Electromotive force produced by shock compression of a substance

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Usp. Fiz. Nauk 119, 75-109 (May 1976)

The phenomena accompanying shock polarization of linear dielectrics and depolarization of nonlinear dielectrics are considered. It is established that the appearance of an emf on the front of a shock wave is a characteristic of a large class of substances, such as linear and nonlinear dielectrics, semiconductors, and metals. It is shown that the emf produced by shock compression of ionic crystals, polar dielectrics, semiconductors, and a number of metals is due to shock polarization. Diffusion of carriers from the front of a shock wave is observed in shock-compressed bismuth, europium, and aluminum. Shock compression of polarization nonlinear dielectrics leads to a stronger effect, namely to the onset of a depolarization emf. The presented phenomenological description of shock polarization is in good agreement with experiment.

PACS numbers: 62.50.+p

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1. INTRODUCTION

A. V. Stepanov seems to be the first to call attention to the fact that deformation of ionic crystals gives rise to a potential difference between the surfaces of the deformed samples (the Stepanov effect).^[1] Caffin and Goodfellow, ^[2] Fischbach and Nowick, ^[3] and Kiss and Urusovskaya,^[4,5] who investigated this effect in ionic crystals, showed that the potential appears both at stresses below the yield point and during the course of plastic deformation of the crystals, and is caused by the motion of charged dislocations. The sign and the amplitude of the potential depend, in particular, on the concentration and type of impurities, on the rate of deformation, and on the sample temperature. Gul' et al. [6] and Novikov et al. [7] have observed electric charges produced when polymethylmethacrylate is compressed. They have shown that appearance of the charges is connected with orientation of the polar molecules during the course of the deformation, and that the time variation of the polarization is determined by the disorientation of the molecules and by the conductivity of the deformed samples. In the studies cited above, the charges were registered with an electrometer. A charge of $10^{-10}-10^{-8}$ C/cm^2 flowed in the measuring circuit during characteristic time intervals on the order of several seconds.

A similar effect, namely the appearance of a potential difference in deformed samples of non-piezoelectric materials, takes place when these materials are dynamically loaded. It appears that this phenomenon was first revealed in electric induced noise, such as in the so-called "cable effect"^[25]—the emf that appears in electric circuits subjected to shock loading. Eichelberger and Hauver^[8] have observed that the motion of a shock wave (SW) between the electrodes of a capacitor filled with a

polar dielectric is accompanied by the appearance of an emf in the external circuit containing such a capacitor (see Fig. 5). Since there are no external emf sources in the circuit, and the resultant emf does not depend on the material of the capacitor electrodes, the effect can be attributed to volume polarization of the dielectric behind the SW front.

The described phenomenon, which is called "shock polarization" in the literature, was registered by us together with Novitskii, Lisitsyn, Yanov, and Bezrukov^[9] and independently by Linde, Murri, and Doran^[10] in another class of dielectrics-ionic crystals. This effect was later observed by us and our co-workers^[11] and by Jones et al.^[12] in shock compression of doped semiconductors (silicon and germanium). Simultaneously, principally in the USA, investigations were made of the behavior of polarized polycrystalline ferroelectrics^[13] and piezoelectrics^[14] in SW. It was established that the main cause of the emf in ferroelectrics is partial or total loss of the ferroelectric properties, i.e., their depolarization in the SW. On the other hand, the shock-polarization effect in these materials is small, albeit comparable with the polarization of linear dielectrics. According to^[8], the mechanism that causes polarization of polar dielectrics is the orientation of the polar molecules along the direction of motion of the SW front. The molecules are rotated by the pressure gradient on the SW front if one end of the molecular dipole has a larger mass than the other. This oriented state of the molecules is in thermodynamic disequilibrium. In the course of time, the thermal motion of the molecules behind the SW front upsets the oriented state, and as a consequence decreases (relaxes) the polarization. The distinguishing feature of shock polarization is that in the case when the

dielectric behind the SW front turns into a conductor the decrease of the polarization behind the SW front can be due not only to the disorientation of the polar molecules, but also to the screening of the polarization field by the carrier field.

Let us estimate the magnitude of the polarization behind the SW front in polymethylmethacrylate, in which shock polarization was first observed. We assume that the SW orients all the polar monomer links of the molecule of this substance along the direction of the SW front motion.^(B) For polymethylmethacrylate, with molecular weight 10^5 g, the number of monomer links per cm³ is $N=6\times10^{21}$ cm⁻³. In this case the polarization is $P=N\mu$ = 3×10^{-6} C/cm², where $\mu = 1.7$ Debye units is the effective dipole moment of the monomer link of the polymethylmethacrylate molecule. Experiment has shown that at a pressure of 200 kbar on the SW front the polarization of polymethylmethacrylate amounts to $P=2\times10^{-7}$ C/cm².

Electric signals of non-thermoelectric nature were observed following shock compression of metals and semimetals.^[15,16] In a number of cases these signals were due to the screening, by the free carriers, of the perturbations produced by the SW in the metal lattice.

Shock polarization has by now served as the basis for the development of dynamic-pressure transducers. [17-19] transducers for the registration of the instants of the passage of an SW front through specified planes (time markers)¹⁾, ^[20-23] and explosive sources of electric energy.^[24] The results of the investigation of shock polarization of materials explain in a number of cases the sources of the electric static in weak-current measurements (e.g., the "cable effect") and make it possible to develop measuring systems that operate reliably under explosive conditions. The results of the investigations of shock polarization permit a better understanding of the non-equilibrium processes that distinguish dynamic loading from static loading. Polarization experiments have yielded information on certain physical properties of shock-compressed substances. Investigations of the emf produced by shock compression permit a new interpretation of such effects as the appearance of charges and of luminescence in the case of fracture of materials, and electrification by friction.

In this paper we analyze the phenomenological theories of the onset of emf following shock compression of linear and nonlinear dielectrics, and review the experimental work done up to 1975. We discuss the difficulties arising in the phenomenological description and in the physical interpretation of the observed phenomena.

2. PHENOMENOLOGY OF SHOCK POLARIZATION OF LINEAR DIELECTRICS AND DEPOLARIZATION OF NONLINEAR DIELECTRICS

A. Linear dielectrics

The passage of a substance through a shock wave front is accompanied by a jumplike change in its thermodynamic parameters with a simultaneous jump in the entropy. In such a transition the compression of substances having strength and viscosity is not hydrostatic, so that the state of the substance behind the shock wave front is described by a stress tensor with principal stresses that differ by an amount equal to the Hugoniot yield point (~ 0.1-100 kbar).

It is logical to assume that the anisotropy of the stresses produced in a shock wave can lead to anisotropy of the physical characteristics of the substance, for example to a disturbance in the spatial distribution of the charges—shock polarization. Since the polarization state is not in thermodynamic equilibrium, it is obvious that the polarization decays completely with time (after the equilibrium is established in the shock-compressed substance).

The first attempts to describe phenomenologically the effect of shock polarization were made by Ivanov and Novitskil^[120] and by Allison.^[26] In^[120] they postulated the existence of a double layer on the SW front, and solved the problem of the current flowing in the circuit (see Fig. 5) when this layer moves with the shock wave. Cases were considered when the medium behind the shock wave front remained a dielectric or was converted into a good conductor. Allison^[26] proposed that the relaxation of the shock polarization P(t) is described by an exponential law with a characteristic time τ :

$$P(t) = P_0 \exp\left(-\frac{t}{\tau}\right), \qquad (2.1)$$

where P_0 is the jump of the polarization on the shock wave front. It is easily seen that formula (2.1) can be obtained by assuming that each volume element relaxes independently and that $dP(t) \sim -P(t)dt$ at each instant of time. In (2.1), τ is the time of the thermal or of the mechanical relaxation. The presence of free carriers behind the shock wave front leads to neutralization of the polarized volumes of the substance (dipoles). This last process is customarily called conductivity relaxation. This type of relaxation was considered in detail by Zel'dovich.^[27] The characteristic time of the process, in cgs esu, is $\theta_2 = \rho_2 \varepsilon_2/4\pi$ where ρ_2 and ε_2 are the bulk resistivity and dielectric constants of the substance behind the shock-wave front.²⁾

The phenomenology of shock polarization, developed in the papers of Allison, ^[26], Zel'dovich, ^[27] Ivanov, Lisitsyn, and Novitskii ^[28] and Zaidel' ^[29] postulates polarization of an isotropic dielectric on the front of a plane shock wave.

Allison considered a non-conducting dielectric placed between the electrodes of a short-circuited capacitor. It was assumed that the dielectric constant and the polarization of the dielectric change jumpwise on the shock-wave front. Thus, in this theory the polarization current density is $j = f(P_0, \varkappa, \tau, t)$, where $\varkappa = \sigma \varepsilon_2 / \varepsilon_1$ and σ is the compression of the substance on the shock-wave front.

¹⁾Transducers for the registration of the instants of the passage of a shock wave front through specified planes.

²⁾The subscripts 1 and 2 will henceforth label the parameters of the substance ahead and behind the shock-wave front, respectively.



FIG. 1. Calculated plots of the polarization currents $j/j_0 = f(t/T)$. ^[28] The values of the parameters ×, τ/T , and θ_2/T are respectively: $1-1.5;\infty;\infty;2-1.0;\infty;\infty;3-2.0; 1.0;1.0; 4-2.0;5.0;0.2; 5-0.9;2.0;2.0; 6-1.0;1.0;1.0; 7-2.0;5.0; 0.05; 8-1.0;5.0;0.05; 9-2.0; 0.05;0.5.$

Zel'dovich assumed $\tau = \infty$, $\rho_1 = \infty$, $\varepsilon_1 = \varepsilon_2$ and $\sigma = 1$, while ρ_2 could take on any constant value.

In the solution of Ivanov *et al.* it was assumed that the decay of the polarization of the shock-compressed dielectric is due to both mechanical and conductivity relaxation. It was assumed for simplicity that $\rho_1 = \infty$. No limitations were imposed on σ and ε_2 , while ρ_2 could assume any constant value. The dependence of the density of the polarization current j in the short-circuited circuit on P_0 , \varkappa , θ_2 , τ , and t was determined.

The initial current-density jump at $t = t_0 = 0$ is independent of the relaxation processes and is connected with P_0 by the expression

$$\mathbf{j}_0 = \frac{P_0}{xT}, \qquad (2.2)$$

where T = l/D is the time of motion of the shock wave front through a sample of thickness l, and D is the velocity of the shock wave front.

Typical plots of $\mathbf{j}(t)$ for certain combinations of parameters are shown in Fig. 1, from which it follows that if τ and θ_2 are noticeably shorter than T, then a dip is produced on the $\mathbf{j}(t)$ curve, and a current peak is observed at the beginning of the plot. The width of this peak is close to the shortest relaxation time (τ or θ_2).

Zaidel' considered the case of an arbitrary load and imposed no restrictions whatever on the variation of P(t); a jumplike change of ε and ρ was assumed, as before, and their values ahead and behind the shock wave front were assumed to be constant. The obtained differential equation contains, as particular cases, the equations that lead to the solutions of $^{[26-28]}$ and make it possible in principle, by using a computer, to obtain P(t), θ_2 , and \times from the experimental plots of j(t).

Thus, the sequence of studies^[120,26-29] deals with more and more general phenomenological models of shock polarization. This is illustrated by Table I.

Problems dealing with the polarization current in a circuit (henceforth referred to as the polarization transducer, see Fig. 5), with a capacitive load were solved for two polarization mechanisms by Lisitsyn *et al.*^[31] Let us stop to discuss some consequences of the considered theories:

1) Within the framework of the theory of ^[26], Yakushev *et al.* ^[30] have derived an expression for the relaxation current density at t > T under the assumption that at t < T the sample moves as a unit

$$\mathbf{j}_{\mathbf{F}}(t) = -\frac{P_0}{T} \left[1 - \exp\left(-\frac{T}{\tau}\right) \right] \exp\left(-\frac{t}{\tau}\right).$$
(2.3)

Somewhat later, Lisitsyn *et al.*^[31] have shown that allowance for the conductivity of the substance behind the shock wave front does not change the result for a shorted circuit. Thus, the relaxation current in the shorted circuit of a polarization transducer is determined only by the relaxation time τ . The relaxation current flows opposite to the polarization current.

