SOVIET PHYSICS JETP VOLUME 26, NUMBER 4 APRIL, 1968

# POLARIZATION OF ALKALI-HALIDE CRYSTALS UNDER IMPACT LOADING. II

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Submitted April 14, 1967

Zh. Eksp. Teor. Fiz. 53, 1242–1248 (October, 1967)

Polarization of ionic single crystals of LiF, KCl, and KBr subjected to shock pressures up to 0.02–1 Mbar is investigated experimentally. As in NaCl, anomalous polarization consisting in a sharp change in the magnitude and direction of the polarization current during compressions $\sigma = 1.42-1.48$ is observed in KBr and KCl. From the obtained results it can be concluded that the polarization current in the investigated substances is determined by the crystal lattice imperfections produced during the plastic deformation in the shock-wave front.

IN this paper we generalize some results of the investigation of impact polarization of alkali-halide compounds which has previously been carried out by the authors only for NaCl.[1, 2] On the basis of an experimental study of this effect in single crystals of LiF, KBr, and KCl (with references to data of other work on NaCl,[2] CsI and KI[3]), an attempt is made to explain the physics of this phenomenon. In addition, we discuss experimental facts related to the anomalous impact polarization of NaCl[1, 2] KBr and KCl (this publication).

## EXPERIMENTAL SETUP

The experimental equipment and the method of carrying out the experiments were the same as in the previous article.[2] The impact polarization of LiF, KBr, and KCl was investigated in the pressure range from 20 to 200 kbar (LiF—up to 1000 kbar). The investigated samples were cut from the respective single crystals along the cleavage planes. The shock wave (SW)[1)] propagated perpendicular to the (100) plane. The sample thickness $l_0$ varied between 0.15 and 1 cm, but the bulk of the experiments was carried out on samples with $l_0 \approx 0.2$ cm.

The crystals were 99.6–99.8 percent pure. The experiments with LiF and KBr were carried out on two batches of crystals. Qualitative spectroscopic analysis showed that both batches did not differ appreciably in their impurity composition (Ba, Ca, Cu, Fe, K, Mg) and content. We note in this connection that the compared polarization currents for various batches of the same crystal lie within the experimental spread.

Special experiments with annealed samples of NaCl and KBr oriented along the [100] (keeping the samples for three hours at 700°C and subsequently cooling them along with the furnace down to room temperature) showed that the previous history of the samples has practically no effect on the amplitude and shape of the time recording of the polarization current I(t).

In calculating the parameters of the investigated ionic crystals behind the shock-wave front (SWF) use was made of the equations of state of LiF, KBr, and KCl from [4]. According to Al'tshuler et al[5] in the range of pressures 20–70 kbar a configuration of two compression waves propagates in KBr and KCl; this is connected with the rearrangement of the crystal lattices of these compounds into the CsI-type structure, there being at the instant of emergence of the first SW from the KBr or KCl sample no less than 70 percent of the substance behind the front of the second SW. Therefore in the 20–70 kbar range the values of the temperature, compression, and polarization currents for these crystals have been referred to the phase with the CsI-type structure.

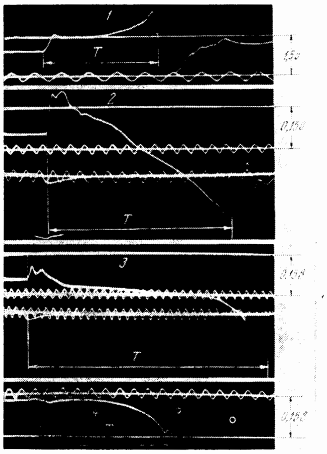

FIG. 1. I(t) oscillograms of experiments with KBr samples. 1, 2, 3 – p = 78 kbar ($\sigma = 1.396$), 4 – p = 150 kbar ($\sigma = 1.58$); 1 – $l_0 = 0.12$ cm; 2 – $l_0 = 0.42$ cm; 3 – $l_0 = 1$ cm; 4 – $l_0 = 0.35$ cm. In all experiments S = 1 cm$^2$. The input resistance of the oscilloscope was 92.2 ohm. Scale time markers – every 0.1 μsec (T is the calculated traversal time of the SW across the sample).

