POLARIZATION OF ALKALI HALIDE CRYSTALS UNDER SHOCK LOADING. I.

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Anomalous polarization of NaCl single crystals subjected to shock loads in the [100] direction was previously observed by the authors of the present paper. The anomaly consisted in a change of sign of the polarization in a narrow region of variation of the compression σ (from 1.26 to 1.3)[10]. More complete data for this direction are presented for the range $\sigma = 1.02$ —1.7. It is shown experimentally that anomalous polarization also occurs in single crystals oriented along [110] and [111] and also in polycrystalline samples. It is also observed at $\sigma \approx 1.03$. It is shown that existing theories describing dielectric polarization due to shock loading are applicable only in some special cases and do not encompass the whole experimental material.

A large number of investigators[1-14] have established recently that the passage of a shock wave through a piezoelectric, a ferroelectric, a polar body, or an ionic crystal causes electric current to flow in an external circuit containing no emf sources (Fig. 1). The cited papers contain assumptions concerning the physical nature of this current, which can be formulated briefly as follows: 1) The shock wave produces in piezoelectrics electric polarization which increases monotonically with increasing pressure[1]. 2) In ferroelectrics, the opposite takes place—depolarization[2,3]. 3) In polar substances the dynamic shock leads to rotation of the polar molecules along the shock direction, if one end of the molecular dipole has a larger mass than the other[4]. 4) In ionic crystals, the inversion center is destroyed[5] and charged dislocations move[6,7].

Neilson and Benedick[8] observed an anomaly in X-oriented quartz crystals, namely, the charge picked off a compressed sample at a pressure $p > 60$ kbar reversed sign. Graham[9] attributed this phenomenon to motion of dislocations on the shock wave front (SWF). A similar effect was described by us earlier[10] and confirmed by Linde et al.[6], who loaded single-crystal NaCl samples. The region of the anomaly was observed at pressures on the order of 100—130 kbar.

Besides describing the experimental results, a number of the cited papers attempt to relate the current I(t) observed in the external circuit[1)] with

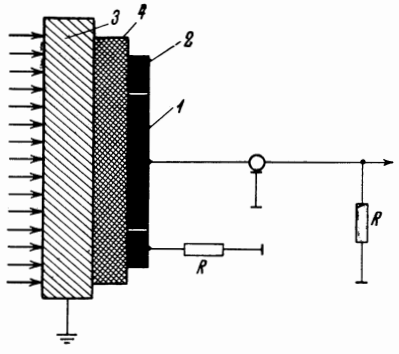

FIG. 1. Experimental setup: 1 – Measuring electrode (S = 1 – 12.5 cm²); 2 – guard ring, of area equal to that of the measuring electrode; 3 – screen of metal with known shock adiabat (aluminum, copper); 4 – NaCl sample (thickness l_0 ranges from 0.1 to 0.8 cm). The arrows show the direction of the motion of the shock wave front.

the geometry of the tested samples and their states ahead and behind the SWF. The authors are aware of three most complete theories describing the polarization current. These are the theories of Allison[11], Zel'dovich[12],[2)] and Halpin[3]. The latter describes experiments with ferroelectrics and piezoelectrics, as is specially stipulated by Halpin, and will therefore not be discussed here.

Allison's theory is based on the following premises: the dielectric is isotropic, the electric displacement vector is continuous on both sides of the SWF (the SWF does not carry free charges), and the circuit is closed. Within the framework of such as-

[1)] We shall henceforth call the current flowing in the external circuit the polarization current.

[2)] It is easy to show that the formulas contained in [1], and under certain simplifying assumptions also in [13], are particular cases of those considered in [11,12].

sumptions, the theory in question can be applied to any class of dielectrics. (Thus, Hauver[14] used it successfully to describe experiments with Plexiglas and polystyrene). The polarization current is connected here with such characteristics of the compressed medium as the polarization P_0 per unit volume on the SWF, the relaxation time in which P_0 decreases exponentially (we shall call it the mechanical relaxation time), and the parameter $\kappa = \epsilon_2\sigma/\epsilon_1$, where ϵ_2 and ϵ_1 are the dielectric constants of the material ahead and behind the SWF, respectively, and σ is the compression of the material on the SWF.

