

ELECTRIC EFFECTS ASSOCIATED WITH PLASTIC DEFORMATION OF IONIC CRYSTALS

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INTEREST has heightened recently in studying electric phenomena accompanying plastic deformation of ionic crystals lacking a piezoeffect.

Studying the electric effects arising from plastic deformation permits us to understand better the nature of hardening, fatigue, and creep in ionic crystals, and permits us to estimate the energy for formation and motion of cation and anion vacancies and the forces binding dislocations to surrounding atmospheres of impurities or vacancies.

These electric phenomena include:

- 1) increase in ionic conductivity during plastic deformation;
- 2) appearance of an electric potential on the surface of the specimens being deformed in the absence of an external electric field.

1. INCREASE IN CONDUCTIVITY (THE GYULAI-HARTLY EFFECT)

In 1926 Joffe and Zechnowitzer^[1] discovered an increase of ionic conductivity in NaCl when plastically deformed. However, Gyulai and Hartly^[2] studied this phenomenon in more detail in 1928. Accordingly, an increase in ionic conductivity upon deformation is often called now the Gyulai-Hartly effect. Following Gyulai and Hartly, A. V. Stepanov^[3-5] observed a change in conductivity during plastic deformation. Gyulai and Hartly had the purpose of studying the mechanism of conduction in ionic crystals. Conversely, Stepanov used the phenomenon of increased conductivity to study the mechanism of plastic deformation.

We shall present the experimental data on the features of this effect, and also some possible reasons for it.

1.1. Experimental Results

Gyulai and Hartly^[2] compressed crystals of natural rock salt between two electrodes. One electrode was connected to an electrometer and the other to the positive terminal of a battery, which had its negative terminal grounded. Upon loading, the conductivity increased by a factor of 10-100 in proportion to the load. A. V. Stepanov^[3-5] observed an even greater increase in conductivity upon compressing NaCl: by a factor of 10^{10} . Here he found that the increase in conductivity begins only after applying a certain load (700 g/mm^2). However, in Quittner's experiments,^[6-8] this effect appeared in NaCl at considerably smaller stresses, 15 g/mm^2 , which is much smaller than the macroscopic creep limit (70 g/mm^2).

Stepanov notes that the conductivity increases not throughout the volume of the specimen, but only in the region of the slip bands. This result was subsequently confirmed by Johnston,^[9] who studied the Gyulai-

Hartly effect in AgBr crystals. Johnston measured the change in conductivity along the slip planes and perpendicular to them. The effect was found only in the former direction. Further, Johnston found a linear increase in the effect with increasing deformation.

All the experimental studies note that the increase in ionic conductivity upon deformation is a time-dependent phenomenon, as the conductivity declines with time under constant load. Increase in conductivity is observed not only in compression, but also in tension.^[10]

Heat-treatment of the specimens affects the increase in conductivity upon deformation. Such experiments have been made both on NaCl crystals and on AgBr crystals, in which Frenkel defects predominate (in contrast to the former).

Boros and Gyulai^[11] studied the ionic conductivity of NaCl annealed at different temperatures from 100° to 500°C for 1-5 hours after plastic deformation and then loaded again. They considered the jump in ionic conductivity to be a measure of the plasticity of the crystal. It increased with higher temperature and longer duration of annealing. The ionic conductivity also increased with increasing load. Under very large loads, some regions of the specimen showed anomalously large jumps in the ionic conductivity, which were ascribed to recrystallization. Heating the specimens during loading diminishes the increase in conductivity, while the effect is completely abolished at 400°C (Caffyn and Goodfellow^[12]).

Kanzaki^[13], who performed experiments on AgBr crystals, studied the effect on the excess ionic conductivity of annealing after deformation. The conductivity rose in these crystals by a factor of 5-6 upon compressive deformation by 35%. The excess conductivity declined upon subsequent annealing, the variation in the excess conductivity taking place non-uniformly with increasing temperature. It was observed to decline most rapidly at temperatures about 30°C , while the conductivity rose again at $100-300^\circ\text{C}$, and the increase in conductivity due to deformation completely vanished only in the third stage of annealing (at 400°C).

Impurities affect both the increase in conductivity and the relaxation time of the conductivity under load. Caffyn and Goodfellow^[12] studied natural and synthetic NaCl crystals and also a series of other synthetic crystals (NaI, KCl, KI, and KBr). They found that the decay time of the temporary increase in conductivity is greater (about one minute) in natural crystals, which contain more impurities, than in synthetic ones, where the decay took about 0.5 sec. Kiss^[14] has studied the effect of cationic and anionic impurities separately. It is interesting to note that the conductivity begins to increase at lower mechanical stresses in the presence of anionic impurities than in "pure" crystals. Furthermore, anionic impurities enhance the increase in con-

ductivity and its relaxation time. Cationic impurities decrease both the amount of excess conductivity and its decay time. We should note that Kiss has studied the Gyulai-Hartly effect in greatest detail and most fully. He has studied the influence of the method of deformation (uniaxial compression, local loading, and plastic bending) and the shape of the specimens. The effect was observed at all stresses (both above the yield point and below it), and the nature of the conductivity change varied in different cases. In the former case, the direction of the excess conduction current did not depend on the polarity of the field, but did so in the latter case. Increased conductivity was observed with all methods of loading and with any shape of specimen at stresses above the yield point. However, the shape of the specimen influenced the size of the effect. It was smallest in flat specimens (in which the thickness was smaller than the diameter), and largest in cube-shaped specimens. Motion pictures of the movement of the electrometer needle showed that the conductivity increases in jumps during deformation. The abrupt variation in the conductivity persisted during the initial stage of the relaxation period.

Kiss carefully studied the relaxation period of the conductivity, to which all previous investigators had paid little attention. He showed that if one follows the decay of conductivity long enough, it turns out that the residual conductivity in the saturation stage is always lower than the original value.

1.2. Treatment of the Experimental Data

Let us summarize the fundamental results of the studies under discussion:

- 1) plastic deformation of ionic crystals increases the ionic conductivity;
- 2) the increase in conductivity decays with time when the specimen is kept under constant load, and the conductivity proves to be lower than the original value after a long enough time;
- 3) the effect increases with increasing load (extent of deformation);
- 4) heating diminishes the effect;
- 5) the thickness of the specimens also shows an effect: cube-shaped specimens show the increased conductivity most clearly;
- 6) the effect of impurities depends on their type: cationic impurities weaken the effect, while anionic impurities enhance it;
- 7) the increase in conductivity is greater along active slip planes than perpendicular to them.

Depending on the level of concepts on crystal properties and defects, various hypotheses have been advanced, as the experimental data have accumulated, on the reason for the increased ionic conductivity upon deformation. Gyulai and Hartly gave the first explanation for this effect.^[2] These authors ascribed the observed effect to the appearance upon deformation of "loosened" sites giving rise to the ionic conductivity. Joffe^[15] took into account Quittner's results on increased conductivity resulting from "elastic" deformation, when no "loosened" sites have yet been created, and proposed that the strained state affects the bulk polarization caused by the external field. That is, he

ascribed the increased conductivity to the piezoeffect. Much later, special experiments were set up to test Joffe's hypothesis.^[16] These experiments did not confirm the appearance of a piezoeffect in rock salt upon deformation. We can consider one of the facts refuting this hypothesis to be that charges of the same sign appear on the compressed and stretched sides of a bent specimen.

