\mathrm{K} = 300^\circ + [\tfrac{1}{2} P_H (v_0 - v) - E_c]/c_v.$$

The analysis carried out shows that in the density range studied the repulsive forces can be represented as $Be^{-r/\rho}$ with the constant $\rho = 0.318$ A. In the same range the Grüneisen constant changes from 1.75 to 1.27.

TABLE II

δ	P_c 10^{10} bars	E_c 10^{10} ergs	γ	P_H 10^{10} bars	T, °K
1.0	0	0	1.75	0.5	300
1.1	2,9	0.04	1.64	3.5	320
1.2	6.8	0,21	1.55	7,8	380
1.3	11,8	0.46	1.48	13,4	550
1,4	17.7	0.82	1.43	20,8	920
1,5	25,1	1.29	1.38	31,1	1500
1.6	33.2	1.81	1.34	43.0	2400
1.7	42.7	2.44	1.30	59.2	3850
1.8	53.7	3.13	1.27	80.7	6150

2. THE ELECTRICAL CONDUCTIVITY OF SODIUM CHLORIDE AT HIGH PRESSURES.

For measuring the electrical conductivity, sodium chloride crystals were attached to plates of aluminum or iron (see Figs. 4, a and b), through which the shock waves passed, produced by the explosive charge or by impact of a plate. The distance between the face of the charge and the center of the crystal being studied was made the same in the conductivity measurements as in the corresponding experiments on the compressibility. The support of crystalline sodium chloride, placed under the 0.02-mm copper foil contact, prevented unloading of the working part of the crystal over the free surface. The crystals were sealed at the sides with ceresin rosin to prevent shorting of the contacts through the air. The crystals were about 3 mm thick and the support 4 — 9 mm.

Special apparatus was required to measure the conductivity behind the shock wave front because of the short duration of the process. We used two arrangements with different measuring ranges.

The first apparatus is shown diagramatically in Fig. 4a.* The principle on which it works is as follows: due to the passage of the shock wave

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*The arrangement was suggested by A. V. Reĭmers.

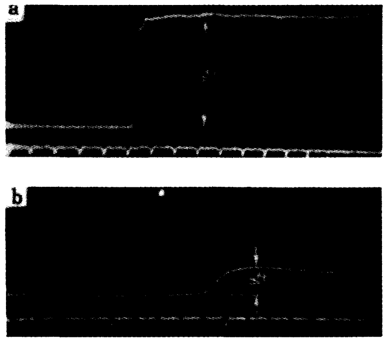

FIG. 5. Oscillograms obtained in experiments by the method of Fig. 4a: a – control, b – working oscillogram. Frequency scale 5 Mcs.

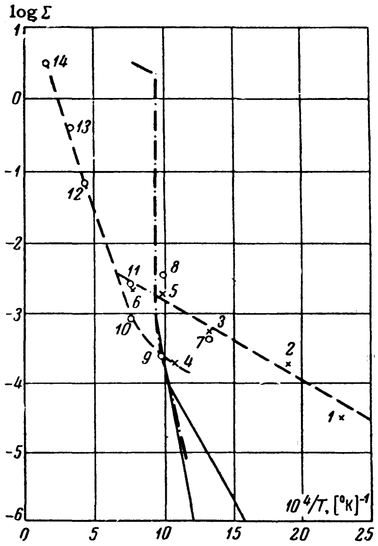

FIG. 6. The dependence of the electrical conductivity of sodium chloride on temperature: dashed curve shows data of the present work (see Table III for the parameters of the experimental points), continuous curve represents Lehfeldt's[15] data and the dashed and fotted curve that of Arndt.[16]

through the crystal there is a sharp reduction in its resistivity, and as a result the capacitors C_1 and C_2 discharge through the crystal. The discharge of capacitor C_2 activates the starter for the whole measuring apparatus. Capacitor C_1 discharges through the resistance $R_1 = 100$ ohms and R_x the resistance of the shock compressed crystal. The value of R_x is determined from the formula

$$R_x = (V_0/V_x - 1)R_1,$$

where V_0 is the deflection on the oscilloscope for shortcircuiting through zero resistance ($R_x \approx 0$) and V_x is the deflection on the picture taken under working conditions. Figure 5 shows oscillograms taken in one of the experiments using this apparatus.