Unlike Allison, Zel'dovich[12] proposes that the decay of P_0 proceeds via compensation of bound charges by free carriers, with a time $\Theta = \rho\epsilon_2/4\pi$, where ρ is the volume resistivity. Unfortunately, no account is taken here in the change in the dielectric constant and the density of the matter ($\epsilon_1 = \epsilon_2$, $\sigma = 1$), and this greatly reduces the range of applicability of this theory.

Apparently, during the polarization decay of a shock-compressed dielectric, both relaxation mechanisms take part, mechanical (with time τ) and conductivity (Θ). How these two mechanisms are related and what the contribution of each is to the depolarization process are questions that must be answered by a more general theory.

The present paper is devoted to an investigation of the depolarization of single crystals of sodium chloride under shock compression conditions. We consider the possibility of using the theories Allison[11] and Zel'dovich[12] for a reduction of the obtained experimental material.

EXPERIMENTAL SETUP

Shock loading of crystals was produced by explosive devices described in the paper of Al'tshuler et al.[15]. The experimental setup is shown in Fig. 1. We used in the experiments calibrated lines with wave resistance 92 and 200 ohms, and the recording apparatus consisted of two types of oscilloscopes with different sensitivity. The rise time of the measuring channel did not exceed 30 nsec.

The parameters of the shock wave in the samples were calculated from the known shock adiabats of the screen and of NaCl[16]. The relatively small thickness of the samples made it possible to avoid lateral relaxation and to neglect the damping of the shock wave during its time of travel through the sample. The differences in the entrance of the shock wave into the tested sample, due to the asymmetry of the shock wave front and possible tilting during the experiments, amounted to 0.02—0.1 μsec, as shown by special experiments.[3)] This fact allows us to assume that conditions close to uniform were realized in most experiments.

Generally speaking, one cannot exclude the possible existence of a two-wave configuration, brought about by a phase transition in NaCl in the pressure range of 20—30 kbar. This question remains debatable to this day; however, if the phase transition does exist, then, according to Larsen et al.[17], the degree of phase transformation in the shock wave is quite insignificant (the difference in the velocities of the two waves is 20 m/sec), making it possible to regard the sample compression as single.

The tested samples were single crystals from four batches. The crystal purity was 99.6—99.8%. Unfortunately, the authors could use only the results of a qualitative spectral analysis, which showed different contents of the main impurities in each of the employed single-crystal batches (Ba, Ca, Cu, Fe, K, Mg, Si). In many experiments we used samples of polycrystals, obtained by pressing kitchen salt ("Ekstra" brand). Their initial density was smaller by a factor 1.04 than the density of the single crystals. The accuracy with which NaC sample were produced with orientation along [110] and [111] was several degrees.

The error in the amplitude measurements, with allowance for all the possible errors, is estimated not to exceed ± 10%.

EXPERIMENTAL RESULTS AND DISCUSSION

1. Oscillograms illustrating the dependence of the polarization current on the time are shown in Fig. 2. It follows from them that with changing loading condition the form of I(t) changes appreciably, although for samples with different orientations but with constant σ it remains similar in many respects (Figs. 2, 6, and 2, 8). To be sure, for samples with orientation along the [110] direction at a pressure p = 276 kbar (σ = 1.5), unlike in Fig. 2(8), a change was noted in the sign of I(t) during the time of passage of the shock wave through the sample[4)].

One of the most important characteristics of the behavior of NaCl in a shock wave, as well as of any other dielectric, is the polarization P_0 on the front of the shock wave. The information con-

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[3)] The difference in time increases with the increasing area of the measuring contact.

[4)] This singularity in the oscillogram trace, like the anomaly in $j_0(\sigma)$ described below, will be specially considered in the second part of the article.