Stepanov^[3-5] gave another explanation. He considered a possible reason for the increased ionic conductivity to be local melting of the crystal along the slip bands. This explanation was based on the similarity of the increase in conductivity of deformed and melted rock salt, and also on the localization of the increased conductivity in the region of the slip bands. However, further experiments refuted this viewpoint as well. Boros and Gyulai^[11] had also advanced as an objection to this explanation the fact that prior annealing increases this effect. Rozhanskiĭ et al.^[17] set up special experiments to reveal heating of the crystal along slip bands in zinc: heating of the crystal should increase the electric resistance during the abrupt shear motions, if Stepanov's hypothesis were true. However, Rozhanskiĭ et al. observed the opposite effect, not involving a temperature change in the slip zone. Further, the theoretical calculations of Eshelby and Pratt^[18] and also those of Cottrell^[19] showed that the local heating of a crystal during motion of dislocations is negligibly small.

Tyler^[20] and also Camagni, Chiarotti, and Manara^[21] suggested that the effect is due to liberation of electrons upon dislocation movement. In Tyler's opinion, this viewpoint is favored by the increase in the conduction current upon irradiation or additive coloration.^[22] However, we should note that vacancies are liberated at the same time as the electrons, and may be responsible for the effect.

Kassel^[10] explained the increased conductivity by an increase in the number of conduction ions detached from lattice defects. The more defects the crystal contains, the greater the number of conduction ions should be.

Seitz^[23,24] relates the effect to an increase upon deformation in the number of vacancies as dislocations intersect. Seitz calculated that each 10% of deformation gives rise to 10^{18} vacancies/cm³. He explains the experimentally observed decline in conductivity under constant load by migration of positive vacancies (which are more mobile in NaCl) toward the negative ones to form neutral pairs of vacancies.

Johnston^[9] and Burmeister^[25] have objected to Seitz's hypothesis. The reason for this was an experiment by Johnston comparing the decay time of the ionic conductivity after loading NaCl crystals with the mobilities of interstitial Na⁺ and Cl⁻ and their vacancies: the time for return of the conductivity was much shorter (10^{-5} sec) than the time of motion of interstitial ions (or vacancies) to meet each other to form neutral pairs (10^{-2} sec). However, the studies of Kanzaki^[13] and Kiss^[14] permit us to conclude that an increase of the number of charge carriers (vacancies in NaCl crystals, but interstitial ions and associated vacancies in the silver halides) actually takes place, but only in the initial stage of deformation, corresponding to the

sharp increase in conductivity. Kiss studied the features of the increased conductivity under different loads, with different polarities of the field, and using specimens of varying thicknesses and various methods of loading. Thereupon he concluded that the increased conductivity is most probably due to creation of point defects arising from the details of encounter of dislocations of opposite mechanical sign migrating from different sources in the same slip plane. Actually, the dislocations always exhibit jogs in a real crystal, and when such dislocations meet one another, they must liberate charge carriers. Kiss ascribes to recombination processes the decline in the number of vacancies after their concentration had temporarily increased. In his opinion, dislocations and divalent impurities play the role of recombination centers.

Assuming that the conductivity in AgBr is due to Frenkel defects (interstitial Ag^+ and Br^- ions and their vacancies), Kanzaki calculated the concentration of interstitial ions and vacancies from the variation in excess ionic conductivity and the energy liberated upon relaxation. Investigation of the interaction of these defects with dislocations permitted Kanzaki to explain the variation in the excess ionic conductivity upon annealing.

In concluding this section, we note that, as Kiss has shown, we should distinguish between the phenomena of increased conductivity observed at stresses above and below the yield point. The phenomenon properly called the Gyulai-Hartly effect is characterized by independence of the direction of the excess conduction current from the polarity of the field and by a long relaxation time under constant load. It is observed only at stresses above the yield point. The dependence of the conduction current on the polarity of the external field and the short relaxation time found when the effect occurs at stresses below the yield point undoubtedly arise from different causes. As Rueda's experiments^[26] have shown, this effect involves charge transport by dislocations. Thus, the nature of the effects at stresses above and below the yield point differs completely: a genuine increase in conductivity owing to increased concentration of charge carriers occurs at high stresses, but the increase in conductivity at low stresses is illusory (the conductivity upon deformation decreases upon changing the direction of the field), and it does not involve a change in the concentration of charge carriers.

2. APPEARANCE OF AN ELECTRIC POTENTIAL ON THE SURFACES OF DEFORMED SPECIMENS IN THE ABSENCE OF AN EXTERNAL ELECTRIC FIELD (THE STEPANOV EFFECT)

The publication in 1933 by A. V. Stepanov^[4] of a phenomenon that he had discovered excited much interest among physicists. Namely, an electric charge appears on the surface of a crystal of rock salt upon plastic deformation in the absence of an external electric field. Stepanov not only discovered this phenomenon, but he also studied its fundamental features. He showed that the charge can vary in sign, he determined the amount of charge, and noted that the amount of charge depends on the geometric dimensions of the

crystal. The charge turns out to be larger in specimens whose shape and dimensions rule out the possibility of blockage of the slip planes by the jaws of the press. An external electric field has no effect on the appearance nor the amount of the charge. A charge was noted at different temperatures in the range 30–170°C at stresses above 200 g/mm² (i.e., above the yield point). The charge disappears on unloading, and only a reloading to a stress above the yield point elicits a charge again. In Stepanov's opinion, the reason for appearance of the charge could be friction of layers of the crystal against internal inhomogeneities, including particles of impurities, and also formation of microcracks.

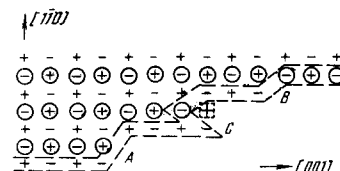
Currently the appearance of the electric charge is ascribed to the existence of charged jogs on the moving dislocations. In this regard, the Stepanov effect has attracted a great amount of attention in recent years. The possibility of using sensitive electrical methods of study opens up new perspectives for studying the mechanism of plastic deformation and for finding certain qualitative and quantitative characteristics of the behavior of dislocations in ionic crystals.

2.1. Origin of the Charged Jogs on Dislocations

As a rule, dislocations develop jogs when they intersect other dislocations. In NaCl-type crystals, intersection can give rise both to neutral jogs (if the Burgers vectors of the intersecting dislocations are mutually perpendicular), and charged jogs (when the Burgers vectors of the intersecting dislocations form an angle of 60° or 120°). In both cases, the offset of the jog is equal in size to the Burgers vector. Figure 1 shows the structure of an edge dislocation having neutral (A) and charged (B, C) jogs. The charged jog has the lesser offset. If an ion is added to the edge of this jog, the charge at the jog reverses. This implies the amount of charge on the jog is half the ionic charge. While a neutral jog could be formed by intersection with another dislocation, a charged small jog could be formed only by diffusion, owing to arrival or departure of a group of ions of both signs. However, the mobility of vacancies in NaCl, especially anion vacancies, is very limited under ordinary conditions at room temperature, and this mechanism of formation of jogs is not very probable. Formation of a charged region on a dislocation owing to dissociation of a neutral jog into two charged jogs seems much more probable. Dissociation can occur if any ion (C) arrives at the neutral jog or leaves it.