2) Hauver, ^[32] analyzing the circuit of Fig. 5 with a constant voltage source E, and assuming that the dielectric polarization (which is independent of E) is described by Allison's solution, has demonstrated the possibility of experimentally determining ε_2 . The expression obtained by him for the dielectric constant behind the shock wave front is

$$\varepsilon_2 = \sigma^{-1} \left[\frac{l \left(Q_E - Q \right)}{E \varepsilon_0} + \varepsilon_1 \right], \tag{2.4}$$

where $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m is the dielectric constant of vacuum, $Q_E = \int_0^T \mathbf{j}_E(t) dt$ (\mathbf{j}_E is the density of the polarization current in the experiment with the *E* source turned off), $Q = \int_0^T j(t) dt$, and *Q* and *E* are in international-system units;

3) The fundamental differential equation (29) in the case when

$$\theta_1 \sim \theta_2, \ \varkappa \sim 1, \ \theta_1 \ll t_1 \ll T,$$
 (2.5)

takes the form^[33]

Я

×

$$Tt_1 \frac{\mathbf{j}(t)}{\theta_1} = P(t),$$
 (2.6)

$$Tt_1 \frac{\mathbf{j}_P(t)}{\theta_1} = P(t) - P(t-T),$$
 (2.7)

where t_1 is the time required for the electric signal to

TABLE I. Some initial premises of the phenomenological theories.

Theory of	τ	θ_2	×	θ ₁	Load
Allison ^[26] Zel'dovich ^[27] Ivanov <i>et al.</i> ^[28] Zaidel' ^[29]	Arbitrary ∞ Arbitrary ''	∞ Arbitrary ''	Arbitrary 1 Arbitrary "	∞ ∞ ∞ Arbitrary	0 0 0 Arbitrary



FIG. 2. Calculated plots of the polarization currents $i/i_0 = f(t/T)$.^[33] The values of the parameters T/η and T/τ are respectively: 1-1;1; 2-1;0; 3-10;0; 4-0.1;0; 5- ∞ ;1; 6- ∞ ; 10; 7- ∞ ;0.1.

become established in the measuring circuit.

We shall show later on that the conditions (2, 5) are realized, in particular, in shock compression of semiconductors.

Thus, for substances having good conductivity on both sides of the shock-wave front, in contrast to dielectrics, P(t) can be obtained from j(t). Even though Eq. (2.6) is valid only at $t_1 \gg \theta_1$, it makes it possible nevertheless to estimate the value of P(t) close to $t = t_0$, since $\theta_1 \ll T$. If it is assumed that a jump of polarization takes place on the shock-wave front, then, in contrast to dielectrics, for which $j_0 = P_0 / \varkappa T$, for substances with good conductivity, other conditions being equal, the jump of jo turns out to be smaller by a factor t_1/θ_1 . In terms of the equivalent electric circuit, the appearance of the factor t_1/θ_1 = $R/\rho_1 l$ can be attributed to the shunting influence of the sample resistance. It is shown in^[33] that in this case the polarization current i(t) does not depend on the area of the investigated sample. In the more general case^[33] the form assumed for P(t) is

$$P(t) = P_0 \exp\left(-\frac{t}{\tau}\right) \left[1 - \exp\left(\frac{t}{\eta}\right)\right].$$
(2.8)

The factor $\exp(-t/\tau)$ is a consequence of the physically plausible assumption that the process of the mechanical depolarization per unit volume of substance is determined by the time that this volume spends behind the shock-wave front.^[26] The second factor $1 - \exp(-t/\eta)$ reflects the process of establishment of the polarization (an exponential increase of P(t) is assumed). The plots of the polarization $(0 \le t \le T)$ and relaxation $(T \le t \le 2T)$ currents calculated from (2.6) and (2.7), with (2.8) taken into account for different values of τ and η , are shown in Fig. 2. We note that if the polarization on the SW front reaches its maximum value within a time $t < t_1$, then a jump of the current i will be observed at the instant t = T, and the sign of the relaxation current will then be the opposite of the polarization current. If $\eta \sim T$, then the polarization current and the relaxation current have the same sign.

The phenomenology of the polarization of piezoelectrics (particularly of quartz) in elastic waves was considered by Anderson, ^[17] Jones *et al.*, ^[36] and Graham *et al.* ^[37] The following was assumed: a) the deformation of the piezoelectric is homogeneous, b) the electric fields produced as a result of the piezoelectric effect have only one component—in the direction of motion of the shock wave front, c) $\varepsilon_1 = \epsilon_2$ and $\rho_1 = \rho_2 = \infty$, d) the piezoelectric polarization depends only on the applied pressure P = kp. It was shown that at $t_0 \le t \le T$ the current i(t) in the shorted circuit is proportional to the pressure p(t) at the boundary between the screen and the piezoelectric:

$$i(t) = p(t) S \frac{k}{T},$$
 (2.9)

where k is the piezomodulus.

Graham^[39] considered the phenomenology of the polarization of the piezoelectric under conditions of a short shock.

B. Nonlinear dielectrics

As noted in the Introduction, the appearance of an emf following application of a shock to a nonlinear dielectric is due mainly to domain-disorientation processes (depolarization) in the shock-wave front. Although the contribution of the polarization remains the same as for linear dielectrics, it turns out to be small in comparison with the depolarization processes.

Let us examine qualitatively the processes accompanying the propagation of a shock wave along a polarized ferroelectric sample. Figure 3 shows schematically the distribution of the charges in a short-circuited ferroelectric sample prior to (a) and during the course (b) of its shock compression. Prior to the compression, the polarization charge on the surface of the sample was neutralized by the free carriers in the electrodes. Neither current nor field is present in the sample. Let the shock wave enter the sample as shown in Fig. 3b, and let it convert the material behind the shock wave front into the linear dielectric. In this case, an electric-polarization field \mathbf{E}_2 is produced behind the shock wave front, and an opposite field E_1 is produced ahead of the shock wave front. This process causes part of the free charge to flow over. The change of the fields and the flow of the charges will continue until the shock wave front leaves the sample. The decrease of the polarization behind the shock wave front can be the result, for example, of a phase transition, of domain reorientation, and/or of a decrease in the dipole moment upon compression of the sample.

Thus, the pictures of the redistribution of the free charges in nonlinear and linear dielectrics at $\tau \gg I$ are qualititatively similar. The only difference is that the material of a linear dielectric is not initially polarized,



FIG. 3. Distribution of the charges in a short-circuited ferroelectric sample prior (a) and during the course (b) of its shock compression. $^{[34]}$



FIG. 4. Calculated depolarization-current curves. ^{E51} The values of the parameters τ' , θ'_1 , and \times^* are respectively: 1-.1; ∞ ; 0.5; 2-0.1; ∞ ; 0.5; 3-0;1; 0.5; 4-0; ∞ ; 2; 5-0;1; 2; 6-.0.1; ∞ ; 2; 7-0; 0.1; 0.5; 8-1; ∞ ; 0.5; 9-0; ∞ ; 8; 10-0;1; 8; 11-0; 0.1; 2; 12-1; ∞ ; 2; 13-0; 0.1; 8. Top-normalized hysteresis loop in coordinates $E'_1 = -(E_1/E_c)$ and $F' = -F/P_s$, where E_c is the coercive field, F' is the surface density of the bound charges, and P_s is the spontaneous polarization.

whereas the material of nonlinear dielectric is polarized but the polarization prior to the experiment is compensated by the free charges.

The phenomenology of the impact depolarization of the nonlinear dielectrics was first considered by Halpin.^[34] The main premises of this theory are the following:

1) The shock wave converts jumpwise a nonlinear isotropic dielectric into linear one; in this case a charge equal to the residual polarization P_0 is released on the shock wave front. 2) The plane shock wave compresses the dielectric once. 3) The static dielectric-hysteresis loop does not change under the conditions of the rapid variation of E ahead of the shock wave front. 4) The dielectric constant and the bulk resistivity ($\rho_1 = \infty$) on the shock wave front change jumpwise. 5) The vectors \mathbf{P}_0 and D are parallel. 6) The load circuit is shorted.

A more general problem was solved by Novitskii *et al.*^[35] They assumed, in particular, that the load circuit contains an active resistance, and that the polarization of each volume element behind the shock wave front depends only on the time that the volume remains in the compressed state. The solution of ^[35] yields, as particular cases, all the shock-polarization theories considered above for linear dielectrics in Halpin's phenomenology. For nonlinear dielectrics at $t = t_0 = 0$ (shorted circuit)^[35] we have

$$j_{0} = \frac{P_{0}}{x^{*T}},$$
 (2.10)

where $\kappa^* = \sigma \varepsilon_2 (\partial D_1 / \partial E_1)_{B_1=0}^{-1}$, while D_1 and E_1 are the induction and the electric field intensity. If it is assumed, as was done by Halpin, that $(\partial D_1 / \partial E_1)_{B_1=0} = 0$, then $j_0 = 0$. The influence of the inductance of the circuit on the form

of i(t) was taken into account in^[35] for several particular cases.

Figure 4 shows the calculated plots of i(t) in accordance with^[35] in the dimensionless coordinates I' and (t/T) for a number of combinations of the parameters $\tau' = \tau/T$, $\theta'_2 = \theta_2/T$, and κ^* for the hysteresis loop shown on the top of Fig. 4. The calculation was performed for the case $t_1 = 0$, $\theta_1^{-1} = 0$, $P(t) = P_0 \exp(-t/\tau)$, $I' = i(t)T/P_0S$.

Stuetzer^[97] considered secondary dynamic pressures that are produced ahead of a shock wave front in a piezoelectric under the influence of fields caused by the presence of the closed circuit. It was assumed in^[17, 34-36] that during the time that the shock wave front moves through the piezoelectric the latter is not compressed ahead of the shock wave front. This is valid for an open circuit. In the case of a shorted circuit, the field induced by the shock wave produces a counterfield in the region ahead of the shock wave front. If the electromechanical coupling coefficient of the material is large, then the counterfield can cause noticeable secondary dynamic pressures that vary with time and influence the shape and magnitude of the polarization current. The solution of this problem at constant p(t) leads to the following form of the polarization current density:

$$\mathbf{j}(t) = \frac{kp}{T} \exp\left(\frac{r^2 t}{T}\right),$$

where r is the electromechanical coupling coefficient. Thus, the depolarization current is not constant in the shorted circuit through which a shock wave with constant p(t) passes. For quartz we have $r^2 = 0.01 (\exp[r^2 t/T] \approx 1 \text{ at } t = T)$, and for lead-zirconate-titanate systems $r^2 = 0.25$ and $\exp[r^2 t/T] \approx 1.3$.^[97]

The effect exerted on i(t) by the fact that not all parts of the SW front enter the sample simultaneously will be considered below.

3. EXPERIMENTAL STUDIES

Experimental investigations of the emf produced upon shock compression of substances followed three directions. In the first direction, the emf is connected with the type of the substance (dielectric, semiconductor, metal) and with the shock-wave parameters. The second direction is an investigation of the dependence of the emf on the physical characteristics of the substances and the shock-parameters, such as the crystallographic direction of the loading, the volume state of the impurities, etc. In the studies of the third direction, measurements are made of the conductivity, dielectric constant, and the polarization parameters of the shock-compressed bodies.

A, Experiments

In all the investigations, electric signals produced by shock compression of the substances were investigated by using the setup illustrated in Fig. 5. The electrode and the guard ring were made of metals whose acoustic rigidity was close to that of the sample material. The quantities registered in the experiment



FIG. 5. Diagram of experimental setup. 1) Electrode, 2) guard ring, 3) metallic screen, 4) sample; $R = 92 \Omega$ —input resistance of the oscilloscope, R_1 —resistance of guard ring. The arrows show the direction of the shock wave front motion.

were the voltage drop U(t) = i(t)R, where i(t) is the polarization current and R is the input resistance of the recording unit. As a rule, U(t) is produced jumpwise at the instant when the shock wave reaches the boundary between the screen and the sample (t_0) . The instant t = T at which the shock wave leaves the boundary between the sample and the electrode corresponds to a break on the U(t) curve. It is shown in^[8,44,68] that the polarization current in dielectrics is directly proportional to the electrode area. Therefore, using the guard ring, at $R = S_1 R_1 / S$, where S and S_1 are respectively the areas of the electrode and of the guard ring, it is possible to avoid the influence of the edge effects on the measurement results. Usually $S_1 = S = 1$ to 3 cm², l=0.1 to 1 cm, and $R_1 = R = 92 \Omega$. In the case of dielectrics and semiconductors with $\rho_2 \approx 10^3 \ \Omega$ -cm, these parameters ensure that the conditions for the circuit to be shorted are satisfied $(t_1 \sim 10^{-9} \sec \ll T)$. In the case of nonlinear dielectrics, the depolarization effect in the shock wave was investigated in a circuit with $R = 1 \Omega$ with an adjustable value of the inductance $L \approx 5-100$ nH.