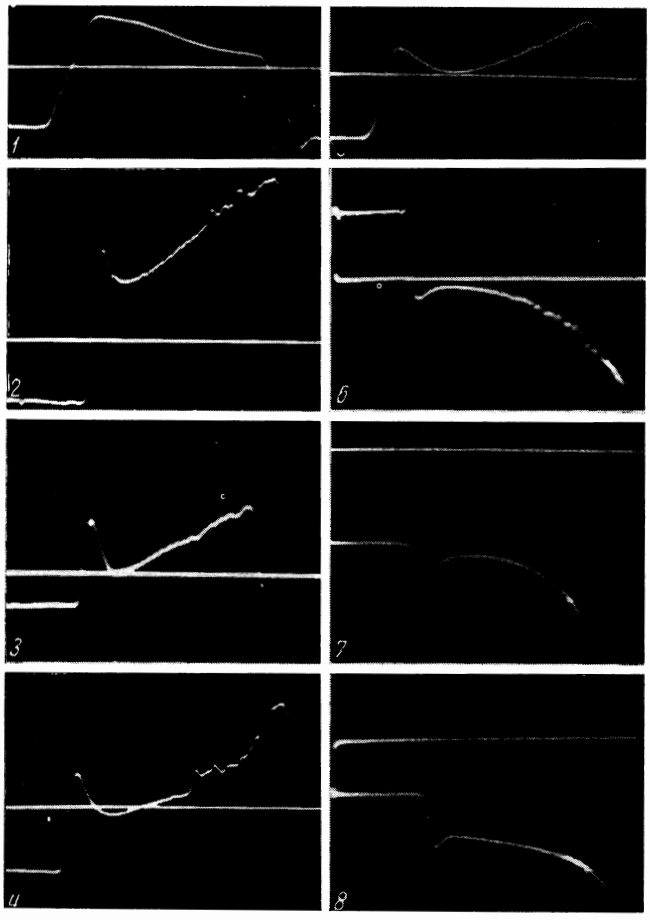

FIG. 2. Typical oscillograms. Oscillograms 1 – 7 were obtained with the samples loaded in the [100] direction, 8 – in the [110] direction. Oscillogram 1 – p = 20 kbar (σ = 1.07, l_0 = 0.31 cm); 2 – p = 53 kbar (σ = 1.16, l_0 = 0.56 cm); 3 – 5 – p = 100 kbar (σ = 1.26, l_0 – respectively 0.55, 0.4, and 0.2 cm); 6 and 8 – p = 153 kbar (σ = 1.34, l_0 – respectively 0.8 and 0.35 cm); 7 – p = 276 kbar (σ = 1.5, l_0 = 0.47 cm). Oscillograms 1, 2, and 7 were obtained in experiments in which S = 3.14 cm^2, in the remaining cases S = 1 cm^2.

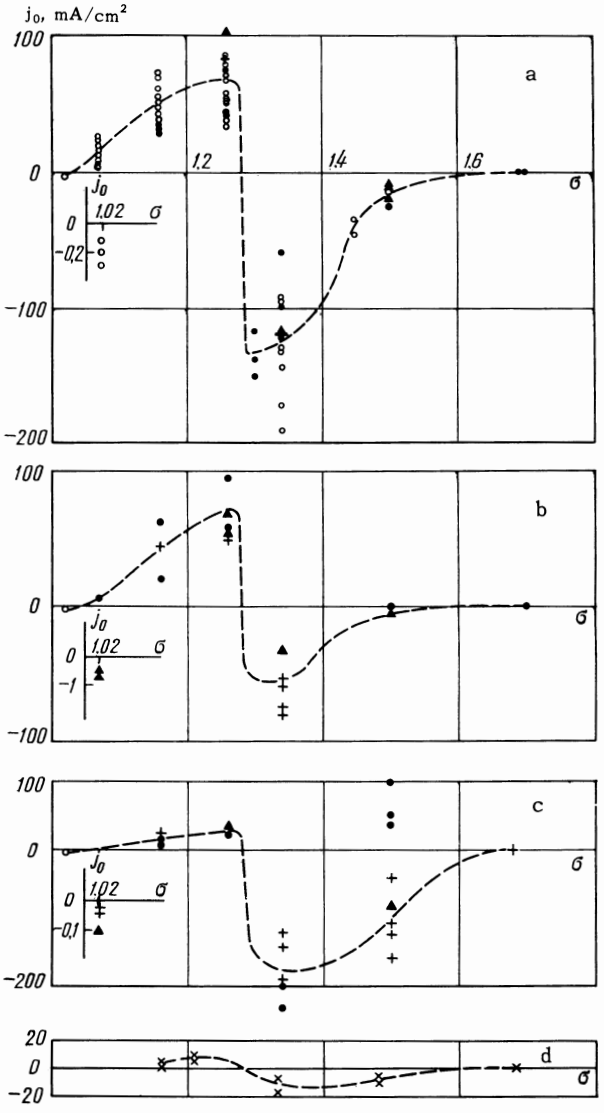

FIG. 3. The initial jump in the density of the polarization current upon loading of sodium chloride; a – in [100] direction, b – in [110] direction, c – in [111] direction, d – polycrystalline samples. Different points correspond to four batches of single crystals. In plots n – c the values of j_0 for σ = 1.02 are shown in an enlarged scale.