As Bassani and Thomson^[27] have shown, both cation and anion vacancies can deposit on dislocations with equal probability, since their binding energy to the core

FIG. 1. Diagram of the structure of neutral (A) and charged (B, C) jogs on dislocations in NaCl-type crystals. The plane of the drawing coincides with the extra half-plane of an edge dislocation passing along the lower edge of the half-plane. The circles outline the positions of ions situated $\frac{1}{2}b$ above and below the plane of the drawing.



of the dislocation is the same. Hence, the number of positively and negatively charged jogs on the dislocations must be the same in pure crystals, and the dislocations as a whole will be electrically neutral. Vacancies of one type are always in excess in a real crystal, owing to the presence of impurities. The deposition (capture upon migration) of these vacancies on neutral jogs may be the most probable reason for the existence of charged jogs on a dislocation.

Eshelby, Newey, Pratt, and Lidiard^[28] suggest that the dislocations should have an excess charge of a particular sign even in pure crystals. These authors explain the appearance of a charge by the "evaporation" of the one type or the other of vacancies from the edge of the extra half-plane. The preferential evaporation of vacancies of a certain type is determined by the energy of formation of the corresponding vacancies. However, we should note that in this study they are discussing a crystal in thermodynamic equilibrium. Hence, the theory of Eshelby et al. is hardly applicable to deformation of crystals at room temperature. The study of Eshelby, Newey, Pratt, and Lidiard has played a large role in the development of studies of charged dislocations. It has stimulated the appearance of numerous experimental and theoretical studies in this field, although debatable in itself. Eshelby et al.^[28] based their work on the results of Mott and Littleton,^[29] who had shown that the energy of formation of cation vacancies is smaller than for anion vacancies in NaCl-type crystals, and also on the data of Lehovec^[30] on the distribution of vacancies throughout the volume of the crystal. Thus they concluded that in NaCl an electric charge must exist in a thin layer on the outer surface and on internal surfaces (on block boundaries and on cylindrical surfaces around individual dislocations). Since cation vacancies can be formed more easily than anion vacancies, they penetrate from the surface (or from the dislocations) into the interior of the crystal, leaving the surface (or dislocation) positively charged. In order to preserve electroneutrality, a layer of vacancies or impurities of the opposite sign (a Debye-Hückel atmosphere) must arise beneath the surface (or around the dislocation).

Lifshitz and Geguzin^[31] consider invalid the assumption of Eshelby et al. that vacancies are absorbed inward from the surface on a macroscale, since this would considerably deplete the outer surface of one type of ions. In line with the fact that the thermodynamic potential cannot vary independently for the vacancies of opposite sign, the concept of energy of absorption from the surface of some particular type of vacancy loses meaning. Lifshitz, Kosevich, and Geguzin^[32] suggest that the charge (accumulation of vacancies of one type) on the outer and inner surfaces involves a differing type of interaction of the ions in these layers, as compared with the bulk of the crystal. The equilibrium concentration proves to differ for the different types of vacancies, owing to the variation in energy of interaction, and consequently an excess of vacancies of one type appears near the surface (or at the dislocations).

The surface and dislocation charges vary with differing crystal face, impurity content, or temperature. The charge distribution along a dislocation must also

vary with varying direction of the dislocation. Indeed, as Kosevich et al.^[33] have shown, the vacancy distribution is inhomogeneous in the Debye-Hückel atmospheres along a curvilinear dislocation (in particular, a prismatic one). Here the charge on the dislocation is not compensated by the charge of the atmosphere. The compensation necessary for electroneutrality of the crystal is attained by formation of charges of opposite sign on other defects throughout the crystal. The jogs on both edge and screw and mixed dislocations can be charged. Only edge and mixed dislocations can transport charge through the crystal, since the charges of ions do not alternate in the motion of edge dislocations (and the edge components of mixed dislocations), and a charged jog moves along with the dislocation. Screw dislocations do not carry charge through the crystal, since ions of opposite sign alternate in their motion, and the sign of the charge on a jog continually varies. A charged jog on a screw dislocation can only move along the dislocation. Spatial arrangements of charged jogs on edge and screw dislocations are given in^[34].

An atmosphere of vacancies or impurities collects around charged dislocations, and compensates their charge. Brown^[35] has calculated the potential of such a dislocation, the charge on the dislocation, and the force acting per unit length of the dislocation required to maintain it in motion.

2.2. Experimental Studies

The first experimental studies relating the appearance of an electric charge upon deformation to the motion of charged deformations were those of Fischbach and Nowick^[36,37] and of Caffyn and Goodfellow.^[12]

Quickly two approaches were distinguished in studying charged dislocations:

1) the appearance and motion of new dislocations during deformation, and 2) the oscillatory motion of old dislocations with respect to their impurity atmospheres. Each of these approaches has its advantages and defects. The advantage of the former approach is that one observes precisely the charge that the dislocations acquire in the deformation process. The defect of these experiments consists in the difficulty of determining the direction of motion of the dislocations, i.e., their mechanical sign, which is highly essential in correctly interpreting the sign of the potential that appears on the surface of the specimen. The latter approach lacks this defect, since in these experiments one observes the motion of dislocations of known mechanical sign. Here one introduces beforehand extra dislocations of one particular mechanical sign by bending the specimens. However, the already existing atmosphere of impurities around the oscillating dislocations can sometimes prevent the total charge from being manifested. The two series of experiments supplement one another.

Direct proof was gained in^[36,37,12] of the existence of a charge on dislocations by using different methods of fixation of the charge. They give facts concerning the mechanism of appearance of charge on the dislocations. They studied how the Stepanov effect is influenced by temperature changes, presence of impurities in the

crystals, application of an electric field, and irradiation with X-rays and gamma rays. They propose methods of estimating the charge density on the dislocations and also some other quantitative characteristics from the experimental data. We shall present the results of all these studies.

2.2.1. The electric charge on the surface and charged dislocations. Sproull^[38] undertook the first attempt to detect charge on dislocations. Assuming that the external electric field must interact with the charge on the dislocations and cause them to move, Sproull expected that a crystal would start to deform when acted on by an electric field. He applied a d.c. field to a bent LiF crystal. The crystal straightened slightly in the electric field. The deformation caused by the field was estimated from the displacement of the end of the crystal being straightened. Sproull assumed that the force F exerted by the field E on a dislocation of charge density q is determined by the expression

$$F = Eq = \frac{-q^2 k^2}{\epsilon} r \left(\ln \frac{k r}{2} + 0.0772 \right), \quad (1)$$

where $k^2 = 8\pi e^2 N_{\alpha} / \epsilon kT$ (N_{α} is the number of cations per cm^3 , ϵ is the dielectric constant, r is the distance that the dislocation moves, k is the Boltzmann constant, and T is the absolute temperature). Thus he estimated the charge density on the dislocations in the crystal that he was studying. It proved to be 2×10^{-3} CGSE/cm. The dislocations were also observed to move in an a.c. electric field.^[39] Schwensfeier and Elbaum^[40] detected motion in an electric field (supplemented by heating) of an entire wall of dislocations comprising the boundary of two disoriented blocks. The direction of displacement of the boundary changed with the sign of the field. The displacement was as much as 115μ . At temperatures of $560-640^{\circ}\text{C}$, the sign of the field had no effect on the direction of displacement of the boundary. In the opinion of these authors, these temperatures correspond to the isoelectric temperature range in which there is no charge on the dislocations (no excess of vacancies of either type). They established from the direction of shift that the boundary is charged negatively below 560°C , and positively above 640°C .