The geometry of the explosive devices ^[40, 41] and the dimensions of the samples were such that the attenuation of the plane shock wave and the influence of the lateral relaxation during the course of the experiment could be neglected. The time spread of the entry of the shock wave into the sample was $t_f \approx 0.02-0.1$ µsec on an area S=12 cm². The influence of the curvature of the shock wave front on i(t) in a linear dielectric and of the tilting of the shock wave front on i(t) in a nonlinear dielectric is discussed in the papers of Yakushev *et al.* ^[42,43] and Halpin. ^[34] It is shown in these papers that t_f plays an essential role in the interpretation of i(t) in the regions $\tau \ll t_f$ and $\theta_2 \ll t_f$. In most cases, however, $\tau > t_f$.

The idea of measuring the time of mechanical relaxation of the polarization was proposed by us and our coworkers^[44] and was first realized by Yakushev *et al.*^[45] The method was based on registering the current in the circuit of Fig. 5 after the shock wave front leaves the sample. The value of τ is calculated from formula (2.3). The method of^[44, 45] does not make it possible to measure $\tau \leq t_f$ and $\tau \leq t_1$. We note that if the investigated substance becomes conducting behind the shock wave front then the relaxation signal can become distorted as a result of electrochemical processes on the shockcompressed boundaries between the screen and the sample and between the sample and the electrode, ^[43] as well as because of violation of the conditions for the shortcircuiting of the circuit.

If a voltage source with calibrated amplitude and with small internal resistance (e.g., a charged capacitor) is connected in series with the circuit of the electrode and the guard ring of Fig. 5, then by registering the voltage drop U(t) across R we can obtain information on the conductivity $\Sigma_2^1(t)$ of shock-compressed substances in a direction normal to the shock-wave front. Such a scheme was first described by Al'tshuler et al. [46] and discussed in detail by Mitchell and Keeler.^[47] This scheme, with suitable choice of the circuit parameters, was used by us and by others^[23,48] to register, in a single experiment, the polarization and the conduction signals. The latter is necessary to eliminate the influence of shock polarization on results of the measurements of Σ_2^1 , inasmuch as the polarization current becomes comparable with the conduction current in a number of cases, and may even exceed it.^[49] Electric-contact^[46] or polarization^[48] pickups were used to determine the spread in the time of passage of the shock wave front to a given area in the sample and in the instant of the increase of the Σ_2^{\perp} behind the shock wave front to the level resolved by the measuring circuit.

A system for measuring the conductivity $\Sigma_2^{"}$ in the direction parallel to the shock wave front was proposed by David and Hamann^[50] and by Juigneau and Thovenin.^[51] The complicated geometry of the electric field in the samples called for an exact calculation of the value of $\Sigma_2^{"}$ by electrolytic simulation.^[52] A mathematical relation between U(t) and $\Sigma_2^{"}$ was obtained in^[53, 54] for the case of a parallel-plate capacitor in which the shock wave propagated parallel to its electrodes.

Hauver^[32] proposed two experimental methods for the determination of ε_2 . The first is based on the use of formula (2.4), and the second consists of exciting, by means of the polarization current, an *LR* network connected in the circuit in the circuit of Fig. 5. Yakushev *et al.*^[55] developed high-frequency methods of measuring ε_2 , namely an amplitude-frequency method and a tank-circuit method. In most cases, use was made of the equations of state of the investigated substances as obtained by Al'tshuler, ^[40] Van Thiel, ^[56] and McQueen and March.^[57]

B. Experimental results

1) Linear dielectrics. Ionic crystals. Shock polarization of ionic single crystals and polycrystals was investigated systematically as a function of the shock wave amplitude (p=5-1000 kbar), of the crystallographic loading direction ([100],[110],[111]), of the microphysical characteristics of the initial samples, of the type of lattice (LiF^[61, 63], NaCl^[9,10,44,58], NaF, KCl^[10, 60], KBr^[61], RbCl, KI^[10, 60], RbI^[60], MgO^[59], Li⁷H, Li⁶D^[60]lattice of NaCl type, NaCl, CsI^[10, 62], CsBr-lattice of CsCl type), of the degree of the ionic bond (NaCl-LiH), of the concentration, sort, and valence of the doping impurities (Ca²⁺, Sr²⁺, Mn²⁺, Mg²⁺, I⁻, F⁻) and of their volume distribution (Table II), and of the dislocation density (10^3-10^7 cm⁻²).

Typical oscillograms of polarization currents are

TABLE II. Concentration of doping impurities in NaCl and LiF samples.

		NaCi											
Doping impurity Concentration of doping	Ca ²⁺	Ca ²⁺	Ca2+	Mn ²⁺	Sr ²⁺	I-	F-	Li+	Mg ²⁺				
impurity, mol.%	5.10-3	5-10-2	5-10-1	8-10-4	1 - 10-2	2.10-1	2.10-2	3-10-2	5.10-2				
Index of sample	11	111	IV	v	VI	VII	VIII	IX	11				
The nominally pure samples (NaCl I and LiF I) contain 5×10^{-4} mol.% of polyvalent impurities.													

shown in Fig. 6. It was established in the experiments that the polarization current begins to flow at the instant when the shock wave enters the sample and decreases abruptly at the instant when the shock wave leaves the sample. The rise time of the leading front U(t) is $\eta \simeq 0.02-0.10 \ \mu$ sec and is governed mainly by the tilt of the shock-wave front. It can therefore be assumed that, accurate to 10^{-8} sec, the current in the circuit to Fig. 5 is produced instantaneously, and the true value of the current at the instant that the shock wave enters



FIG. 6. Typical oscillograms of the voltages U(t). 1-3) Ionic crystals (1-NaCl I, p = 100 kbar, S = 1 cm²; 2-KBr, p = 78kbar, $S=1 \text{ cm}^2$; 3-NaCl I, p=116 kbar, $S=1 \text{ cm}^2$). 4-6) Polar organic dielectrics 4)—polyamide resin, p = 45 kbar, S = 12.5 cm^2 ; 5) dibutylphthalate, p = 100 kbar, S = 12.5 cm²; 6) TNT, p = 36 kbar, S = 12.5 cm²). 7-9) Ferroelectrics; (7-lead zirconate titanate TsTS-19, p=5.5 kbar, T/t=2; 8-TsTS-19, p=5.5 kbar, $S=1.3 \text{ cm}^2$, $T/t_1=10$; 9-LiNbO₃-the arrows correspond to the successive instants of entrance of the shock wave into the sample from an iron screen with pressures 20, 110, and 190 kbar). 10-12) Semiconductors (10-KDB, $\rho_1 = 0.02$ Ω -cm, p = 20 kbar; 11-KDB, $\rho_1 = 35 \times 10^3 \Omega$ -cm, p = 40 kbar; 12-KDB, $\rho_1 = 7.5 \Omega$ -cm, p = 46 kbar. 13-15) Metals (13-europium, p = 170 kbar; 14-ytterbium, p = 120 kbar; 15-ytterbium, p = 200 kbar). Time markers 1 to 10 and 12 to 15-0.1 μ sec, 11-1 µsec; sweep from left to right. Arrows-instants of entrance and exit of shock wave from the sample. U-amplitude calibration: 1-3.2V, 2, 10, 11, 12-0.15 V; 3-7.9 V, 4,5-1.5 V; 6-1.1 V; 7-9-70 V, 13-15-0.11 V.



FIG. 7. Dependence of Q_0 on the compression σ for NaCl II loaded along the crystallographic directions [100] (a), [110] (b), and [111] (c). ^[66] Each point on the plot of the result of a separate explosion experiment.

the sample can be obtained by extrapolating the plot of i(t) to the instant t_0 . The results of experiments with NaCl and KBr have shown that $i_0 = i(t_0) \sim S/T$. This has made it possible, by using expression (2.2) $Q_0 = j_0 T$ = P_0/\varkappa = const at σ = const, to compare the values of Q_0 in experiments with different *l* or *S*. Plots of $Q_0(\sigma)$ for the three principal crystallographic directions of NaCl are shown in Fig. 7. The main results of the experimental investigation of nominally pure crystals with NaCl lattices are the following:

a) For a given crystal, $Q_0(\sigma)$ increases monotonically to a certain value $Q_{0 \text{ max}}$ (at $\sigma \approx 1.3$), and changes abruptly in sign and magnitude at $\sigma \approx 1.3$ (the so called $Q_0(\sigma)$ anomaly⁹). Exceptions are LiF and MgO, where the sign of Q_0 does not change when the maximum is reached (at $\sigma \approx 1.3$). We note that $\Theta_2 \ll T$ for the investigated crystals at $\sigma \ge 1.5$. According to the phenomenological theories, at $\theta_2 \ll T$ the polarization signal degenerates into two sharp peaks that occur at the instants when the shock wave enters and leaves the sample. Owing to the limited bandwidth of the measuring circuit and to the fact that the shock wave does not enter into the sample instantaneously, these peaks cannot be resolved by the apparatus. Therefore the dependence of $Q_0(\sigma)$ in the region of σ where $\theta_2 \ll T$ is not known sufficiently reliably.

b) In the interval $\sigma \approx 1.03-1.3$, all the investigated crystals have a positive Q_0 .

c) In KCl and KBr, reversal of the sign of i(t) was observed in the course of the motion of the shock wave front through the sample. This phenomenon takes place only at $l \ge 0.3$ cm (KBr). In terms of σ , the reversal of the polarity of i(t) in KBr precedes the $Q_0(\sigma)$ anomaly.

d) $Q_{0\max}$ depends on the type of crystal—the difference can reach two orders of magnitude (MgO and RbI). In the case of one and the same crystal, $Q_{0\max}$ depends on the loading direction. In NaCl at $\sigma \leq 1.3$ the value of Q_0 correlates with the degree of ease of the plastic deformation at different loading directions, namely, the "soft" direction [100] corresponds to $Q_0[100] > Q_0[111]$. To the

TABLE III. Values of Q_0 for shock loading of Li^7H and Li^6D single crystals along [100].

Crystal	Li	۶H	Li ⁶ D						
σ	1,	31	1.31						
$Q_0 \cdot 10^8$, Coul/cm ²	31.0	23.8	18.0	24.8	21.7				

contrary, past the $Q_0(\sigma)$ anomaly, the maximum value of Q_0 corresponds to the "hardest" direction [111].

In contrast to NaCl, the anisotropy of the polarization of LiF up to $\sigma \leq 1.3$ is not constant. In particular, in the region of small σ ($\sigma \leq 1.16$) we have $Q_0[111] \gg Q_0[100]$, i.e., under these compressions the anisotropy of the polarization does not correspond to the anisotropy of the plasticity.

e) If NaCl is loaded along [111], the sign of Q_0 reverses once more at $\sigma = 1.47$.

Plots of $Q_0(\sigma)$ for CSI loaded along [100], [110], and [111] are shown in Fig. 8. Let us note the most important features of shock polarization of CSI and CSBr: a) Q_0 is a complicated function of σ and of the direction of loading. $Q_{0\text{max}}$ is comparable in magnitude with that for NaCl. b) The anisotropy of the polarization changes with increasing compression: at $\sigma = 1.05 - 1.25$ the value of Q_0 is larger for loading along the "hard" [100] direction than for loading along the "soft" [111] direction; at $\sigma = 1.25 - 1.4$, the $Q_0(\sigma)$ curves are arranged in the order of the hardness of the directions: $Q_0[100] < Q_0[110]$ $< Q_0[111]$.