## EXPERIMENTAL RESULTS

Oscillograms of the experiments with LiF, KBr, and KCl in the investigated range of compression are in general similar to I(t) traces for NaCl. A new fact is the change in the sign of the polarization current in the course of the propagation of the SW along the sample observed in KBr and KCl [Fig. 1, below—pole reversal of I(t)].

As follows from [2], quantitatively the polarization of various substances in a SW is most simply characterized by the quantity[2)] $j_0 = I_0/S$, where $I_0$ is the polarization current at t = 0, and S is the area of the electrode. Experiment indicates that in LiF, KBr, and KCl, as well as in NaCl, $j_0 l_0 = \text{const}$ for a given compression $\sigma$; it turned out therefore to be possible to de-

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[1)] Below we shall make use of the notation introduced in [2].

[2)] The method of obtaining $j_0$ from the oscillograms and the accuracy of measurements in this work do not differ from those in [2].

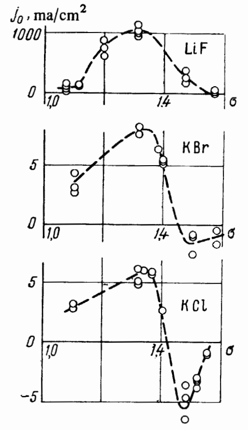

FIG. 2. Dependence of the density of the initial jump of the polarization current $j_0$ on the compression $\sigma$ under load in LiF, KBr, and KCl ($l_0 = 0.18$ cm).

scribe a series of experiments with one form of ionic crystals and different sample geometry for $\sigma$ = const by using a single value of $j_0$ calculated for a given $l_0$. In Fig. 2 the experimental data are presented in the $j_0-\sigma$ plane ($l_0 = 0.18$ cm).

Let us note the following features of the polarization of LiF, KBr, KCl, and NaCl in SW.

A. The dependence of $j_0$ on the SW amplitude. A similarity of the $j_0(\sigma)$ curves is noted in the three crystals—NaCl, KBr, and KCl: a monotonic increase of $j_0$ for $1.1 \leq \sigma \leq 1.3$ to some value $j_{0\,\max}$ followed by a change in the sign of $j_0$ [$j_0(\sigma)$ anomaly], and a subsequent decrease of the absolute value of $j_0$. In LiF there is no $j_0(\sigma)$ anomaly. In all the investigated crystals the value of $j_{0\,\max}$ is attained for $\sigma \approx 1.30$, and amounts (in mA/cm²) to 1050 in LiF, 80 in NaCl, 7.5 in KBr, and 5.5 in KCl. For $\sigma \approx 1.6$ the value of $j_0$ in LiF becomes less than the sensitivity threshold of the apparatus (100 mV/cm).

B. The sign of $j_0$. According to the results of this work, as well as those of [2, 3], in all alkali-halide crystals in which impact polarization was investigated (LiF, NaCl, KBr, KCl, CsI, and KI) a positive sign of $j_0$ was recorded in the range $\sigma = 1.1-1.3$ independently of the type of lattice, the ratio of masses of the anion ($m_-$) and the cation ($m_+$), and the direction of the impact loading.

C. The relationship between $j_0$ and the characteristics of the ideal lattice. Experimental results on the most fully investigated ionic crystals up to a compression $\sigma = 1.3$ indicate for $\sigma$ = const a correlation between $j_0$ and a large number of parameters characterizing the crystal lattice of these compounds under normal conditions: $(r_- - r_+)/r_-$ ($r_-$ and $r_+$ are the radii of the anion and cation, the reduced mass M ($1/M = 1/m_+ + 1/m_-$), the activation energy required by the cation to overcome the potential barrier ($E_A$), the low-frequency dielectric constant ($\varepsilon_1$), etc. We note that for $\sigma > 1.3$ there is no such correlation. Some data on such a correlation for $j_0 = j_{0\,\max}$ are presented in Fig. 3.