Shvidkovskii et al.^[41] and Zagoruiko^[42,43] have observed motion of single dislocations when acted on by an external electric field. When LiF and NaCl crystals are put in an etching agent,^[41] signs of motion of dislocations are noted upon action of a 6 kV field for 20 minutes. Zagoruiko determined the minimum field that can displace dislocations in LiF: on the average it is about 10^3 V/cm, but can be somewhat larger or smaller, depending on the rigidity of the crystal. The dislocations moved greater distances in lower electric fields in crystals having lower yield points. The higher the electric field is, the greater the number of dislocations

in motion. The number of moving dislocations and their path lengths increase with increasing time of action of the field. However, after the field has been turned on three times, as a rule, the dislocations stop moving and become fixed. Observing the direction of motion of the dislocations with respect to the field direction made it possible to determine the sign of the charge on the dislocations. Both positively and negatively charged dislocations were observed to move in one and the same crystal. Zagoruiko notes that only edge dislocations move.

Blistanov, Soifer, and Shaskol'skaya^[44] supplemented the experiments observing motion of single dislocations in NaCl and LiF crystals by measuring the internal friction at frequencies of 5 kHz and 1 Hz in a specimen placed in a condenser with an internal field of 10 kV/cm. Applying the electric field caused a sharp increase in the internal friction. The authors explained this phenomenon by a decrease in the degree of fixation of the dislocations, owing to the fact that the charged clouds were drawn away from them by the external field. When the field was turned off, the internal friction declined, and after the field has been turned on and off repeatedly, the rate of relaxation of the internal friction decreased. Drawing the clouds away from the dislocations is also evidenced by the shift in the internal friction peak to lower temperatures when the electric field is applied.^[45]

Observation of motion of individual dislocations in a electric field is a direct proof of the existence of charge on the dislocations. A more indirect but still convincing proof of the charge on dislocations is the discovery of an electric charge in single slip lines. Godefroy^[46] observed a charge in slip lines using an oscillating probe, and Saucier and Dupuy^[47,48,49] observed it by depositing electrically sensitive powders (mainly a mixture of sulfur and red lead). Such powders had previously been used to reveal charge on the surfaces of deformed specimens.^[50,51] Saucier and Dupuy studied crystals of LiF, NaCl, KCl, KBr, and MgO. In order to obtain single slip lines, LiF monocrystals were irradiated with gamma rays. The middle region of the crystals was annealed at a moderate temperature ($250-300^{\circ}\text{C}$) to produce local softening. It was precisely in the softened region of the crystals that single slip lines appeared on compression. They traced these by transmitted polarized light. The stress pattern indicated the presence in these slip lines of dislocation sources (Fig. 2). Dislocations of opposite mechanical sign were located on the two sides of these. They found by xerography a negative charge near the source and a positive charge at a distance from the source.

FIG. 2. Diagram of the distribution of stresses (a) and dislocations (b) along a single slip line in an LiF crystal. T - region of tensile stresses, C - region of compressive stresses, S - dislocation source (according to [49]).

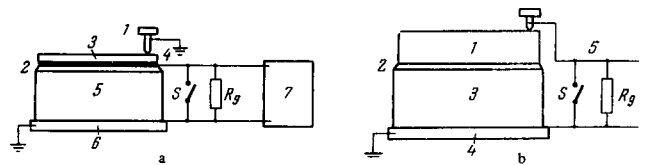
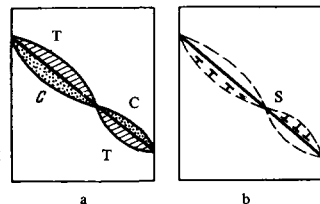


FIG. 3. Diagram of an experiment by Rueda and Dekeyser^[52] to observe the electric charge that appears upon action of a concentrated load. The numbers denote, in (a): 1 - indenter, 2 - cement (araldite), 3 - crystal, 4 - electrode (gold film), 5 - glass support, 6 - specimen table, 7 - electrometer; in (b): 1 - crystal, 2 - cement (araldite), 3 - glass support, 4 - specimen table, 5 - electrometer leads.

This means that the mobile dislocations in the studied crystal of LiF carry a positive charge, leaving a negative charge in the region of the dislocation source.

The relation of the charge on the surface to the charged dislocations that have arrived there is confirmed by comparing the surface charge with the motion of dislocations upon deformation. Such experiments have been performed by Rueda and Dekeyser^[52] and by Kiss^[53] on NaCl crystals deformed by a concentrated load. Rueda and Dekeyser used two methods for determining the electric signal produced by impact of an indenter. In one case, a gold electrode was placed on the NaCl surface opposite the one struck, and it was connected to an amplifier and oscilloscope (Fig. 3a). In this case the indenter was a diamond pyramid. In the other case, the charge arising in the crystal was transmitted directly to the electric circuit through the indenter, which was made of steel (Fig. 3b). Comparison of the electric signal with the distribution of dislocation etch pits on the surface of the NaCl opposite the one struck showed that this face almost always shows new dislocation etch pits. They are arranged in a pattern which is a projection of the rosette of dislocations. If the crystal is placed in a metallic ring (grounded), and an electrode is placed in the center of it, then this electrode sometimes picks up positive signals, and sometimes mixed (first positive and then negative) when the indenter strikes the upper surface. Etching the lower surface showed that a positive signal is observed when deformation occurs at the lower surface of the crystal (as in three-point bending), i.e., when the dislocations move from the electrode into the crystal. A negative signal appears when the distribution of dislocations corresponds to the "projection" of a rosette of dislocations arising at the upper surface (i.e., when the dislocations move toward the electrode). A mixed pattern of dislocations is observed with a mixed electric signal.

All the material presented above gives us grounds for supposing that the charge on the surface of alkali-halide crystals that appears during deformation actually involves motion of charged dislocations.

2.2.2. Behavior of the charge with different methods of deformation. The Stepanov effect has been studied with different methods of deformation: compression, bending, concentrated loads, and with longitudinal and bending vibrations. The objects of study were crystals of NaCl, LiF, KCl, KBr, MgO, and AgCl. In the first three methods, the effect was due to new dislocations, and to old dislocations in the latter two. As experiments on compression of NaCl crystals have shown,^[36,37,53-55] electric charges appear at sites of

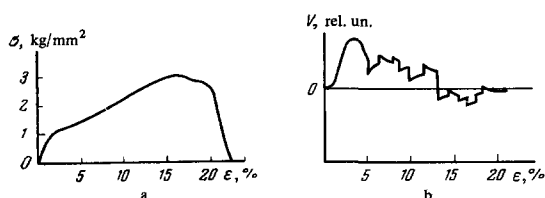


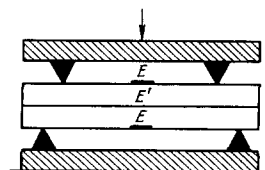
FIG. 4. a) Deformation curve of an LiF crystal (rate of deformation is 5×10^{-3} mm/sec); b) variation in potential at the ends of the specimen during compression (according to [56]).