The values of Q_0 in Li⁷H and Li⁶D at $\sigma = 1.31$ are listed in Table III. If it is assumed that $\varkappa_{Li^7H} = \varkappa_{Li^6D}$, which is quite likely in view of the similarity of the physical properties of these compounds, then it follows from Table III that the values of P_0 for Li⁷H and Li⁶D are equal, apart from the experimental scatter. Hence, taking into account the insignificant change in the cation mass and the appreciable change in the anion mass on going from



FIG. 8. Plots of Q_0 against the compression σ for NaCl I loaded along the crystallographic directions [100] (a), [110] (b), and [111] (c).^[62]



FIG. 9. Curves illustrating the connection between $Q_{0\max}$ and the characteristics of the host lattice of the investigated crystals: r_{\star} (curve 1), ϵ_1 (curve 2), γ (curve 3). $Q_{0\max}$ is given in coulombs/cm².

 $Li^{7}H$ and $Li^{6}D$, we can conclude that the effect does not depend on the anion mass. This conclusion confirms the constancy of Q_{0} in the sequence KCl-KBr-KI at constant σ , where the mass of the anion increases 3.5 times while the mass of the cation remains constant.

An analysis of the data on impact polarization of nominally pure ionic crystals shows that at constant σ and constant orientation of the samples relative to the shock wave propagation the value of $Q_{0 \max}$ is connected with the characteristics of the lattice under normal conditions (Fig. 9): a) For compounds with NaCl-type lattice at a given cation, $Q_{0 \max}$ remains unchanged when the anion is replaced. b) In the same compounds, $Q_{0 \max}$ decreases with increasing cation radius. c) Regardless of the type of lattice, $Q_{0 \max}$ decreases with decreasing parameter $\gamma = \Delta \varepsilon / \Delta E \cdot a$, where $\Delta \varepsilon$ is the difference between the low-frequency and high-frequency dielectric constants, ΔE is the width of the forbidden band in the electron spectrum of the crystal, and a is the lattice parameter.

The role of the impurities in the effect was investigated by Tyunyaev *et al.*^[62-65] and Wong *et al.*^[8] It was established that Q_0 of NaCl and LiF doped with divalent metallic impurities depends on the concentration (c) and on the volume state. In NaCl: Ca²⁺, the $Q_0(\sigma)$ curves for different values of c are approximately equidistant up to $\sigma \approx 1.3$ (Fig. 10). From the course of these curves it follows that the impurity component of the polarization Q_0^{imp} is due to Ca²⁺. The quantity Q_0^{imp} can be defined as $Q_0^{imp}(c) = Q_0(c) - Q_0^p$, where $Q_0(c) = Q_0$ in doped



FIG. 10. Dependence of Q_0 on the compression σ for NaCl: Ca⁺⁺ loaded along [100].^[66] 1-NaCl I, 2-NaCl II, 3-NaCl III, +-NaCl IV.

TABLE IV. Dielectric parameters of shock-compressed NaCl I and NaCl III.

	p, kbar:	20	53	100	152
NaCl I	τ, μsec	0.27 (maximum estimate)	0.09 ± 0.02	0.08 ± 0.03	0.08±0.02
NaCl II	ε ₂ θ ₂ , sec τ, μsec	10±3 10 ⁻⁶ 0.18±0.09	0.19±0.12		

NaCl, and $Q_0^p = Q_0$ in ideally pure NaCl. Recognizing that even in nominally pure NaCl we have $c \approx 5 \times 10^{-4}$ mol. %, and on the other hand that Q_0 in this substance does not depend on the volume state of the divalent metallic impurities, we can set Q_0^p equal to the value of Q_0 of nominally pure NaCl. According to^[54], in NaCl: Ca²⁺ the value of Q_0^{imp} depends on the Ca²⁺ concentration and on its volume state in the lattice (isolated Ca²⁺ ions, isolated dipoles: Ca²⁺-cation vacancy, aggregates of dipoles). At constant σ , an anisotropy of the impurity polarization is observed: $|Q_0^p|[100] \gg |Q_0^p|[110]$, and $|Q_0^p|[111] = 0$ accurate to within the limits of experimental error.

Experiments with NaCl crystals doped with monovalent impurities (NaCl VII, VIII and IX), or bombarded with γ rays (NaCl I, irradiation dose 10⁸ rad, *F*-center concentrations not less than 10¹⁸ cm⁻³), and with NaCl II crystals, in which the density of the aged dislocations ranged from 10³ cm⁻² to 10⁷ cm⁻², has shown that, other conditions being equal, these factors do not change the form of i(t) or the value of Q_0 . It is shown in^[66] that in NaCl I at p = 20 kbar the value of ε changes jumpwise behind the shock wave front and amounts to $\varepsilon_2 = 10 \pm 3$. The values of t determined for NaCl I and NaCl III are shown in Table IV.

A review of the experimental data on the conductivity of shock-compressed substances, including ionic crystals, was written by Doran and Linde.^[67] However, most papers cited in^[67] on ionic crystals, just as in^[53], do not contain data of importance from the point of view of the conductivity of the ionic crystals, such as the chemical compositions of the samples. For this reason we shall dwell only on the results of Tyunyaev *et al.*^[54]

Tyunyaev et al. [54] investigated the crystals NaCl II, III, and γ -irradiated NaCl I at p = 20, 45, 53, 100, 116,and 276 kbar. The results of the experiments are shown in Fig. 11: a) A $\rho_2^{\perp}(t)$ distribution exists at p = 20-276kbar; b) the $\rho_2^1(t)$ curves for NaCl I and NaCl II coincide at p = 20 and 116 kbar within the limits of experimental error; c) at p = 20-116 kbar, a 100-fold increase of the Ca^{2*} concentration leads (at constant p) to a decrease in the minimum value of $\rho_2^{\perp}(t)$ by a factor of approximately 6; d) at p = 53 kbar, the conductivity is anisotropic: at conductivity of NaCl I in the direction parallel to the 0.5 < t < 1.5 sec, the shock wave front is higher than in the direction normal to the front and the maximum difference reaches two orders of magnitude; e) the rate of decrease of $\rho_2^{"}(t)$ is much less for NaCl I than for NaCl п.

1.1) Polar dielectrics. Investigations were made of

polymethylmethacrylate (organic glass), $^{[6,43,45,68-70]}$ polystyrene, $^{[68,71,72]}$ polyethylene and *o*-nitroanisole, $^{[32]}$ epoxy resins (their components), $^{[71]}$ vinyl plastic, teflon, polyvinyl chloride plastic, lavsan polyester, caprolone, $^{[21,72]}$ explosives (TNT^[23,73-75,48] and hexolite^[761]), and water^[8,43,77-80,85]. Some oscillograms of the signals are shown in Fig. 6. Investigations of these compounds in the interval p = 20-500 kbar have shown the following:

a) The registered values of Q_0 lie in the interval from $\sim 10^{-7}~{\rm coulomb/cm^2}$ (organic glass) to $10^{-11}~{\rm coulomb/cm^2}$ (polypropylene); b) in a number of cases (for example epoxy resins, polyethylene, and TNT), the $Q_0(\sigma)$ anomaly and the reversal of the sign of i(t) are observed; c) in polystyrene (p = 20-170 kbar), $Q_0(\sigma)$ is independent of the molecular weight as the latter is increased from 70 thousand to 2 million; the maximum value Q_0 in toluene, which is the initial product used to manufacture TNT, is smaller by at least two orders of magnitude than in TNT; d) when polystyrene is used as a filler in certain epoxy resins (p = 20-50 kbar), oscillograms with j = 0and with subsequent monotonic increase of j(t) are observed; e) in organic glass (p = 150 kbar), the shock wave reflected from the electrode produces at t = T polarization of the same sign as the incident shock wave; f) in the case of shock compression of water, the magnitude of the signal $(\sim 1 \text{ V})$, depends on the metallic screen material and the electrode material, and differs, for example, by 0.5 V for the systems Cu-H₂O-Cu and $Al-H_2O-Al$ at p=100 kbar. When the surface-active sodium stearate is added to the water, the polarity of the signal is reversed. The conductivity of the water at p = 100 kbar is the same as the conductivity of 5N solution of HCl in water at room temperature $(\Sigma \sim 1 \ \Omega^{-1} \ cm^{-1})$.^[103]

Yakushev *et al.*^[30] have shown that $\tau = 1 \mu \sec$ in organic glass (p = 100-170 kbar), and $\tau = 0.15 \mu \sec$ in vinyl plastic (p = 150 kbar). $\tau = 0.25$ sec in epoxy resin (p = 30 kbar).^[43] Measurements of ε_2 in nitrobenzene^[55] at pressures up to 120 kbar have shown that $\varepsilon_2/\varepsilon_1 \sim \sigma$.

The electric conductivity of the TNT explosion products was measured by Brish *et al.*^[52] When *p* changed from 100 to 500 kbar, the value of Σ_2'' of TNT increased from 5 Ω^{-1} cm⁻¹ to 50 Ω^{-1} cm⁻¹. Ivanov *et al.*^[23, 48] ob-



FIG. 11. Plot of ρ_2 vs the time t. ^[54] 2,3,5,6-NaCl I; 4-NaCl II; 1,7-NaCl I (γ -irradiation); 1-S) ρ_2^1 ; 6,7) $\rho_2^{"}$; p(kbar): 1,2,4) 20; 6,7) 4.5; 5) 276.

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TABLE V. Distance δ (or time interval Δt) over which the resistivity ρ_2^{\downarrow} of TNT is $\leq 10 \ \Omega$ -cm.

p, kbar	Δt , $\mu \sec$	ð, cm				
17	0.63	0.23				
36	0.46	0.17				
190	0.07	0.05				

served experimentally a transition conduction band in TNT in p = 17.36 and 190 kbar (detonation pressure). In the latter studies it was found that the final value of ρ_2^{\perp} is $\leq 10 \ \Omega$ -cm, regardless of the shock wave pressure. However, the distance δ (or the time interval Δt) from the shock wave front at which this value of ρ_2^1 is reached increases with decreasing pressure (Table V). A distribution of ρ_2^1 was observed by Zubkov *et al.*^[81] in PETN and in hexogene, by Dremin et al. [82] in nitromethane by Yakushev^[43] in nitrobenzene, and by Kuleshova^[53] in teflon. Keeler and Mitchell^[83] and Champion^[102] have shown that the electric conductivity of polyethylene and teflon behind a shock wave front (p \simeq 300-500 kbar) increases by 12-14 order of magnitude. The measured dielectric parameters of polyethylene and o-nitroanisole are listed in Table VI.

The electric signals in nonpolar organic dielectrics (carbon tetrachloride, ^[84, 69] benzene^[42, 43]) are observed only in the shock wave reflected from the electrode. The amplitudes and signs of these signals depend on the properties of the electrode metal.

Kochnev^[85] observed emf in shock compression of metal-electrolyte (solutions of H_2SO_4 or HBr)-metal systems. It was established that the emf depends on the type of electrode material, on the electrolyte, on the shock wave parameters, and varies in the interval from 1 V to $-2 V (p \le 50 \text{ kbar})$.

Thus, the results of the investigations have shown that the polarization of ionic crystals and of polar dielectrics in a shock wave is approximately of the same magnitude and is characterized by the $Q_0(\sigma)$ anomaly and by the reversal of the polarity of i(t). It has been shown that polarization of ionic crystals in shock waves is connected with the lattice of these compounds. However, attempts to trace the connection between the polarization and the macroscopic characteristics of the investigated polar dielectrics have not succeeded.

1.2) *Piezoelectrics*. The most completely studied were the properties of shock-compressed tourmaline

TABLE VI. Dielectric parameters of shock-compressed substances.

Substance	p, kbar	ρ⊥, Ω-cm	τ, μsec *)	Q ₀ , Coul/cm ²	θ ₂ , μsec	Ref.
Polyethylene o-nitroanisole	47 67	$\sim 10^{7}$ **) 10^{1} $- 10^{2}$	0.01 0.01	10 ⁻¹¹ 10 ⁻⁸	10 ⁻⁶ -10 ⁻⁵	32 32
*The values given in ^[32] **Estimated	of τ and \cdot	$d Q_0$ were	calculated i	from the po	larization s	' ignals

TABLE VII. Dependence of the piezomodulus of quartz (x-cut) on the initial temperature.