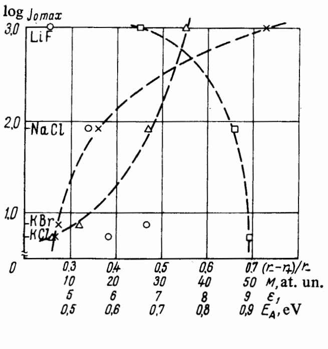

FIG. 3. Curves illustrating the correlation between $j_{0\,\max}$ and some parameters characterizing the lattice of the investigated ionic crystals: Δ – $(r_- - r_+)/r_-$, ○ – M, × – $\epsilon_1$, □ – $E_A$.

D. Pole reversal of I(t). This effect was recorded by the authors in KCl ([100] direction, p = 198 kbar), KBr ([100] direction, p = 78 kbar), and subsequently in NaCl ([110] direction, p = 276 kbar),[3] but was studied in detail only in KBr. The following features of pole reversal of I(t) in KBr are noted:

a) the change in the sign of the polarization current occurs only for $l_0 > 0.27$ cm, whereas for $l_0 < 0.27$ cm the I(t) trace does not differ from oscillograms obtained with other crystals for $\sigma < 1.3$ (Fig. 1, No. 1);

b) with increasing $l_0$ from 0.27 to 1 cm when I(t) = 0 the moment remains approximately constant: $t_{I=0} = 0.5\ \mu$sec ($l_0 = 0.16$ cm, Fig. 1, Nos. 2 and 3);

c) the pole reversal of I(t) precedes the $\sigma$ anomaly of $j_0(\sigma)$.

E. The phase transition and the $j_0(\sigma)$ anomaly. From the formal point of view there is a correspondence between the presence in the crystal of a phase transition and the $j_0(\sigma)$ anomaly. Thus in KBr and KCl—ionic crystals which undergo polymorphous transformations in the investigated pressure range,[4-6] the $j_0(\sigma)$ anomaly has been observed; in LiF, on the other hand, where up to ~ 1000 kbar there is no phase transition,[6] the $j_0(\sigma)$ anomaly has indeed not been recorded. The question of the existence of a phase transition in NaCl in the 100–130 kbar region [the region of the $j_0(\sigma)$ anomaly] remains open.[7]

However, the possible conclusion that the $j_0(\sigma)$ anomaly is in some way related to the appearance in KBr, KCl, and possibly in NaCl, of a phase with the CsI structure is not confirmed by the only experiments with polycrystalline CsI: Linde, Murri, and Doran[3] observed a change of the sign of $j_0(\sigma)$ in CsI (in the range of 107–215 kbar).

A. The region of compressions $\sigma = 1.1-1.3$. The experimental material presented above indicates that up to compressions $\sigma \approx 1.3$ the mechanism of the impact polarization in the investigated ionic crystals is connected with the particular crystal lattice of these compounds.

The authors know only of one paper in which the impact polarization of dielectrics is considered on the microstructure level (Harris[8]). In ionic crystals Harris connects the effect with the relative displacement within the limits of elasticity of the oppositely charged ions of the lattice in the SWF. He assumed that the sign of the polarization depends on the ratio of the anion and cation mass and is determined from the expression $(m_- - m_+)/(m_- + m_+)$. As a result of the developed considerations Harris predicts the absence of polarization effects in the [100] and [110] directions for a NaCl-type lattice. However, the model considered is apparently inapplicable to the impact polarization of

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[3] The analogous phenomenon in NaCl at pressures of 10, 13, and 16 kbar is communicated in [3].

ionic crystals, inasmuch as it is contradicted by a series of experimental facts, namely:

a) a difference of six or seven orders of magnitude between the relaxation time of the impact polarization ($\sim 10^{-6}$ sec[2]) and the relaxation time of the ion polarization ($\sim 10^{-13}$ sec[9]);

b) the presence of a polarization current in NaCl in the [100] and [110] directions [2, 10];

c) the positive sign of $j_0$ in KCl (this communication).