inhomogeneous deformation (e.g., in regions of localized slip), when the external stress reaches the yield point. If the crystal is held under a constant load, then the charge quickly declines, and completely vanishes after several minutes. If, however, the load is removed after the charge has appeared, then the charge on the surface disappears in a fraction of a second. Caffyn and Goodfellow^[12,54,55] have found that the sign and amount of charge depend on a great many factors: on the purity of the crystal, the temperature of experiment, the stress state of the specimen, the input resistance of the circuit including the electrometer, the thickness of the specimen, the rate of loading, etc. The charge on the surface increases with increasing extent and rate of deformation, and this variation is not uniform. As Dupuy^[49] has shown, abrupt bursts or decreases of charge appear during deformation. The decreases in the charge (with rapid restoration to the former level) corresponded to the passage of slip through the entire specimen (the appearance of a slip band), while the bursts corresponded to the onset of a new slip system. Sometimes continuing fluctuations of charge from positive to negative have been observed during compression with longitudinal bending. Martyshchev^[50] has also found a differing behavior of the charge during compression of lithium fluoride (Fig. 4). The potential jumps occurred at the moment when light flashes appeared in the crystal. The author ascribed this to the appearance of cracks.

The behavior of the charge upon bending deformation was more uniform. Figure 5 shows a diagram of some vibratory bending experiments by Caffyn and Goodfellow.^[54,55] The specimens in these experiments had the shape of a bar with an electrode cemented to the middle. The charge was determined on the outer and central electrodes. The surface proved to be positively charged. The authors explain the positive charge on the outer surfaces having the maximum stresses by the motion of positively charged dislocations from the neutral line to the surface of the specimen. However, doubt is raised by Caffyn and Goodfellow's assumption that the dislocations move from the least stressed regions (from the neutral line) into strongly distorted regions (to the stretched or compressed surface). As we know, dislocations move away from their sources.^[57] This means that the dislocations bore a negative charge in Caffyn and Goodfellow's experiments. The authors themselves later came to this conclusion.^[58]

The characteristics of behavior of the electric signal when a concentrated load acts on an NaCl crystal have been described by Rueda and Dekeyser^[52,59-62] and also by Kiss.^[53] McGowan^[63] and Sonoike^[64] have done the same for AgCl. These experiments made it possible to relate the surface potential to the motion of charged dislocations (see the previous section), and also provided extensive material on the influence on the Step-

FIG. 5. Diagram of experiments by Caffyn and Goodfellow to study the appearance of an electric signal upon bending a crystal (according to [12]). E and E' are electrodes.



anov effect of impurities, the temperature, etc., as will be discussed below. Here we shall merely note that, as Sonoike found,^[64] the electric signal from the impact of the indenter can vary in shape: as sharp peaks or as smooth maxima, depending on the nature of the motion of the dislocations in the crystal. The author ascribes the sharp peaks to large displacements of dislocations, and smooth maxima to small displacements of the dislocations with respect to the atmospheres of impurities.

The behavior of the electric potential as dislocations vibrate with respect to the atmosphere of impurities (or vacancies) has been studied mainly by the Belgian scientists Amelinckx, Dekeyser, Vennik, Remaut, Strumane, and De Batist. These authors studied the electric effect in NaCl upon cyclic loading with a small amplitude of deformation. The specimens were first bent to introduce an excess of dislocations of one particular mechanical sign. The authors assumed that these dislocations remain electrically neutral upon bending deformation, and exist as charged jogs that attract atmospheres of vacancies (or impurities) of the opposite sign. Upon cyclic deformation (alternating bending^[16,65-68] or bending-unbending^[69-71] with a small amplitude of deformation so that the acting shear stress does not exceed the yield point), the dislocations should be shifted only slightly with respect to the surrounding atmosphere. That is, the dislocation-atmosphere dipole should oscillate (Fig. 6). As bending is increased, the dislocations should move toward the center of the specimen (Fig. 6a), and from the center of unbending (Fig. 6b). That is, the sign of the charge on the surface should vary periodically upon cyclic deformation. Indeed, these authors observed a periodic variation in the electric charge on the surface of NaCl upon cyclic deformation at a frequency of 10–10,000 Hz (Fig. 7).

Let us point some features of behavior of the electric signal upon cyclic deformation:^[16]

1) The amplitude of the signal declines during testing, but rest restores the signal; the decline in the signal is explained by gradual decrease in the dislocation-atmosphere dipole moment owing to spreading of the atmosphere over the entire path of motion of the dislocations. Rest collects the atmosphere again into one site.

2) An electric signal is observed at amplitudes of deformation above a certain critical value (corresponding to the onset of dislocation movement), and the signal rapidly increases with increase in the amplitude (the dislocation-atmosphere dipole moment is increased).

3) There is a phase shift between the deformation and the electric signal, such that the beginning of the horizontal region of the electric signal coincides with the maximum deformation. This phase shift does not depend on the frequency. The phase shift of the electric signal with respect to the signal of the mechanical vibrations is explained by the non-uniformity of motion of the dislocations. The electric signal appears at the moment when the dislocations start moving. The dislocations continue to move until the maximum stress (or strain) is attained, but they stand still during the subsequent fall in stress, while the charge maintains its maximum value (the horizontal region of the signal),

which corresponds to the maximum dipole moment. The charge begins to decrease when the critical shear stress is reached in the other direction.

4) The electric signal shows flat maxima and minima, and the width of the flat region decreases with increasing amplitude of deformation. This is because the dislocations remain in motion longer at large deformations, and stand still for a shorter time, under the same vibration schedule. Here the phase shift between the electric and mechanical signals correspondingly decreases (since the phase shift is determined by the stopping time of the dislocations).

5) The opposite sides of the specimen show charges of the same sign. That is, the dislocations from the compressed and the stretched sides move simultaneously from or to the surface. This fact indicates that the observed effect is not of piezoelectric origin, since in the latter case the charge on the opposite sides would differ.

6) Comparison of the sign of the mechanical vibrations with the sign of the electric signal makes it possible to determine the sign of the charge on the dislocations. In the specimens studied by the authors of^[16], the dislocations bore a positive charge.

In longitudinal vibrations of NaCl specimens^[66] (compression-tension deformation), the charge on the opposite sides of the specimen differs in sign. That is, in these experiments the dislocations of a particular mechanical sign must move to one particular side (Fig. 6b). They established in these experiments that appearance of an electric signal corresponds to a shear stress of 75 g/mm², i.e., the yield point of NaCl.

An electric signal also appears on the surface of specimens under pulsed loading^[66,67] (pulses of the same or of alternating signs). For one particular amplitude, the pulse duration substantially affects the size of the electric signal^[68]: the shorter the action

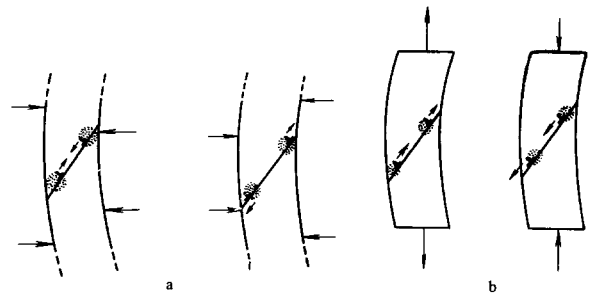
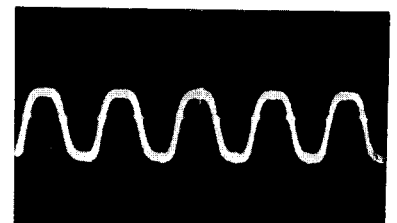


FIG. 6. Diagram of the motion of dislocations with respect to their surrounding atmosphere of compensating charge during oscillatory bending (a) (according to^[65]) and during longitudinal vibrations (b) (according to^[66]).