<i>Т</i> , °К	h, Coul/cm ² kbar	Ref.
573 373 298 79 4.2—1.5	$\begin{array}{c} 1.895 \cdot 10^{-8} \pm 1.47 \cdot 10^{-10} p \\ (2.05 \pm 0.1) \cdot 10^{-8} \\ 2.01 \cdot 10^{-8} \pm 1.1 \cdot 10^{-11} p \\ 2.11 \cdot 10^{-8} \pm 5.5 \cdot 10^{-11} p \\ 2.32 \cdot 10^{-8} \end{array}$	87 88 87, 89 87, 89 87, 89 88

and quartz. It was shown that in the case of z-cut tourmaline the electric charge Q (Coul/cm²) realized in the external circuit is $Q = 2.85 \times 10^{-8} p$ at p < 7 kbar and Q= 10.1 $10^{-8} + 1.36 \cdot 10^{-8} p$ at 7 kbar kbar.^[86]

The results of investigations of the piezoelectric properties of x-cut synthetic α quartz in plane shock waves were reported by Anderson. ^[17] We denote, as in^[17], the quartz orientation by "+x" in the case when the shock wave propagates along the quartz in a direction from the plane in which the negative charge is released to the plane where the charge is positive. In the opposite case the quartz orientation is designated "- x." Experiment has shown that for the "+x" orientation the value of Q depends linearly on p in the range p = 8-25 kbar. For the "-x" orientation, the Q(p) dependence is linear only at 8 kbar kbar (the polarity effect). The piezoelectric modulus of the "+ x"-cut quartz is $k = 2.4 \times 10^{-8}$ Coul/cm²kbar at p < 6 kbar and $k = 2.15 \times 10^{-8}$ Coul/ $cm^{2}kbar$ at 9 kbar < p < 18 kbar.^[37] The dependence of the piezoelectric modulus of "+x"-cut quartz on the initial temperature is given in Table VII.

Anderson^[17] has shown that the piezoelectric modulus of "+ x"-cut α quartz under conditions of shock loading corresponds to the theoretical value of the piezomodulus calculated using elasticity theory.

2) Nonlinear dielectrics. In 1957, Neilson reported depolarization of barium titanate in shock waves.^[13] Reynolds *et al.*^[90] and Doran^[91] found that the Hugoniot yield point $p_{\rm HYP}$ of barium titanate is equal to 25–30 kbar, and the two-wave configuration (elastic and plastic waves) is preserved up to $p \approx 500$ kbar. At $p = p_{\rm HYP}$, complete depolarization of the barium titanate takes place, in which case $\epsilon_2 \approx 2\epsilon_1$ and $p_2^{\rm L} \approx 10^4 \ \Omega$ -cm.^[92] Linde advanced some experimental evidence that the depolarization of barium titanate is irreversible.^[93] The piezomodulus of barium titanate is larger by approximately two orders of magnitude that the piezomodulus of quartz and amounts to $k = (0.8-1.2) \times 10^{-6}$ Coul/cm²kbar.^[94]

Neilson^[13] has observed that samples of the polarized lead-zirconate-titanate (LZT) system become depolarized in shock waves. The investigations of Reynolds *et al.*^[90] and of Novitskii *et al.*^[85] have shown that the Hugoniot yield point of LZT 52/48 (LZT-19)³⁾ is p_{HYP} = 19-20 kbar. An increase of the lead zirconate content in the investigated system to 95 mol.% (LZT 95/5) increases the Hugonoit yield point to p_{HYP} = 40 kbar.^[91]

³⁾LZT 52/48 is a solid solution consisting of 52 mol.% lead zirconate and 48 mol.% lead titanate.



FIG. 12. Dependence of the realized charge Q and of the internal resistance of LZT-19 on the pressure in the shock-wave front.^[95] L (nH): 1-50-100, $2-\leq 3$, l=1.5 mm; R=1 Ω (for curves 1 and 2).

The two-wave configuration (elastic and plastic waves) exists for LZT 52/48 up to $p \approx 200-220$ kbar and for LZT 95/5 up to $p \approx 140$ kbar. Complete depolarization of LTZ takes place at $p = p_{\text{HYP}}$. ^[90,91,95] The dependence of the realized charge in the circuit on the pressure in the shock wave front Q(p) for LZT-19 is shown in Fig. 12. At $p > p_{HYP}$ the value of Q decreases; the smallest value of Q is observed at a pressure sufficient to compress the ceramic to crystal density. The value of Qthen increases, and reaches a maximum at $p \approx 150$ kbar. This is followed by a decrease of Q. These data were obtained with LZT samples with orientation "+" (analogy with quartz). The charge realized on samples with orientation "+" (prepared by the hot-pressing technology), other conditions being equal, is less than for samples with orientation "-." The internal resistance of a shock-compressed LZT-19 sample of 15 mm diameter and 1.5 mm thickness lies in the interval from 75 to 150 Ω at p = 50-150 kbar (Fig. 12).^[95] The function Q(p) for LZT 52/48 is linear in the interval $p \simeq 1-10$ kbar. The piezomodulus in this case is $k = 3 \times 10^{-6}$ Coul/ cm²kbar.^[90] Investigations^[90, 96] have shown that the piezomodulus of LZT 52/48 depends on the pressure rise time. Thus, for example, $Q \approx 8 \times 10^{-6}$ Coul/cm², is produced at a pressure 3 kbar in the shock wave, but when the same pressure is applied with a rise time 3 μ sec the result is $Q \approx 25 \times 10^{-6}$ Coul/cm². Under static conditions, $Q \simeq 28 \times 10^{-6}$ Coul/cm². These data indicate that at a pressure ~ 3 kbar the relaxation time of the depolarization (of the domain processes) of the American piezoceramic LZT 52/48 is of the order of milliseconds.^[90] The results of similar investigations by Khokhlov, Luchinin, and ourselves have shown that in the pressure range 0.003-0.48 kbar and at a pressure rise time $0.1-25000 \ \mu sec$, the most pronounced relaxation time of the Soviet piezoceramic LZT-19 amounts to ~ 40 µsec.

For a correct determination of the time dependence of the depolarization current i(t), the parameters of the measurement circuit must satisfy the condition $T/t_1 \gg 1$, where $t_1 = 2L/R$ is the time needed to reach the steady state and L is the inductance of the measurement circuit. As shown by Novitskii *et al.*, ^[95] this condition was not satisfied in^[34] in the investigation of the depolarization of the piezoceramic LZT 52/48 in a shock wave. It is shown in^[95] that at $T/t_1 \simeq 10-100$ a current jump i_0 is registered on the i(t) oscillograms at $t = t_0$. At $T/t_1 \gg 1$, a condition that prevailed in^[34], the i(t) curves were bell-shaped. We note that at $p < p_{\rm HTP}$, regardless of the value of t_1 , the maximum values of i(t) lie at $t_0 < t < T$, whereas in linear dielectrics the maximum of i(t) occurs either at $t = t_0$ or at t = T.

The residual polarization of the ferroelectric samples preserved after the experiments, according to Linde,^[93] is 30%, 70%, and 0% of P_0 , respectively, for LZT 52/48 (p = 9.5 kbar), LZT 95/5 (p = 11.5 kbar), and BaTiO₃ (18 kbar). Assuming that the rarefaction wave does not influence the depolarization process, Linde has concluded that the depolarization of the investigated systems is due to reorientation of the domains.

The electric signals from unpolarized LZT-19 samples have a form characteristic of linear dielectrics. In this case $Q \approx 10^{-8}$ Coul/cm².

Novitskii *et al.*^[98] investigated the depolarization of the single-crystal ferroelectrics BaTiO₃, PbTiO₃, and LiNbO₃ after double compression in a shock wave (elastic waves from steel with p = 12-20 kbar). It was established that: a) with increasing ferroelectric rigidity of the crystals, their depolarization decreases: $Q \sim 0.1P_0$ (2.6 μ Coul/cm²) for BaTiO₃, $Q < 10^{-3}P_0$ (0.07 Coul/cm²) for PbTiO₃ and LiNbO₃; b) when PbTiO₃ and LiNbO₃ are compressed by a second shock wave from steel with p=110 kbar, a charge $Q \sim P_0$ is delivered to the external circuit.

Thus, experiments with nonlinear dielectrics have shown that under certain conditions an electric charge equal to the initial polarization of these substances is delivered to the external circuit. In particular, for LZT systems, complete depolarization takes place irreversibly at $p = p_{HYP}$.

3) Semiconductors. Electric signals produced by shock loading of single-crystals of p-Si (with boron content $N=6\times10^{18}-5\times10^{11}$ cm⁻³)^[33,100,101] and of n-Si (with phosphorus content $N = 2 \times 10^{14} \text{ cm}^{-3})^{[33]}$ were investigated. The shock waves (p=5, 10, 40, and 200 kbar) were applied to the samples along [111]. [33] The Hugoniot yield point of p-Si with $N=5\times10^{11}$ cm⁻³ along [111], is p_{HYP} = 50 kbar at l = 10 mm and $p_{HYP} = 76$ kbar at l = 2 mm. Oscillograms of the voltage drop U(t) across the input resistance of the oscilloscope are shown in Fig. 6. Certain parameters of the initial samples and the values of $P_0 = P(t_0)$, calculated from formula (2.6) under the assumption that $\varepsilon_2 \simeq \varepsilon_1$, are given in Table VIII. The dependence of the voltage U_0 at $t = t_0$ for certain p-Si samples on the compression on the shock-wave front is shown in Fig. 13. Since⁴ $R \gg \rho_1 l/S$, it follows that U(t)is equal to the emf produced in the shock-compressed samples.

An analysis of the experimental data on p-Si has shown the following: a) In contrast to the polarization signals

⁴⁾It is shown $\ln^{[104]}$ that $\rho_1 \approx \rho_2$ in the case of semiconductors that are compressed by weak shock waves.

TABLE VIII. Bulk resistivity (ρ_1) and number of impurity atoms in the initial samples (N), experimental (P_0) and calculated (P) values of the polarization, the field strength (E), and the thickness of the double layer (Δ) in shock-compressed samples at p=40 kbar.

Si	ρ:, Ω-cm	N, cm-3	P ₀ , C-cm ²	P, C-cm ²	E, V-cm ⁻¹	Δ, cm
<i>p</i> -type	$2 \cdot 10^{-2}$ 4.5 7.5	6-1018 1.1016 7.1015	$2 \cdot 10^{-7}$ $4 \cdot 10^{-8}$ $-3 \cdot 10^{-8}$	5 · 10-7 7 · 10-9 6 · 10-9	$2 \cdot 10^7$ $4 \cdot 10^4$ $3 \cdot 10^4$	$2 \cdot 10^{-8}$ $4 \cdot 10^{-6}$ $6 \cdot 10^{-6}$
n-type	$2 \cdot 10^3$ 3.5 \cdot 10^4 4.5 7.5 45	$ \begin{array}{r} 1 \cdot 10^{13} \\ 5 \cdot 10^{11} \\ 2 \cdot 10^{15} \\ 9 \cdot 10^{14} \\ 1 \cdot 10^{14} \end{array} $	$\begin{array}{r} 3.10^{-12} \\ -2.10^{-12} \\ -2.10^{-12} \\ -5.10^8 \\ -5.10^8 \\ -1.10^{-9} \end{array}$	8. 10-11 1 · 10-11 2. 10-9 3. 10-9 4. 10-10	3 2 5 • 104 5 • 104 3 • 10 ³	$\begin{array}{c} 2 \cdot 10^{-3} \\ 3 \cdot 10^{-2} \\ 4 \cdot 10^{-6} \\ 6 \cdot 10^{-6} \\ 4 \cdot 10^{-5} \end{array}$

*The first and second values correspond to calculations with and without allowance for the influence of the conductivity on the polarization signal.

from dielectrics, the character of the plots of U(t) and the magnitude of U_0 do not depend on I(0.2-1 cm), $S(1-7 \text{ cm}^2)$, or $R(93-1053 \Omega)$; b) $U(t) \neq 0$ at t > T (starting with t = T and for approximately one microsecond the samples were compressed as units).

c) All the U(t) plots can be approximated by a single relation

$$U(t) = U_0 \exp\left(-\frac{t}{\tau}\right) \left[1 - \exp\left(-\frac{t}{\eta}\right)\right]$$

at the following values of the constants:

1) $\eta \ll T$, i.e., $1 - \exp(-t/\tau) \rightarrow 1$ and $\tau \approx 0.2-0.4 \ \mu \text{sec}$, p = 20 and 40 kbar, $\rho_1 = 4.5-45 \ \Omega - \text{cm}$ for the *n*-type and p = 20-200 kbar, $\rho_1 = 4.5 \text{ and } 2 \times 10^{-2} \ \Omega - \text{cm}$ for the *p*-type.