These facts, as well as other results of experiments in the range $\sigma = 1.1-1.3$ can be qualitatively explained if it is assumed that the polarization of the crystals in a SW is a result of the directional displacement of charged lattice defects appearing according to Pratt[11] in plastic deformation of ionic crystals.

From the data of Pratt[11] and Klein[12] it follows that the number of defects n (including vacancies of positive ions) produced in 1 cm$^3$ during plastic flow of the crystal is a function of the deformation and of the rate of deformation. The most probable reason for the production of these vacancies is at present considered to be the capture of cations by dislocation steps.[13, 14] Because of the presence of a force field (a pressure gradient) in the front of the SW the captured ions will be preferentially displaced in the direction of propagation of the SW. Independent of the displacement mechanism of the cations[14] there occurs as a result of this process behind the front of the SW a nonuniform ion distribution analogous, for instance, to the ion distribution in thermal polarization.[9]

These circumstances make it possible to represent formally the impact polarization of ionic crystals as a result of two simultaneously occurring processes: 1) the production of cation dipoles—a cation vacancy due to the displacement of cations from the lattice sites; 2) the orientation of these dipoles in the direction of motion of the SW.

We note that analogous arguments are also applicable to other classes of substances which contain as the basic or impurity material ionized atoms. This remark refers in particular to the impact polarization of silicon and germanium.[15]

Taking into account the above, one can write the polarization $P_0$ on a SWF of given intensity as

$$P_0 = \bar{\mu} n, \tag{1}$$

where $\bar{\mu}$ is the average component of the dipole moment in the direction of propagation of the SW, the averaging being carried out twice: over the magnitudes of the cation displacements ($\delta_i$), and over all possible dipole orientations.

The quantity n exceeds the equilibrium defect concentration $n_{eq}$. In purely ionic crystals $n_{eq}$ is determined by the impurity ion concentration (up to a temperature of about 450°C[11]). The decrease in the number of defects from n to $n_{eq}$ will occur according to an exponential law[2, 16] with some relaxation time which corresponds here to the "mechanical" relaxation time from [2]. We note that the value of $\tau = 0.75 \times 10^{-6}$ sec (NaCl, p = 20 kbar) obtained experimentally in [2] is within the time interval of the relaxation of the thermal polarization ($10^{-2}-10^{-7}$ sec[9]).

It is clear from general physical considerations that the quantities n and $\delta_i$ (and the $P_0$ and $j_0$[4] related with them) should in the final analysis be determined by the height U of the local potential barrier (which can for cations to a first approximation be considered equal to $E_A$). In alkali-halide crystals under normal conditions U decreases with increasing parameter $(r_- - r_+)/r_-$.[18] If it is assumed that for $\sigma$ = const the ratio of the heights of barriers in different crystals does not change compared with normal conditions (which appears probable), then the experimentally observed relationship of $j_0$ and the parameter $(r_- - r_+)/r_-$ becomes understandable.

As a result of the anisotropy of the ionic crystal the quantity U should also depend on the crystallographic direction. Taking into account all that has been said about the connection between U and $j_0$ from a comparison of the values of $j_0$ measured under impact loading of NaCl of various orientation,[2] it follows that the values of U in the [100] and [110] directions are approximately equal and appreciably smaller than U in the [111] direction. (It is curious that one can arrive at the same conclusion by considering the displacement of the ions in the geometrical model of the NaCl-type lattice.)

Based on the above, one can conclude that up to $\sigma \approx 1.3$ the determining parameter of the polarization of alkali-halide compounds in a SW are the ion dimensions. This point of view could be confirmed with crystals in which the parameter $(r_- - r_+)/r_-$ takes on an extremal value, for example in KF $[(r_- - r_+)/r_- = 0.02]$ and LiH (0.713).