The second arrangement (see Fig. 4b) was similar to that used earlier[14] for measuring the electrical conductivity of explosion products.

The resistance R_{sh} varied in different experiments between 0.8 and 6 ohms and the resistance $R_a = 50\ R_{sh}$ was used to obtain time markers on the oscillogram corresponding to the instant when the shock wave reaches the specimen surface. Measurements showed that the greatest deflection indicating the reduction in resistivity of the crystal, occurred at the moment when the shock wave reached the copper foil contact. The resistance of the crystal R_x was derived from the relation

$$R_x = V_{xsh}\,[(V_{sh} - V_{xsh})\,(1/R_{sh} + 1/R_a)]^{-1},$$

where V_{sh} and V_{xsh} are the electrode voltages before and after the passage of the shock wave through the crystal.

The specific conductivity, Σ, of the crystal was calculated from the formula

$$\Sigma = L/R_x S,$$

where R_x is the measured resistance of the shock compressed crystal, S is the area of the copper foil contact (which varied between 0.2 and 7 cm^2) and L is the thickness of the crystal (between the plate and the metal contact). Several series of experiments were made with various shock wave parameters, just as in the measurements of dynamic compressibility.

The experimental results are collected in Table III, which gives the relative compression v_0/v, the pressure P_H, the temperature in the crystal behind the shock wave front, T, and the specific conductivity of the crystal, Σ. The apparatus shown in Fig. 4a was used for the first six experiments (these points are marked by crosses in Fig. 6), and the previously described apparatus[14] was used for series 7 — 14.

The results of the present experiments are shown in Fig. 6 as log Σ vs. $10^4 T^{-1}$, together with the data of Lehfeldt[15] who measured the conductivity at atmospheric pressure, and of Arndt[16] who measured the conductivity of fused sodium chloride. It can be seen that for relatively low pressures and temperatures there is considerable scatter in the

TABLE III

Point No.	v_0/v	T, °K	P_H, 10^{10} bars	Σ, $\Omega^{-1}\cdot$cm^{-1}	Point No.	v_0/v	T, °K	P_H, 10^{10} bars	Σ, $\Omega^{-1}\cdot$cm^{-1}
1	1,26	440	10,0	$2{,}0\cdot10^{-5}$	8	1.45	1020	23,6	$3.5\cdot10^{-3}$
2	1.31	530	13,7	$1{,}9\cdot10^{-4}$	9	1.45	1020	23.6	$2.6\cdot10^{-4}$
3	1.39	760	18.2	$5.7\cdot10^{-4}$	10	1.50	1320	27.6	$8.6\cdot10^{-4}$
4	1.43	940	20.9	$2.0\cdot10^{-4}$	11	1,50	1320	27.6	$2{,}5\cdot10^{-3}$
5	1.45	1020	23.6	$1{,}9\cdot10^{-3}$	12	1.62	2280	43,3	$6{,}8\cdot10^{-2}$
6	1.50	1320	27.6	$2{,}5\cdot10^{-3}$	13	1,68	3030	54.5	$4{,}1\cdot10^{-1}$
7	1.39	760	18.2	$4{,}4\cdot10^{-4}$	14	1.85	6150	79.0	3,26

magnitude of the conductivity, especially in experiments with crystals taken from different sources.

The experimental results obtained show that the electrical conductivity of a crystal compressed by intense shock waves increases by several orders of magnitude. We found a similar effect earlier in Plexiglas and in caesium iodide.

In the high temperature region the log Σ (T^{-1}) curve has a constant slope, corresponding to an activation energy of 1.2 ev. This leads us to presume that the main factor determining the increase in conductivity is temperature. Judging by the activation energy, the conductivity of sodium chloride is of an ionic nature, just as under normal conditions.

The log Σ (T^{-1}) dependence does not show the rapid changes in conductivity or activation energy, characteristic for the melting process.

The authors consider it a pleasant duty to express their thanks to academician Ya. B. Zel'dovich for his interest and advice in the work and to V. P. Drakin for help with the experiments.

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