2) $\tau \gg T$, i.e., $\exp(-t/\tau) - 1$ and $\eta \approx 0.1 \ \mu \text{sec}$, $p = 200 \ \text{kbar}$, $\rho_1 = 3.5 \times 10^4 \ \Omega - \text{cm}$, p-type.

3) $\eta \ll T \ll \tau$, i.e., $U = U_0$, p = 40 or 200 kbar, $\rho_1 = 4.5 \Omega$ -cm, p-type.

d) For plots in the form $U \sim \exp(-t/\tau)$ the current in the circuit at t > T, is directed opposite to the current at t < T. In the remaining cases, the directions of the currents in the measuring circuit are the same at t > T and t < T.

e) Reversal of the sign of U(t) in Si with $\rho_1 = 3.5 \times 10^4$ Ω -cm at p = 40 kbar during the course of motion of the shock wave through the sample.

f) $U_0(\sigma)$ have anomalies for Si with $\rho_1 = 7.5$ and 3.5 $\times 10^4 \ \Omega$ -cm (*p*-type) and $\rho_1 = 4.5$, 7.5, and 45 Ω -cm (*n*-type).

Coleburn *et al.*^[100] in analogous experiments on ptype Si (boron concentration $N \simeq 10^{14}$ cm⁻³) at p = 8-55kbar obtained values $U_0 = 2.6-3.2$ V, which were larger by one order of magnitude than the values of U_0 registered by us at $N \gg 10^{14}$ cm⁻³ and $N \ll 10^{14}$ cm⁻³. So large a discrepancy can be explained by assuming that the compared Si samples differed in type and (or) concentration of the minority carriers, the presence of which can greatly change the magnitude and even the sign of U(t).^[101] Experiments with Ge of p- and n-type^[11, 105] have shown that the polarization current in these crystals is of the same order as in p-Si.

Tyunyaev and the present authors investigated the influence of the crystallographic loading direction in the elastic region on the bulk electric polarization of doped Ge in shock waves. The n-Ge samples doped with antimony (initial resistivity 3Ω -cm) were loaded with plane shock waves along the [100], [110], and [111] directions at shock-wave pressures ≈ 6 and ≈ 12 kbar. The Hugoniot yield points of Ge shock-loaded along [100], [110], and [111] are 58, 48, and 47 kbar, respectively.^[99] It was observed that the magnitude, sign, and temporal characteristics of the polarization produced by the shock wave depend on the direction of the shock compression. In particular, $U(t) \simeq 5$ mV = const in the case of loading along [100] at a pressure 6 kbar, and U(t) reverses sign during the motion of the shock wave through the sample in the case of loading along [110].

Jacquesson *et al.*^[105] registered, in shock compression of *n*-PbTe, a value $U_0 \simeq -0.04$ V in the interval p = 75-170 kbar. Reversal of the polarity of i(t) was observed in *n*-PbTe at p = 170 kbar.

The results of the investigations have shown that the emf of shock-compressed doped silicon and germanium single crystals depend on the impurity concentration. It is curious that at certain pressures, e.g., at p = 200 kbar, the U(t) signals have the same polarity regardless of the type of initial conductivity of the silicon. Just as in the case of shock polarization of ionic crystals and polar dielectrics, the reversal of the sign of i(t) and the $U_0(\sigma)$ anomaly are observed in semiconductors.

4) Metals. The emf produced by shock compression of metals was investigated by Jacquesson, $^{[105-111]}$ Ilyukhin and Kologrivov, $^{[112]}$ Buzhinskiĭ and Samylov, $^{[113]}$ Palmer and Turner, $^{[114]}$ Deribas *et al.*, $^{[115]}$ Nesterenko *et al.*, $^{[116, 117]}$ Kanel' and Dremin, $^{[133]}$ Bordzilovskiĭ and Karakhanov, $^{[143]}$ and by ourselves and others. $^{[15, 16, 118]}$ The experimental values of the emf are given in Table IX. Some oscillograms of U(t) are shown in Fig. 6. Experiments with time markers are shown that U(t) appears at the instant when the shock wave arrives at the boundary between the screen and the sample. The in-



FIG. 13. Dependence^[101] of the voltage u_0 at the instant of the entrance of the elastic wave into the silicon sample on σ at boron-atom concentrations in the samples 1×10^{16} (1), 1×10^{13} (2), and 5×10^{11} cm⁻³ cm (3).

Investi-	Screen													r), kba	ar													Refer
material	rial	50	60	70	100	120	130	140	140	170	180	190	200	210	240	280	300	320	340	360	380	390	400	670	780	970	1160	2000	ence
۲.	Cu								-10																				109
Ni	Cu		-9			-19	-26				24	1			-26		-39	1	-32				35				90		109,110
Bi	Cu				< 10						11												-100				-170		100, 118
Bi	Αl		1					10					1	1		-30										-60			118, 115
Sb	Al									< 10							13		ļ					ł	[80	118, 115
Cal	AI							20				Ì	1			20													118
Cd	Cu	< 10				1								•															118
Ви	AI		1									20																	118
pl,	Cu			-25													:												118
Z.1	Cu																										90		109
Constan- tan	Cu	-15	20		- 30	-33			-36		-43		-10		50		-60		-65				-73				-180		109, 111
Constan- tan	Fe		ļ	-	—3ā	ļ	-50													-500									109, 111
Chromel	Fe						+20							·															109
Yb	AI					-100							-300												130				117
Cu	Al									60				ļ				170						150					117
Ce	AI					15								15								-15							117
Sm	AI						1	< 10												< 10									117

TABLE IX.	Emf ((in mV) in shock	compression	of metals.
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stant of emergence of the shock wave to the boundary between the screen and the electrode corresponds to a break of U(t). In the case of cadmium, beryllium, and lead, the plots of U(t) are similar and are characterized by a decrease of U(t) at $t > t_0$. In bismuth at p = 140, 260, and 970 kbar, we have $U(t) > U(t_0)$; at p = 490 kbar U(t) reverses sign at $t_0 < t < T$. In europium (p = 170kbar) and in bismuth (p = 260 and 340 kbar), U(t) increases noticeably at $0.1-0.15 \ \mu$ sec (europium) and $0.3-0.5 \ \mu$ sec (bismuth) prior to the emergence of the shock wave front from the samples, regardless of their thickness. U(t) is constant in experiments with antimony, europium (p = 620 and 670 kbar) and cerium (p = 120and 210 kbar).

The growth of U(t) in the case of bismuth and europium when the shock wave front approaches the electrode can be attributed to the penetration of the precursor charge into the unperturbed substance ahead of the shock-wave front. Experiments using a capacitive transducer have shown that in bismuth and antimony there is indeed a diffusion of the carriers through the shock-wave front. ^[15, 115] The increase in the amplitude of the precursor signal in bismuth with decreasing temperature of the sample from 300 to 77 °K also indicates, within the framework of the theory, ^[116] diffusion of the carriers through the shock wave front. Coleburn *et al.* ^[144] have observed diffusion of the carriers from the shock-wave front into aluminum (p = 270 kbar).

The signal-growth times (τ) following the entry of the shock wave into the sample and the decay time (η) of U(t) at t > T are indicated in Table X. Attention is called to the large values of τ and η in the case of shock compression of ytterbium. In the case of shock compression of constantan and nickel (copper screen), the emf is approximately proportional to the pressure in these materials.

Kanel' and Dremin^[113] modified the scheme of Fig. 5, placing the electrode between two samples of the investigated metal. Insulating liners were placed between the electrodes and the samples. The shock waves propagated perpendicular to the surfaces of the sample and the electrode. This scheme ($p \simeq 300$ kbar, $t_1 \simeq T$) was used to register signals of amplitude $\simeq 1$ V produced by shock compression of aluminium, iron, nickel, and copper. Replacement of the copper electrode with an aluminium one in experiments with copper samples and aluminum samples did not change appreciably the amplitude or the character of the signal. No noticeable changes were observed also when the materials of the insulating liners (mica, teflon) were replaced.

Thus, metals, which are good conductors, also respond to compression by shock waves by production of an emf that depends not only on the shock wave parameters but also on the type of metal.

The influence of the parameters of the measuring circuit, of the tilt of the shock wave front, and of the skin effect on the emf of a compressed copper-nickel pair was investigated in^[143].

Metal	Pressure p, kbar	τ , μ sec	η, μsec
Ytterbium	120-780	~ 1	~ 1
	170	≤ 0.05	0.03
Europium	320-670	€0.05	0.15
Beryllium	190	0.2-0.3	
Cadmium	50-260	0.2-0.3	
Lead	190	0.2-0.3	

TABLE X. Rise times (τ) and fall-off times (η) of signals in certain metals.

4. INTERPRETATION OF THE EXPERIMENTAL DATA

A. Static and dynamic emf sources

It is clear from general considerations that the sources of the electric signals in shock compression of linear dielectrics, semiconductors, and metals are connected either with the thermoelectric power (1), or else with electric phenomena due to dynamic compression of the substance: deformation of the surface double electric layers in the shock wave (2), hopping of the carriers by inertia on the shock wave front (3), dragging of the carriers by the deformed lattice (an effect of the acoustoelectric type) (4), shock polarization (separation of the positive and negative charges in the volume of the substance behind the shock wave front) (5), or diffusion of the carriers from the shock wave front (6).

We shall show that in the case of linear dielectrics the observed effect is due to shock polarization. Let us estimate the effective resistance (R_{eff}) of the capacitor made up of the electrode and the shock-wave front.

According to^[119, 120] we have

$$R_{\text{eff}} = \left(\frac{dC}{dt}\right)_{t=0}^{-1} = \frac{4\pi l^2}{\epsilon_1 SD} \,.$$

At $S=1 \text{ cm}^2$, l=0.2 cm, $\varepsilon_1=6$, and $D=5\times10^5 \text{ cm/sec}$ we obtain $R_{\text{eff}}=1.5\times10^5 \Omega - \text{cm}^2$. This means that an emf source of 10^3-10^5 V acts in the circuit at the experimentally registered values $\mathbf{j}=10^1-10^3 \text{ mA/cm}^2$. It is difficult to explain the appearance of such an emf source by means of known effects. Thus, according to Yakushev's estimates, ^[43] the contact emf in shock compression of a metal-dielectric system is $E_1 \approx 2 \times 10^{-2} \text{ V}$.

Even as we assume that the dielectric becomes an electrolyte behind the shock-wave front, then in this case, too, $E_1 \approx 2 \text{ V}$.^[85] Another important argument favoring shock polarization is the following. Within the framework of shock polarization it is possible to explain qualitatively not only the form of the $\mathbf{j}(t)$ curves and their dependence on τ and ρ_2 , but also the $Q_0(\sigma)$ anomaly for a number of substances, as well as the reversal of the polarity of $\mathbf{j}(t)$.^[31] Finally, the phenomenology of shock polarization predicts a $\mathbf{j}_0(T)$ dependence in the form $\mathbf{j}_0 \sim T^{-1}$. This is precisely the $\mathbf{j}_0(T)$ dependence obtained in experiment.