FIG. 7. Shape of the electric signal that appears on the lateral surface of an NaCl crystal upon cyclic deformation (according to^[65]).



time of the pulse, the less the charge is. Upon deformation by pulses of identical amplitude and duration (of alternating sign), the amplitude of the electric signal gradually declines, and reaches an equilibrium value after 10–12 cycles. If one thereupon increases the amplitude of the mechanical pulse, then the shape of the electric signal suddenly and markedly changes. It is assumed that the decrease with time of the amplitude of the electric signal involves a continual pinning of the dislocations, while the complex shape of the signal at the moment that the amplitude of deformation is increased involves breakthrough of the dislocations through the barrier (the pinning points). In these experiments, charge appeared at stresses below the yield point, and the sign of the charge corresponded to negatively charged dislocations. However, reversal of sign of the charge was sometimes observed in experiments at larger amplitudes. This phenomenon involves entry into action of new slip systems.

Strumane and DeBatist^[69] have studied in detail the relation of the electric signal to the amplitude of deformation. They also studied the effect of the amplitude of deformation on the resonance frequency and the logarithmic decrement of decay. The variation of the decrement with the amplitude of deformation reflects the rate of redistribution of the atmosphere of impurities about the oscillating dislocations. The found increase in the decrement with increasing deformation indicates a "spreading" of the atmosphere along the path of motion of the dislocations.

Study of the appearance of charge under different methods of deformation has led most of the authors to the conclusion that the dislocations become charged during motion, owing to the fact that vacancies that they meet on the path of motion deposit on them (or on their jogs). One of the proofs of this mechanism is the decrease in the concentration of vacancies during deformation under a constant load, as discovered by Kiss.^[14] Then the sign of the charge must be determined by the sign of the charge of the vacancies along the way. Since an overall effect throughout the volume of the crystal has been observed in the experiments, predominance of vacancies of one type must be of importance. In a real crystal containing various impurities, the concentration of vacancies is determined by the concentration of impurities (mainly divalent cation or anion additives). Hence, the macrocharge in real crystals must depend on the impurities present. The influence of impurities and also irradiation on the Stepanov effect has been discussed in numerous studies, whose results are given in the next section.

2.2.3. The effect of impurities and irradiation on the charge arising upon deformation. Impurities (divalent) affect both the stress required for appearance of a charge and the size and sign of the charge. The effect of impurities on the stress giving rise to a charge involves their hardening effect, which reduces the mobility of the dislocations in the crystals. Caffyn and Goodfellow have observed such an effect of CaCl_2 and SrCl_2 impurities in sodium chloride.^[12] Addition of anionic impurities (OH^- ions,^[58] sodium peroxide Na_2O_2 ^[52,53,60,72,73]) to NaCl crystals make the dislocations in them positively charged, while addition of cationic impurities (CdCl_2) makes them negatively

charged.^[52,53,60,72] The differing sign of the charge on the dislocations in the experiments of different authors apparently might involve the differing composition of these crystals.

In the case of AgCl crystals, addition of sulfide ions S^{2-} puts a positive charge on the dislocations, while cadmium ions Cd^{2+} make them negative.^[64] Presence of Mg^{2+} ions in LiF crystals^[60] increases the negative charge on the dislocations. Here the higher the concentration of impurities is, the greater the signal obtained upon deformation, in line with the number of vacancies created by the impurity.

If one compares crystals of KCl , NaCl , and LiF , then the latter crystals prove to show much more surface charge at equal extents of deformation.^[67,73] This might involve the fact that the impurities are more firmly bound to the atomic sites of the structure and more often occupy these sites in more rigid crystals having a larger lattice energy. Hence, they give rise to a greater number of vacancies compensating the charge of the divalent impurity.

Excess vacancies are introduced not only by adding impurities, but also by irradiation of the crystals by x-rays and gamma rays,^[49,62,74] which produce color centers in the crystals. However, since the color centers in alkali halide crystals are electrically neutral, the dislocations in the crystals have the same charge immediately after irradiation as before it. The dislocations in irradiated crystals show changes only after annealing: whenever the dislocations were negatively charged before irradiation, they became positively charged after irradiation and annealing. On the other hand, if the dislocations were positively charged even before irradiation, then the positive charge was increased after annealing following irradiation.* The weakening of negative charge and enhancement of positive charge in these experiments involves breakdown of the F and M centers upon annealing, which liberates positively charged anion vacancies.

2.2.4. Effect of temperature on the charge on the dislocations. Heating the crystals before or during deformation substantially affects the state of the impurities in crystals, and hence also the concentration of the vacancies bound to these impurities. In line with the differing composition of the tested crystals, the results of different authors studying the effect of the temperature on the charge on the dislocations proved to differ. Caffyn and Goodfellow,^[12] who did not know the sign of the charge on the dislocations in NaCl , found that in these crystals the charge remains about the same up to 180°C , while it declines with increasing temperature and vanishes entirely at 250°C . In Davidge's experiments^[76] (deformation by longitudinal vibrations), the dislocations have a negative sign below $400\text{--}550^\circ\text{C}$, but a positive sign above. Strumane and De Batist^[70] studied in greater detail the effect of the temperature on the charge on the dislocations. They deformed NaCl crystals with longitudinal vibrations at temperatures from -193° to 600°C . The dislocations in these experiments were positively charged up to 250° and above 600°C , but were negatively charged be-

* Cases have been observed of non-uniform behavior of the size and sign of the charge upon gradual increase of the annealing temperature.^[62]

tween these temperatures. The temperatures 250° and 600°C are the isoelectric points. It is interesting to note that the first isoelectric point is also manifested when one studies the electrical conductivity. As Dreyfus and Nowick^[57] showed, the conductivity-temperature curve has a break at 250°C . Strumane and De Batist ascribe the positive charge on the dislocations at low temperatures to capture by the moving dislocations of positively-charged cation vacancies. The latter are in excess because of their lower energy of formation as compared with the anion vacancies. At low temperatures, the impurities do not affect the concentration of vacancies, since they exist in the form of particles of precipitate imbedded in the NaCl crystal. The impurities begin to dissolve with rising temperature, and the liberated divalent cations occupy Na^+ ion sites. Simultaneously, they give rise to Na^+ vacancies to compensate the excess charge of the impurity. These Na^+ vacancies are captured by the dislocations, and cause a lowering of the total positive charge and appearance of a negative charge on the dislocations. In Smoluchowski's opinion, the appearance of the positive charge above the second isoelectric point is due to lowering of the number of free vacancies in the crystal at high temperature.