From (1) and from the expression $P_0 = j_0 \kappa T$[2] we find

$$\bar{\mu} = \bar{\delta} q = j_0 T \varkappa / n, \tag{2}$$

where $\bar{\delta}$ is the average displacement of the cation in the direction of motion of the SW and q is the cation charge. Equation (2) allows one to estimate the value of $\bar{\delta}$. It follows from [11, 12] that under conditions of impact loading no less than $10^{17}$ defects/cm$^3$ are formed for each percent of plastic deformation of an ionic crystal. Thus, for $\sigma = 1.1$ (10 percent plastic deformation in the SWF) n will be of the order of $10^{18}$ cm$^{-3}$. Taking $\varepsilon_2 = \varepsilon_1$ (see above) and making use of the experimentally measured values of $j_0T$, it is readily found from (2) that for $\sigma = 1.1$ the value of $\bar{\delta}$ is of the order of 1−10 lattice constants.

Substituting in (2) the average values of $j_0T$ from the interval $\sigma = 1.1-1.3$ for each investigated crystal, we find the following orders of magnitude of the polarization $P_0$(coul/cm$^2$): $\sim 10^{-7}$ for LiF, $\sim 10^{-8}$ for NaCl, and $\sim 10^{-9}$ for KBr and KCl.

B. The region of compressions $\sigma = 1.3-1.6$. In this region, unlike in the region $\sigma = 1.1-1.3$ there is no unique form of the $j_0(\sigma)$ curves and I(t) traces; therefore here a unique interpretation of the experimental data is difficult.

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[4] $j_0 = P_0/\kappa T$ ($\kappa = \epsilon_2\sigma/\epsilon_1$ where $\epsilon_2$ and $\epsilon_1$ are the dielectric constants before and after the passage of the SWF, and T is the calculated traversal time of the SW across the sample).[2] Since $\epsilon_2$ apparently changes weakly with the pressure, [2,17] $\kappa \approx \sigma$.

1. From a consideration of the equivalent circuit of the polarization pickup[19] it follows that the reasons for the pole reversal of I(t) can be either a) change of sign of the effective circuit resistance, or b) a change of sign of the effective emf. Case a) can occur theoretically[16] for $\kappa < 1$, however for reasons presented in [2, 20] the applicability of this theory to ionic crystals at pressures higher than 20–30 kbar is in doubt. Case b) is possible if it is assumed that the polarization of the crystal in a SW is produced by two independent processes with appreciably different relaxation times and by charge carriers of opposite sign, carriers of one sign only being generated in each process. Such an explanation of the pole reversal of I(t) appears most probable.

2. Considerations analogous to case b) can also be applied to the $j_0(\sigma)$ anomaly. Actually, we assume that $P_0$ is a sum of two polarizations of different sign ($P_0 = P_+ + P_-$). The $j_0(\sigma)$ anomaly can then be explained by a change in the relative values of $P_+$ and $P_-$ with the increase in the compression behind the SWF.

Such facts as the absence of a correlation of $j_0$ with the lattice characteristics of the ionic crystal for $\sigma > 1.3$, the effect of impurities on the $j_0(\sigma)$ anomaly in NaCl at $\sigma = 1.50$,[2] and the existence of a polarization current in silicon and germanium in which it is difficult to imagine a source of this current other than the activation of impurities in the SW, set one thinking about the determining role of the latter in the impact polarization of ionic crystals for $\sigma > 1.3$. We note that the excitation of the impurities contained in silicon and germanium ($\sim 10^{-4}$ percent[15]), and in the employed ionic crystals ($\sim 0.3$ percent) are sufficient in their order of magnitude for the production of the observed currents. Within the framework of the "impurity" hypothesis the proposed connection between the phase transition and the $j_0(\sigma)$ anomaly can be explained by a change in the binding energy ($E_b$) of the impurities with vacancies during the rearrangement of the crystal lattice. According to K'o T'ing-sui[21] $E_b$ is a function of the structure of the lattice.

In order to verify these assumptions, it is essential to carry out experiments with ionic crystals of graded purity.

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Translated by Z. Barnea
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