Experiments on ionic crystals make it possible to estimate the time of establishment of the polarization on the shock-wave front. To this end, we turn to the dependence of Q_{0max} on the cation radius (curve 1 in Fig. 9). The lower part of curve 1 corresponds to crystals. KCl, KBr, KI, RbI) that experience polymorphic transformations in the range $\sigma < 1.3$. On the other hand, in the CsI crystal, which has a lattice of the CsCl type even under normal conditions (the lattices of the crystals mentioned above are transformed into this lattice under pressure), the value of $Q_{0 \max}$ is approximately 50 times larger than that expected from curve 1 for CsI. This circumstance indicates that the polarization of the aforementioned crystals occurs apparently in the initial type-NaCl lattice, and not in the restructured one. From Kormer's experiments on the reflection of light from a shock wave front in KCl and KBr it is known that the

time of the phase transition of these crystals at $p \approx 100$ kbar is $t < 10^{-12}$ sec.^[121] Thus, the time required for polarization to set in for these two crystals $t < 10^{-12}$ sec, so that the postulate concerning the jump of the polarization on the shock wave front in a linear dielectric, assumed in a number of phenomenological theories, is physically justified at $p \approx 100$ kbar. This postulate of the theory is also justified for shock compression of NaCl (p = 20 kbar), as shown by experiment.^[66] To be sure, in polystyrene and in some epoxy resins at $p \approx 50$ kbar, Novitskii *et al.*^[71] observed a stretched-out polarization front with $\eta \approx 1$ µsec.

An analysis of the contribution of sources (1)-(5) to the emf produced by shock compression of silicon and germanium is reported in^[33, 101], where it is shown that the investigated effect is due to shock polarization. In particular, the increase of the electric field intensity in shock-compressed silicon with increasing impurity concentration (see Table VIII) indicates that the observed emf is not the result of an acoustoelectric effect.^[101]

An analysis of the possible sources of emf in metals is presented in^[117,118], where it is shown that the emf produced by the mechanisms (2) and (3) is small (< 1 mV)and could not be registered in our experiments. The emf produced by mechanism (1) was estimated within the framework of the theory of free electrons. Calculations of E_1 for cadmium, beryllium, lead, and for the investigated lanthanoids yielded $E_1 \approx 1$ mV. These values of E_1 are smaller by one or two orders of magnitude than the experimentally registered emf. Nonetheless, it is impossible to separate the contributions of the dynamic ((4)-(6)) and the static ((1)) sources of the emf in shock compression of cadmium, beryllium, lead, ytterbium, and cerium. Favoring the shock polarization of these metals are the large growth and fall-off times of the signals U(t) (see Table X) in comparison with the time required to establish the contact electric processes $(\approx 10^{-13} \text{ sec})$. [118] In accordance with the universal theory of relaxation times in conductors, the redistribution of the charge produced in a conductor decreases exponentially with a time constant θ . Using Ohm's law for the case of a constant charge density, we have for good conductors $\theta \approx 10^{-19}$ sec. It is physically clear, however, that θ cannot be less than the average time τ_{e} between the carrier collisions. [118] For bismuth and antimony $\tau_e \approx 10^{-10}~{\rm sec},$ while for cadmium, beryllium, and lead $\tau_e \simeq 10^{-4}$ sec. Allowance for the frequency dependence of the conductivity of the metal and for the collective character of the reaction of the electrons to the nonstationary character of the charge distribution in the conductor leads to $\theta \approx 10^{-12}$ sec. ^[122, 123] Therefore the fact that $\tau \approx \eta \gg \tau_e$ in these metals, just as in semiconductors, ^[33] means that, within the framework of the mechanism (5), the registered U(t) dependence is due to the depolarization of the shock-compressed metals. One cannot exclude, however, the possibility that the Fermi energy of the shock-compressed metals can change as their lattice goes over to the new equilibrium state. Then the value of τ will characterize within the framework of the mechanism (1) the relaxation of the last process. [118]



FIG. 14. Comparison of the experimental j(t/T) curves for NaCl at p = 20 kbar with the curves calculated from Allison's theory. ^[66] 1-4) experiment; 5,6) calculation. The parameters of the calculated curves are: 5) $P_0 = 3 \times 10^{-3}$ Coul/cm², $\times = 2$, $\tau = 1 \times 10^{-7}$ sec; 6) $P_0 = 1.78 \times 10^{-3}$ Coul/cm², $\times = 1.9$, $\tau = 1 \times 10^{-7}$ sec.

As noted in Chap. 2, the effect of the shock-wave precursor in bismuth, antimony, europium, and aluminum is due to carrier diffusion from the shock-wave front. ^[15,115-116,144] Jacquesson *et al.* ^[109-111] and Conze *et al.* ^[124] propose that the emf observed in shock-compressed nickel (copper screen) and constantan (ion and copper screens) is connected with mechanism (4).

Kanel' and Dremin^[133] have shown that the signals (≈ 1 V) produced upon shock compression of aluminum, copper, nickel, and iron are not connected with the thermal emf and with electrochemical effects, and are due to dynamic redistribution of the volume charges on the shock-wave front (mechanisms (3)-(5)).

B. Applicability of the phenomenological theories

In order for the phenomenological theories of shock polarization to be applicable to the description of the experimental data it is necessary to satisfy two conditions: a) agreement between the initial premises of the theory and the physical conditions in the experiment, b) agreement between the calculated and experimental j(t) dependences. Allison's phenomenology was used by Horie^[77] to describe the electric signals produced in shock compression of water, and by Hauver^[32] to describe the polarization signals in shock compression of polyethylene and o-nitroanisole. In^[77], however, the condition (a) was not satisfied. It was shown above that the aggregate of the experimental data on the electric signals produced in shock compression of water does not make it possible to attribute them unambiguously to shock polarization. Even if it is assumed, as was done by Horie, ^[77] that the signals observed in water are due to shock polarization, then, by making use of Hamman's data on the conductivity of water at p = 100 kbar $(\rho_2^1 \simeq 1 \ \Omega\text{-cm})^{[103]}$ we have $\theta \simeq 10^{-9}$ sec at $T = 4 \times 10^{-7}$ sec. The condition for the applicability of Allison's theory $(\theta_2 \gg T)$ is not satisfied in this case.

A comparison of Allison's theory with experiment was carried out by Tyunyaev *et al.* using as an example NaCl at p = 20 kbar.^[66] It was shown earlier that in the case of shock compression of ionic crystals, a jump of the polarization (with a transient time < 10^{-12} sec) and a jump

of the dielectric constant take place on the shock wave front. It is seen from Fig. 14 that within the limits of the experimental scatter, the calculated curves plotted using the data of Table III agree with the experimental j(t) curves.

At p > 20 kbar for NaCl and for a number of linear dielectrics at $p \ge 100$ kbar, the shock-polarization theories that take rigorously into account the mechanical and conductivity relaxations cannot be used for a quantitative description of the experimental data, since the conductivity jump on the shock wave front, which is assumed in the phenomenology, is not realized at these values of p, and the subsequent value of ρ_2 is constant. Nonetheless, these theories describe qualitatively the evolution of the experimental $\mathbf{j}(t)$ curve with increasing conductivity. With increasing pressure, the conductivity increases and the current peaks in the plots of j(t), at $t = t_0$ and t = T, become sharper and the j(t) dip at $t_0 < t$ < T becomes larger. We note that the phenomenological theory of shock polarization^[26-28] was constructed with the assumption of only one polarization method. At the same time, the $Q_0(\sigma)$ anomaly, the reversal of the sign of j(t), and the dependence of Q_0 on the concentration of the calcium ions in NaCl can be attributed to the existence of at least two independent polarization mechanisms with different signs and characteristic times of the carrier mechanical relaxation. [31] Within the framework of this assumption, the reversal of the sign of Q_0 at values of σ corresponding to the $Q_0(\sigma)$ anomaly is the result of a change in the leading mechanism of the polarization.

The applicability of the theory of shock polarization to semiconductors and of shock depolarization to nonlinear dielectrics has not been discussed in detail. In these cases the temporal characteristics of the polarization (depolarization) and the dielectric constants of the substances were determined by comparing the calculated and experimental j(t) curves.^[33-35] Thus, Novitskii *et al.*^[95] have shown that Halpin's phenomenology of shock depolarization does not describe the results of the experiment at $T/t \approx 10-100$. An analysis of Halpin's premises yields $\varepsilon_1 = 0$, whereas the dielectric constant of the initial piezoceramic is $\varepsilon_1 \approx 1000$.

C. Diffusion of ions in shock compression of ionic crystals

An analysis by Tyunyaev has shown that shock polarization of ionic crystals can occur in principle at any one of four structural levels of the medium: 1) at the microscopic level—when the crystal cracks or is crushed^[125]; 2) at the block-structural level—when charged interblock walls move^[126] (the possibility of polarization at this level was discussed also in^[58]; 3) at the atomic level—when individual ions or charged dislocations move; 4) at the electronic level.

An estimate has shown that the times of the onset of polarization in accordance with mechanisms (1) and (2) are longer by at least two orders of magnitude than the experimentally observed time of the onset of polarization ($\eta \simeq 2 \times 10^{-8} - 1 \times 10^{-7}$ sec). Comparison of the re-

laxation times of the shock polarization ($\tau \approx 10^{-7} \text{ sec}$) with the relaxation times of the electron polarization (~ 10^{-14} sec in the case of bound electrons and ~ 10^{-8} in the case of free electrons) shows that the effect is not connected with electrons. Favoring this assumption are the results of experiments with γ -irradiated NaCl I samples.

The atomic model of the polarization of ionic crystals in shock waves, whereby ions of opposite sign are displaced relative to one another within the elastic limits, was proposed by Harris.^[127] The conclusions of this theory, however, do not agree with experiment.^[61]

Linde *et al.*^[10] and Wong *et al.*^[58] have proposed that shock polarization of nominally pure ionic crystals is due to formation of dipoles consisting of a charged dislocation (aged) and a compensating cloud). The role of the dislocations in shock polarization of nominally pure ionic crystals was investigated by Tyunyaev *et al.*^[62, 63] The results of the investigations have shown the following:

a) A discrepancy between the anisotropy of the polarization and the anisotropy of the plasticity in CsI and LiF crystals at low pressures in the shock wave.

b) A disparity between the directions of the change of Q_0 and of the change of the plasticity of the properties of the ionic crystals in the sequence RbI-KI-KBr-NaCl-LiF (the crystals are arranged in increasing order of rigidity).

c) A disparity between the sign of the polarization in the region of low pressures and the sign of the charge at the dislocations, both fresh and aged. Thus, the polarization of nominally pure ionic crystals in shock waves is apparently connected with diffusion of the ions. The positive sign in the circuit of Fig. 5 corresponds to a resultant displacement of the cations relative to the anions (at $\sigma < 1.3$) in the direction of motion of the shock wave. The decisive role of the cations in the effect, up to the $Q_0(\sigma)$ anomaly ($\sigma < 1.3$), confirms the $Q_{0 \max}(r_+)$ dependence (Fig. 9). The most probable elementary shock-polarization mechanism is here the diffusion of the cations over the vacancies. An estimate given in^[61], using the data of Pratt^[128] and Klein^[129] on the number of point defects in shock compression of ionic crystals, agrees with this hypothesis. To explain the values of $Q_{0 \max}$ it must be assumed that the cations are displaced 1-10 lattice periods relative to the anions. It is possible that the relative shift of the cations and anions extends even over larger distances. Then, however, breakdown electric fields can be produced and consequently a lowering of the polarization level. Favoring the latter assumption is the connection between $Q_{0 \max}$ and the parameter γ , which characterizes, according to Whitehead, [130] the dielectric strength of ionic crystals.

Within the framework of the diffusion mechanism, the negative sign of the polarization at $\sigma > 1.3$ is due to the accelerated diffusion of the anions in comparison with the cations in the direction of motion of the shock wave.