McGowan^[63] has studied the effect of temperature on the charge on the dislocations in AgCl crystals. He deformed the specimens with a silver cone, which served as the electrode to detect the signal. He performed the experiments at temperatures from -56° to 140°C . The charge was negative at low temperatures. The charge decreased with rising temperature, and vanished at temperatures from 70° to 140°C (depending on the purity of the crystal). The signal changed sign with further temperature rise, and corresponded to positively charged dislocations. The positive charge increased with further temperature increase. McGowan explains the negative charge on the dislocations at temperatures below the isoelectric point by capture of excess cation vacancies by the dislocations. He ascribes the reduction in the charge as the point is approached to appearance of interstitial Ag^+ ions (with

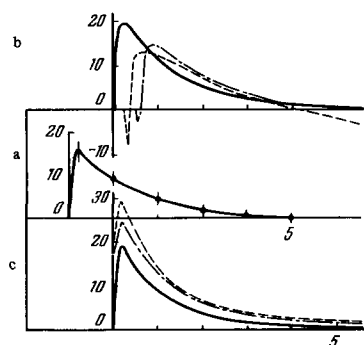


FIG. 8. Signals obtained from an NaCl specimen 1 mm thick. a) Without applying an electric field; b), c) upon applying a 120-V electric field to the lower electrode (b) +120 V, c) -120 V). The solid lines in Figs. b) and c) indicate the signals appearing when the field has been on for 10 min, the dotted lines when it has been on for 270 min, and the signals indicated by dot-dash lines were obtained 10 min after the field had been turned off (according to [26]).

increase in the number of Frenkel defects), which are captured by the moving dislocations. When the number of positively charged jogs equals the number of negatively charged ones, the dislocations become electrically neutral. In McGowan's opinion, the appearance of a positive charge and its increase with rising temperature may involve additional detachment of silver vacancies from the dislocations.

The effect of quenching of NaCl specimens on the charge on the dislocations has been studied. Quenching did not affect the sign of the charge in "pure" crystals,^[58,73] whereas the sign of the charge in crystals containing OH^- ions as an impurity reversed upon quenching.^[58]

2.2.5. Effect of an external electric field on the appearance of a charge upon deformation. Rueda^[26] has performed experiments on the application of an external d. c. electric field. He studied the charge upon deformation by a concentrated load at various times elapsed after applying the electric field. Figure 8 shows the shape of the electric signal when volume polarization is absent or present. We see that the external field affects the charge that appears upon impact by the indenter. When the applied electric potential had the same sign as the charge appearing on this side of the specimen, the signal from the impact of the indenter was increased by presence of the volume polarization (Fig. 8b). The thickness of the specimen affected the size of the signal in these experiments: the thicker the specimen was, the larger the negative portion of the signal. Rueda concluded from the obtained results that the discovered interrelation between the volume polarization and the electric effect from the impact of the indenter indicates that deformation distorts the volume polarization.

In his opinion, the observed electric effect involves transport of charged defects by the dislocations. These charged dislocations interact with the charged layers of the crystal at the negative electrode.

2.2.6. Estimate of the charge density and other quantitative characteristics of a crystal. In many experimental studies, the authors give quantitative data on the charge density on the dislocations, on the energy of formation of cation and anion vacancies, etc. McGowan^[63] proposes a very simple way to determine the charge density on the dislocations in the case of deformation by a concentrated load. The charge density is estimated from the size of the electric signal and the depth of the depression made by the impact of the indenter. If we divide the depth of the depression by the Burgers vector of the dislocations, we get an approximate number for the dislocation loops produced by the indenter. The total length of the produced dislocations is found by multiplying the number of dislocations by the length of the edge region of a dislocation

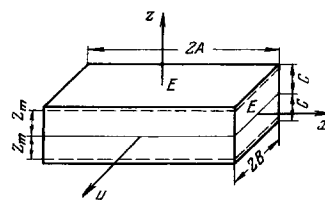


FIG. 9. A system by Strumane and De Batist^[70] to calculate the charge density on the dislocations.

loop. The latter is taken to be approximately half the thickness of the crystal. One can find from the measured potential V the total charge $Q = VC$, where C is the capacity, which equals $\epsilon S/4\pi d n f$ (ϵ is the dielectric constant, S is the area of the plate, and d is the distance that the dislocations have traveled). The charge density is found by dividing the total charge Q by the total length of the dislocation lines (or more correctly, their edge components). In silver chloride crystals containing 0.01% divalent impurities, the charge density on the dislocations proved to be 7.65×10^{-6} CGSE/cm.

Strumane and De Batist suggest a way to calculate the charge density on the dislocations upon deformation by longitudinal vibrations.^[70] If the crystal has the shape portrayed in Fig. 9, then a charge will appear on the surface of the specimen upon bending and subsequent cyclic loading. It is due to dislocations lying in the surface layers alone (e.g., in the layer $|z| > z_m$). Let the sample be deformed with an amplitude γ , and let γ_m denote the deformation at which a charge on the surface becomes noticeable. Then z_m is related to the amplitude of deformation as follows:

$$\frac{z_m}{c} = \frac{\gamma_m - \gamma f}{\gamma - \gamma f}, \quad (2)$$

where

$$\gamma f = -\gamma_m \left[\frac{\gamma - \gamma_m}{(1 - 2\Delta f/f)\gamma - \gamma_m} - 1 \right]; \quad (2')$$

and $\Delta f/f$ is the relative variation in the resonance frequency corresponding to the deformation γ .

If Λ is the density of excess dislocations of one particular mechanical sign introduced by bending, and m is the number of excess jogs of one particular electrical sign per unit length of dislocation, then a unit volume will have the charge $\Lambda m q$. When a dislocation is displaced with respect to its compensating atmosphere of impurities (or vacancies) by a distance l , a dipole moment will arise, being per unit volume equal to:

$$P = \frac{dM}{dv} = \Lambda m q l. \quad (3)$$

A potential will arise on the surface of the crystal, which is separated from the dipole by the distance r , with the value:

$$V = \frac{1}{\epsilon} \int_S \frac{P_n dS}{r} + \frac{1}{\epsilon} \int_V \frac{-\text{div } P}{r} dv, \quad (4)$$

where P_n is the normal component of P (with respect to the surface of the crystal). According to the assumptions stated above,

$$l = \alpha (|z| - z_m) u \quad \text{for } |z| > z_m, \\ l = 0 \quad \text{for } |z| \leq z_m. \quad (5)$$

Here α is a proportionality coefficient, and u is a unit vector in the direction of slip. If l_0 is the mean elongation of the dislocation arc when $z = C$, then $\alpha = l_0 / (C - z_m)$. As Niblett and Wilks^[77] have shown, the maximum elongation of a dislocation arc of length L during a deformation γ is $\gamma L^2/4b$ (b is the Burgers vector). Strumane and De Batist assume l_0 to be $2/3$ of this quantity, and get

$$\alpha = \frac{1}{6} \frac{\gamma L^2}{b(C - z_m)}. \quad (6)$$

Experimentally, one measures the potential difference

between two points on the surface of the crystal (e.g., between E and E' in Fig. 9). Upon substituting $\Lambda = \sqrt{2/Rb}$ (according to^[18], and taking account of the fact that the slip plane is $\{110\}$ in NaCl; R is the bending radius of the specimen) and combining Eqs. (3)–(6), they get

$$V_E - V_{E'} = \frac{1}{6\epsilon} \frac{qL^2}{Rb^2} \gamma I, \quad (7)$$

where q is the charge per unit length of dislocation, γ is the deformation measured for $z = C$, and

$$I = \frac{1}{C - z_m} \int_{v'} \left(\frac{1}{r_E} - \frac{1}{r_{E'}} \right) dv - \int_{S'} \left(\frac{1}{r_E} - \frac{1}{r_{E'}} \right) dS, \quad (8)$$

here v' is the fraction of the volume of the crystal having $|z| > z_m$, and S' corresponds to the two faces of the crystal perpendicular to the z axis.