cerning the polarization is easiest to obtain in shock-loading experiments by determining in each experiment the initial density of the polarization current j_0,[5)], since this value is not affected by relaxation processes that require finite time intervals for their development. According to [11,12], we can put $P_0 = j_0 \kappa T$. At a known value of κ, we obtain P_0 from this relation uniquely, otherwise we obtain it accurate to κ (at small compressions κ is apparently close to unity).

The results of [4,6,14] and of our own direct experiments with NaCl single crystals have shown that, other conditions being equal, $I_0(T)$ and $I_0(S)$ are respectively in reciprocal and direct linear relation with the argument, within the limits of experimental error. This circumstance allows us to describe a series of experiments with different sample geometries by means of a single quantity j_0 at a certain nominal value l_0 and a given compression. Therefore, in spite of the difficulties that arise in determining j_0 (see below), the authors deemed it advisable to refer all the experimental data to the j_0-σ plane (for l_0 = 0.18 cm), as was done in Fig. 3. Each point here is the result of a separate measurement.

From the plots of Fig. 3 we get the following:

[5)] j_0, and subsequently $j_{0,s}$ and j_f, determine the density of the polarization current for the respective instants of time t = 0, t = 0.5T, and t = T = l_0/D (D–velocity of shock wave in the sample).

a) The polarization current exists when the NaCl is loaded in any single-crystal direction ([100], [110], [111]), and also in loaded polycrystalline samples. In the latter case the values of $j_0(\sigma)$ are much smaller.

b) An anomaly exists in the course of $j_0(\sigma)$, pointing to the existence of an anomaly of $P_0(\sigma)$. The anomaly consists in the reversal of the sign of j_0 when σ varies in the interval 1.26—1.30.[10] A similar change in the sign of j_0 was registered in the region of $\sigma \approx 1.03$. Neither anomaly depends on the direction of the loading or on the crystal batch.

c) The values of j_0 for different directions (with σ = const) differ greatly from one another, reaching a maximum (in absolute value) of ~ 0.2 A/cm^2 when the samples are loaded in the [111] direction to pressures ~ 152 kbar ($\sigma = 1.34$).

d) All four experimental plots $j_0(\sigma)$ curves are similar in many respects, if we disregard the results of three experiments at $\sigma = 1.5$ on Fig. 3c, where a change takes place not only in the value of j_0 but also in its sign.

e) In all cases, the polarization current drops to zero when σ approaches 1.6—1.7. We recall that sodium chloride begins to melt at these compressions[18], and the conductivity of the compressed material reaches a value on the order of 10^{-2} -10^{-1} ohm^{-1} cm^{-1} [19].

2. The results of the experiments have shown that the pulse rise time is 0.03—0.15 μsec. It is clear therefore, that to find j_0 it is necessary in each case to extrapolate I(t) to t = 0.

Most oscillograms (Fig. 2) have a characteristic singularity, namely a current peak at the start of the trace; this greatly complicates the determination of j_0. It is natural to expect the current density j_0 to turn out to be too low. By way of a criterion for an estimate of its magnitude it is useful to employ the relation $j_0 T$ = const, if a series of experiments is made at σ = const and at variable T.

3. Let us estimate the limits of applicability of the theories of Allison[11] and Zel'dovich[12] to the reduction of the obtained experimental material. We start here from the following facts: a) in most oscillograms one registers in the experiments the current peak at the start of the trace; b) the $j_f(T)$ dependence remains approximately the reciprocal of linear in the entire investigated pressure region; c) the conductivity of NaCl is sufficiently high at $p \geq 100$ kbar[19].

The current peak at the start of the trace is due to the small value of either τ or Θ (compared with T). The analysis presented below shows that it is difficult to determine which of the temporal parameters determines the course of the I(t) plot.