The physical nature of the $Q_0(\sigma)$ anomaly in NaCl was considered by Tyunyaev *et al.*^[145] According to^[145], the change in the sign of the polarization of NaCl at σ

>1.3 is due to the formation of interstitial anions in shock-compressed NaCl at $p > p_{HYP}$. The mobility of the interstitial anions in NaCl depends strongly on the crystallographic direction of their motion. It is shown in [145] that in NaCl at $\sigma \approx 1.3$ we should have in accordance with the proposed mechanism $|Q_{0[111]}| > |Q_{0[100]}|$. Experiment has yielded $|Q_{0[111]}| = 2 \cdot |Q_{0[100]}|$. It cannot be excluded, however, that the change of the sign of the polarization is due to the mobility of the cations and anions with increasing temperature behind the shock wave front. We note in this connection that the conductivity of NaCl at room temperature and at normal pressure is due to the Na⁺ ions, while the contribution of the Cl⁻ ions becomes noticeable at temperatures above 700 °K. ^[131] At $\sigma > 1.3$, the temperature in NaCl exceeds 550 °K. ^[46]

The possible mechanisms whereby divalent metallic impurities participate in the shock polarization of ionic crystals have been considered by Tyunyaev et al. [65] It was shown that impurity polarization in shock compression of doped NaCl is due to reorientation of impurities plus cation vacancy dipoles in the elastic fields of the dislocations moving the shock-wave front. This mechanism explains the anisotropy of Q_0^{imp} . The point is that an energywise lower orientation is assumed by the dipoles when the dislocations glide over $\{110\}$ planes, and the magnitude of the shear stress (τ_{shear}) in these planes, and consequently the possibility of gliding, depends strongly on the direction of the shock loading. In particular, in loading along [100] we have τ_{shear110} = 0.369 p, and in loading along [111] we have $\tau_{\rm shear110} = 0.$

D. Sources of emf in shock compression of polar dielectrics and electrolytes

The ideas concerning the mechanism of shock polarization of polar dielectrics are confined to the hypothesis of Eichelberger and Hauver, wherein the polar molecules are rotated by the pressure gradient in the shock wave front.^[6]

The results of experiments with TNT (molecule dipole moment 1.2 Debye units) and with toluene^[23] (0.3 Debye units) offer evidence in favor of this hypothesis. The independence of polystyrene polarization of its molecular weight (dipole moment^[132]) can be explained from this point of view as being due to the destruction of the polystyrene molecule behind the shock wave front.^[139] It is known that the polarization of polystyrene behind the shock wave front takes place not jumpwise, but increases smoothly with time ($\eta \simeq 1 \ \mu$ sec). Therefore the question of polar dielectrics calls for further research.

The leading mechanisms that produce electric signals in shock compression of water and certain electrolytes, as shown by Breusov *et al.*^[80] and Kochnev *et al.*,^[85] are electrochemical processes on the shock-compressed screen-liquid and liquid-electrode boundaries. An interesting fact is the presence of an emf in systems in which the screen and the electrodes are of the same metal (aluminum or copper). This shows that the produced galvanic potentials on the shock-compressed boundaries are not stationary even in a time interval ~ 1 $\mu \text{sec.}$

E. Release of bound charges behind the shock wave front in nonlinear dielectrics

The release of charges in shock compression of nonlinear dielectrics can be due to the decrease of the combined dipole moment as a result of compression (the piezoeffect), to domain processes, or to phase transitions.

It was shown in¹⁹⁰¹ (with allowance for the dependence of the Curie temperature on the static pressure) that to initiate the transition of lead-zirconate-titanate from a ferroelectric to paraelectric state it is necessary to have on the shock wave front a pressure 200-300 kbar. It follows from experiment, however, that even at pressures smaller by one order of magnitude the charge realized in the circuit is equal to the value of the initial polarization.

Reynolds and Seay, [90] on the basis of the linear dependence of the realized charge on the pressure on the shock wave front in LZT 52/48, have concluded that the time of the explosion experiment pressure action time ~ 10^{-6} sec, pressure buildup time ~ 10^{-7} -10⁻⁸ sec) was insufficient to switch over the domains, and that the realized charge was due to the piezoeffect. Their comparison of the Q(p) dependences for shock experiments and the Q(p) dependences obtained by Berlincourt and Krueger^[96] under static conditions has shown that the relaxation time of the domain processes in the LZT 52/48 ceramic at $p \approx 3$ kbar is ≈ 3.5 msec. However, it would be incorrect to characterize the domain processes by only a single relaxation time, since it is known that this time depends on the electric field intensity in the sample, which in turn depends on the pressure at $p < p_{HYP}$. Thus, for example, the domain switching time (t_s) in BaTiO₃ in fields $E < 10^2$ V/cm is described by the exponential law t_s^{-1} ~ exp(- α/E), where $\alpha \approx 10^4$ V/cm is the activation field^[134] and $t_s \sim E^{-3/2}$ at $E \approx 10^5$ V/cm.^[136] An estimate of the electric fields in a shock-compressed LZT ceramic was carried out $in^{[34, 135]}$. It was shown that for the LZT 65/35 system $E \approx 5 \times 10^4$ V/cm at $p < p_{HYP}$, i.e., it is of the order of the breakdown field under normal conditions. Assume that such fields are realized in shockcompressed $BaTiO_3$, for example on account of the piezoeffect. Then, using Stadler's relation^[136] to estimate t_s we obtain $t_s \approx 10^{-7}$ sec. This result indicates that intervals $T \approx 10^{-6}$ sec are sufficient to complete the domain processes in shock-compressed BaTiO₂. Favoring this conclusion are measurements of the residual polarization of the BaTiO₃ samples preserved after shock loading.^[93]

The presence of strong electric fields behind the shock wave front in nonlinear dielectrics, as shown by Canfield^[137] and by Cutchen, ^[138] can lead to ionization of impurities and to generation of carriers behind the front, and as a consequence to different functions Q(p), depending on the direction of shock-wave motion relative to the polarization vectors in quartz and LZT samples.

F. Emf in shock compression of semiconductors and metals

An analysis of the experimental data on the emf produced in shock compression of doped semiconductors shows that the observed phenomenon does not reduce to any of the known electric effects (acoustoelectric effect and the Stepanov effect).^[101]

The increase of P_0 with increasing N and the large times τ and η in silicon compared with the electron relaxation time give grounds for assuming that the emf in shock-compressed doped silicon is the result of a volume redistribution of the impurity ions in the shock wave. It can be further assumed that the volume polarization mechanism consists of the following:

1) Formation, by the impurities, of bound or separated Frenkel pairs having an electric moment,

2) Orientation of these pairs in the direction of motion of the shock wave.

We note in this connection that with increasing degree of doping of the silicon the number of point defects produced after the shock loading increases.^[140] Similar dipoles can be produced in metals by ions of the host substances or of the impurity and by their vacancies.^[141] It is known that plastic deformation results in much more vacancies than interstitial atoms, this being caused by the large difference between the energies required to produce these defects (a bibliography on defect production by shock deformation can be found in Mogilevskii's paper^[142]). The electric field produced upon polarization will be compensated after a time θ_2 by the carrier field. The depolarization process will cause a change in the electric field of the carriers. If $\tau \gg \theta_2$, as is the case of the experiment, then the law governing the time dependence of the compensating field will coincide with the law governing the variation of the polarization.

Let us estimate the order of magnitude of the polarization of silicon within the framework of the considered mechanism. Assume that the impurity ions are displaced by one lattice period. Then the polarization is equal to $P = qN^{2/3}$, where N is the number of impurity ions per cm^{-3} with charge q equal to the electron charge. The results of the calculations are given in Table VIII, which lists also the values of P_0 obtained by reducing the experimental data with the aid of the phenomenological theory. As seen from Table VIII, the compared values P and P_0 are of the same order of magnitude. Shock polarization in a medium with good conductivity behind and ahead of the shock wave front means that a double acoustic layer of thickness $\Delta = \theta_2 D$ moves together with the front in such a substance (at $\eta = 0$). Assuming that the potential difference across this layer is equal to the experimentally observed value U_0 , we estimate the field intensity E in this layer at $E \ge U_0/\Delta$. The obtained values of Δ and *E* for the investigated silicon samples are given in Table VIII. Analogous estimates of P for metals^[118] show that this hypothesis is not contradictory.

On the other hand, the diffusion of the carriers from the shock wave front, according to Nesterenko *et* al_* , ^[116, 117] can be attributed to the production of a thermal wave propagating through the electron gas in the material ahead of the shock wave front, and this propagation is determined by the collisions of the electrons with one another. A similar approach is developed in the papers of Jacquesson *et al.*^[109-111] and Conze *et al.*, ^[124] in which it is assumed that the entire increment of the internal energy of the substance in the shock wave (or only 50% of it^[124]) is transferred to the directional motion of the carriers. The question of the coefficient of energy transfer from the lattice to the carriers is debatable. Nonetheless, in ^[109-111, 124] they obtained a qualitative agreement between the calculation and the results of measurements of the emf in shock-compressed copper-constantan (nickel, aluminum) and iron-constantan pairs.

5. CONCLUSIONS

As a result of the investigation of the emf produced in the shock compression of matter, a number of general laws governing this phenomenon have been established. The interpretation of these laws has made it possible to come closer to the understanding of both the nature of shock-induced emf and the physics of shock compression.

a) The onset of an emf in a shock wave is typical not only of nonlinear dielectrics, but also of a large class of substances, such as linear dielectrics, semiconductors, and metals. This indicates the absence of a rigorous thermodynamic equilibrium behind the shock-wave front in the investigated substances. This is also demonstrated by the nonstationary character of the electric conductivity of shock-compressed ionic crystals and polar dielectrics.

b) The polarization of all the investigated ionic crystals at $\sigma < 1.3$ has a positive sign and depends on certain parameters of the initial lattices. In most of the investigated ionic crystals, the sign of the polarization reverses at $\sigma \approx 1.3$, regardless of whether the degree of ionic bond or the crystallographic direction of the shock compression changes in these crystals. These facts indicate that the processes that lead to the polarization of these compounds are of common origin.

An analysis of the aggregate of the experimental data indicates that the shock polarization of nominally pure ionic crystals at $\sigma < 1.3$ is due to a displacement of the cations relative to the anions. The formation of interstitial anions in plastic deformation of ionic crystals in the shock wave front leads to a change in the sign of the polarization.

c) The polarization of ionic crystals that undergo a polymorphic transformation takes place in the initial lattice within a time ~ 10^{-12} sec. However, in the case of such polar dielectrics as polystyrene and epoxy resins, the time of establishment of the polarization is comparable with the time of motion of the shock wave through the sample (~ 10^{-6} sec).

d) The electric signals produced in shock compression of nonpolar organic dielectrics (carbon tetrachloride and benzene) are observed only in the shock wave reflected from the electrode and are connected with electrochemical processes that occur on the boundaries between the screen and the sample and between the sample and the electrode in a time interval ~1 μ sec.

e) In the case of shock compressed doped semiconductors and a number of metals, the observed emf is not connected with thermoelectricity, but is due to the volume distribution of the changes on the shock wave front. Diffusion of the carriers from the shock wave front was observed in aluminum, bismuth, antimony, and europium.

f) Phenomenological theories were developed for shock polarization of linear dielectrics and for the depolarization of nonlinear dielectrics; these theories are in qualitative agreement with experiment. In some cases the agreement is also quantitative.

g) Although no emf was observed upon compression of certain materials, this results indicates more readily that the shock polarization is small rather than actually absent.

We note that such processes as rupture, crushing, and splitting of the material, which are accompanied by relaxation waves, should lead to shock polarization and are apparently responsible for the electrification of the materials. The prolonged preservation of the charges indicates that the insulating properties of the dielectrics are insignificantly altered, in contrast to strong shock action. In the latter case, the strong increase of the conductivity is apparently not of thermal origin and leads to a rapid relaxation of the charges. The nonequilibrium radiation from the substances when they are rapidly deformed plastically or are cracked can also be attributed to discharges between like-charged surfaces. ^[121, 146, 147] We note that an analogous effect was observed also in metals. ^[146]

Research on the emf produced by shock compression of substances calls for the solution of the following problems: 1) The development of a phenomenological theory of shock polarization and depolarization with arbitrary laws of variation of the polarization, of the dielectric constant, and of the conductivity of the substance behind the shock wave front. 2) An investigation of the dielectric properties of shock-compressed substances. 3) The development of physical models for the appearance of the emf in shock compression of substances.

The authors thank their colleagues E. Z. Novitskil, U. N. Tyunyaev, and U. V. Lisitsyn for fruitful collaboration, and G. A. Adadurov, L. V. Al'tchuler, O. N. Breusov, A. A. Deribas, A. N. Dremin, R. M. Zaidel', Ya. B. Zel'dovich, O. K. Rosanov, A. A. Urusovskaya, and V. V. Yakushev for valuable discussions.

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Translated by J. G. Adashko