Upon substituting into Eq. (7) the experimental values $2A = 3.3$ cm, $2B = 1$ cm, $2C = 0.17$ cm, $R = 8$ cm, $\gamma = 0.826 \times 10^{-5}$, $\gamma_m = 0.024 \times 10^{-5}$, $\Delta f/f = 6.93 \times 10^{-2}$, $L = 5.47 \times 10^{-4}$ cm,^[88] and $V_E - V_{E'} = 708$ mV, Strumane and De Batist found that $q = 1 \times 10^{-3}$ CGSE/cm. This corresponds to 4.2×10^6 excess steps per cm.

By using Brown's theory,^[85] Strumane and De Batist calculated the free energy of formation of cation vacancies in NaCl crystals, using their own experimental data. As Brown had shown, the potential in the bulk of the crystal far from the surface and from dislocations in a region of intrinsic and pseudointrinsic conductivity is

$$V_\infty = \frac{1}{2e} (g_+ - g_-) \quad (9)$$

(where e is the charge of an electron, and g_+ and g_- are the intrinsic energies of formation of cation and anion vacancies, respectively). The charge Q on the dislocations is related to V_∞ as follows:

$$Q = -\frac{eV_\infty}{2K_0(a)}, \quad (10)$$

where K_0 is a Bessel function in Watson's notation,^[78] and a is the lattice parameter. Since $g_+ = g_+^0 - kT \ln A_+$ ^[18] (g_+^0 corresponds to 0°K), $(A_+ A_-)^{1/2} = 22.2$,^[75] $A_+ = 7.6$,^[76] and $K_0(a) = 0.065$ for an impurity concentration of 5×10^{-5} , then when $q = 1.45 \times 10^3$ CGSE/cm (taken from experiment) we get

$$g_-^0 - g_+^0 = 0.26 \pm 0.12 \text{ eV},$$

Also, since, according to^[75], $g_-^0 + g_+^0 = 2.12 \pm 0.06$ eV, then

$$g_-^0 = 0.93 \pm 0.09 \text{ eV and } g_+^0 = 1.19 \pm 0.09 \text{ eV}.$$

Davidge has also estimated g_+^0 for NaCl from the temperature at which the charge on the dislocations changes sign:^[76] $g_+^0 = 0.95 \pm 0.1$ eV.

Eshelby et al.^[28] suggest that the electrostatic interaction of charged dislocations with their atmospheres of impurities (or vacancies) is responsible to a considerable degree for the mechanical properties of ionic crystals. These authors derived a formula for the shear stress capable of detaching dislocations from the surrounding charged atmosphere:

$$y = \frac{0.80q^2 \hbar}{\epsilon b} \quad (11)$$

(ϵ and \hbar are defined in (1), and b is the Burgers vector).

However, Sproull^[38] and Koehler and his associates^[79] state that Eq. (11) holds only at temperatures close to the isoelectric point under conditions of thermodynamic equilibrium. In line with this, they find unconvincing the hypothesis of Eshelby et al. that the electrostatic interaction between the dislocations and the atmosphere of impurities plays a decisive role in hardening. Soifer^[80] suggests that the electrostatic interaction can differ in different crystals, depending on their electric resistance and the state of their point defects.

2.3. Conclusions from the Studies of the Stepanov Effect

The observations of the appearance of an electric potential on the surface of NaCl-type crystals upon deformation (the Stepanov effect) permit us to draw the following conclusions:

1. Plastic deformation gives rise to an electric charge on the surface of specimens. The charge declines and disappears under constant load or after removing the load.

2. Comparison of the dislocation distribution and the electric signal produced has made it possible to establish that the potential is due to motion of dislocations bearing an electric charge. This is also indicated by the fact that the observed charge corresponds to the motion of edge dislocations alone.*

3. Most of the data indicate that the dislocations acquire charge during motion by capturing excess vacancies along the way.

4. The theoretical calculations of Bassani and Thomson, as well as the experimental observations of Zagoruiko, have shown that NaCl-type crystals simultaneously contain both positively and negatively charged dislocations.

5. An electric charge of a particular sign manifested on the surface indicates that dislocations of one particular sign predominate in the crystals. The sign of the charge on the dislocations depends on the crystal being studied, the impurity content, the temperature, and irradiation.

6. The size and sign of the charge vary with the temperature, owing to variation of the concentration of excess vacancies, as related to variation in the state of the impurities. The impurities determine the charge at intermediate temperatures, at which they occupy sites of the structure. The impurities are present as particles of precipitate at low temperatures, while the number of free vacancies declines at high temperatures.

7. Charged dislocations are surrounded by an atmosphere of vacancies or impurities of opposite electric charge. Electrostatic interaction between the charges on the dislocations and in the atmosphere can limit the mobility of the dislocations and harden the crystal.

3. CONCLUSION

Until recently, electrical effects arising from deformation have been studied exclusively on NaCl-type crystals. However, reports have recently been pub-

lished on existence of an electric charge on dislocations in crystals of CsI^[84] and CaF₂ containing a rare-earth impurity.^[85] The electric charge on the dislocations in CsI crystals was studied both under a concentrated load and with longitudinal and bending vibrations. It was found that the dislocations in the studied CsI crystals are positively charged from room temperature to 400°C. The relation of the size of the observed potential to the deformation and the test temperature was studied. The charge density at room temperature was 10⁻⁶ CGSE/cm. Impurities (Cd, Fe, Cr, Mn, Ag, Cu) do not change the sign of the charge on the dislocations, but only affect the charge density.^[86] Electrostatic interaction of the dislocations with the charged atmosphere does not lead to appreciable hardening in cesium iodide.

There are only some indirect indications on the existence of charge on the dislocations in fluorite crystals. The dislocations are assumed to be charged in semiconductor crystals.^[87,88]

Thus, the studies treated in this review convincingly show that the electric effects accompanying plastic deformation of ionic crystals are due to movement of dislocations, just as deformation itself is. The increase in ionic conductivity (the Gyulai-Hartly effect) involves production of vacancies or interstitial atoms when dislocations having jogs meet in a single slip plane. The appearance of an electric potential (the Stepanov effect) is due to capture of vacancies by moving dislocations. Studying these effects makes it possible to elucidate the mechanism of hardening of ionic crystals upon deformation, and also the mechanism of creep and fatigue. Comparison of the temperature dependence of the yield point and the electric potential^[28] has shown that they are correlated: a greater electric potential corresponds to a higher yield point. This means that electrostatic interaction between the charged dislocations and the surrounding atmosphere is actually one of the causes of hardening of ionic crystals.

Kiss's work has shown that deformation under constant load (creep) is accompanied by gradual elimination of vacancies from ionic crystals.

The features of behavior of the electric signal under cyclic loading help in understanding the behavior of dislocations and point defects in fatigue tests of crystals.

All of this indicates the great importance of the Gyulai-Hartly effect and the Stepanov effect in studying plastic deformation of ionic crystals. Studies along this line are continuing, and undoubtedly much more new information will be obtained on micro- and macro-processes of plastic change of shape of crystals.

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