Indeed, it follows from [11] that the I(t) dependence has the same form for $\tau \ll T$ (in the region $\tau \ll t \ll T$) and for $\tau \gg T$:

$$I(t) = A[\varkappa T + t(1-\varkappa)]^{-2}, \qquad (1)$$

where $A = P_0 S\tau(\kappa - 1)$ for $\tau \ll T$ and $A = P_0 S\kappa T$ for $\tau \gg T$. A characteristic feature here is the fact that in the former case ($\tau \ll T$) j_f is inversely proportional to the square of T, and the I(t) curve has a clearly pronounced current peak of some duration at the beginning of the trace. In the second case, the current density j_f is inversely proportional to the first power of T,[6] and there is no current peak. Further, if there is no distinct minimum[7] on the I(t) oscillogram, this means that the conditions realized in the experiment are close to one of the two limiting cases. A reciprocal linear dependence of j_f on T in our experiments, and the presence of a current peak at the beginning of the trace, are thus, from the point of view of Allison's theory[11], in contradiction.

One might think that the latter contradiction can be eliminated by the presence of high conductivity in compressed NaCl and by using Zel'dovich's theory[12] for the reduction of the experimental data. However, it is impossible to state here unequivocally allowance for the compression of the matter behind the SWF in Zel'dovich's exact solution conserves the reciprocal linear variation of j_f with T. Furthermore, whereas in Allison's theory, using known data on the conductivity of NaCl, it is possible to establish the limits for the applicability of the theory (by calculating the value of Θ), the same cannot be said with respect to Zel'dovich's theory, since the question of the value of τ remains open[8].

It thus becomes perfectly obvious that the bulk of the experimental material requires for its applicability a more general theory, which contains at least two time parameters (τ and Θ), and also the polarization of the matter P_0 and its compression behind the SWF ($\sigma \neq 1$, $\epsilon_1 \neq \epsilon_2$). It is not excluded that the influence of the mechanical relaxation process on the course of I(t) turns out to be insignificant where the conductivity is high, and vice

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[6] If the condition $\tau \gg T$ or $\tau \ll T$ is satisfied, we get from (1) $\kappa = 2(j_f/j_{0.5})^{-1/2} - 1$.

[7] It is easy to visualize a case when the current peak at the start of the trace cannot be resolved by the apparatus.

[8] We recall that the Zel'dovich theory [12] is valid for $\tau \gg T$.

versa. However, by virtue of the differences in the physical nature of the relaxation processes under consideration, this problem can obviously be solved only after a more general theory is developed.

Long-range extrapolation of the results of Al'tshuler et al.[19] into the region of low pressures makes it possible to establish that, in first approximation, the value of Θ can be comparable with or larger than the time of passage of the shock wave through the sample only for p = 20 kbar and below. Starting from this, we have performed calculations on the oscillogram 1 of Fig. 2 (p = 20 kbar), and obtained

$$P_0 = 8.5 \cdot 10^{-9}\ \text{k/cm}^2, \qquad \tau = 0.75\ \mu\text{sec}, \qquad \varepsilon_2 = 1.09\varepsilon_1.$$

We see that in this case the conductivity has exerted its influence on the course of I(t), since the obtained value of τ turned out to be of the same order as T (according to Zel'dovich, one should expect $\tau \gg T$).

4. The determination of the unknown τ and ρ by independent methods would greatly facilitate the determination of P_0 and ϵ_2.

The value of τ can be registered directly by measuring the decrease in the polarization current for $t > T$, provided the reflection of the shock wave from the second electrodes of the capacitor (1 on Fig. 1) is eliminated. There will be no electric field in the closed circuit inside the dielectric, since there will likewise be no conduction current in the circuit (even in the presence of free carriers in the volume of the dielectric). This gives grounds for assuming that with decreasing polarization of the dielectric (with a time τ) there will flow in the external circuit a relaxation current I_r in a direction opposite to the current I(t). An experiment performed at p = 100 kbar ($\sigma = 1.26$) yielded a value $\tau = 0.62\ \mu$sec.

By expanding the conductivity-measurement range in experiments similar to those of Al'tshuler et al.[19] into the region of low pressures, one can decrease the number of unknown parameters by 1.

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