Charged dislocations and properties of alkali halide crystals

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Theoretical and experimental investigations of charged dislocations in alkali halide crystals are reviewed. A description is given of the fine structure of an edge dislocation with defects on the dislocation line. A systematic account is given of theories of a sessile charged dislocation ranging from its representation by an infinitely long charged filament to an allowance for the fine structure of the dislocation line. Phenomenological models dealing with a charge on a moving dislocation are discussed. Forces acting on a dislocation are considered and the characteristics of its motion under the influence of an external mechanical load and of an electric field are dealt with. The direct and converse dislocation piezoelectric effects are described for a crystal containing mobile charged dislocations. In presentation of experimental results special attention is given to studies providing quantitative estimates of the linear charge density on a dislocation.

CONTENTS

1. INTRODUCTION

It is known that plastic deformation of crystals is largely due to mobile dislocations. The motion and inter-action of dislocations determine not only the change in the shape, but also the real atomic structure and many physical properties of crystals. Dislocation dynamics is consequently one of the most rapidly growing branches of solid-state physics. The laws governing dislocation dynamics are determined by the nature of the interatomic binding forces in solids. Defects, including dislocations, in crystals with heteropolar (ionic) bonds which include alkali halides carry an electric charge. This gives rise to special features of the motion and interaction of dislocations and is responsible for "cross" effects, such as the transfer of charge on application of mechanical loads and plastic flow under the influence of an electric field. The discovery of these effects is firmly linked to the names of A.F. Ioffe,[1] A.V. Stepanov,[2,3] and Gyulai and Hartly.[4] The effects are attracting continuing interest of researchers because of the extensive use of alkali halide crystals in infrared laser technology, solid state storage devices, etc.

The progress made in the study and explanation of electrical effects in alkali halide crystals is largely due to the recent results obtained on charged dislocations. We shall provide a systematic account of theoretical and experimental investigations of charged dislocations carried out in the Soviet Union and abroad. We shall concentrate our atten-

tion on the fundamental work carried out in recent years. Earlier investigations had been reviewed in 1958 (Refs. 5 and 6), 1968 (Ref. 7), 1974 (Ref. 8), and 1975 (Ref. 9).

2. THEORY OF CHARGED DISLOCATIONS

2.1. Fine structure of dislocations in alkali halide crystals. Influence of impurities on the dislocation charge

Ionic crystals consist of oppositely charged ions. The appearance of defects (including point defects, dislocations, block boundaries, etc.) in an ionic crystal disturbs the charge equilibrium so that defects (including dislocations) acquire an electric charge. The charge on an edge dislocation is transported by the dislocation as it moves, but screw dislocations do not transport charges. We shall deal mainly with the dynamic effects, so that screw dislocations will not be considered.

Easy slip planes along which edge dislocations glide preferentially in alkali halide crystals belong to the $\{110\}$ family. These planes are shown in Fig. 1. The direction of an edge dislocation is described by a unit vector $\Delta l = \langle 100 \rangle$ and its Burgers vector $b = (a/2)[1\bar{1}0]$ (a is the lattice period) is not the smallest translation vector. This is due to the fact that the direction of the vector b in alkali halide crystals is determined not only by the condition for a minimum of the dislocation energy, but also by the electrical neutrality condition. The latter imposes certain requirements also on the
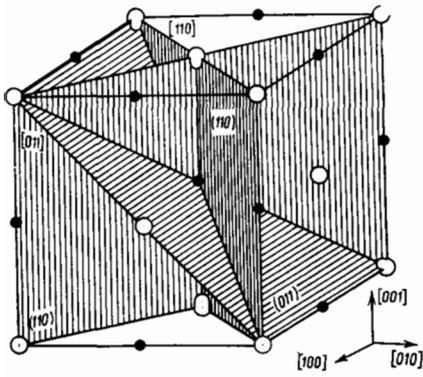
FIG. 1. Easy slip systems in alkali halide crystals. The cleavage planes are {100}.

FIG. 2. Edge dislocation with $\Delta l = [001]$ and $\mathbf{b} = (a/2)[\bar{1}10]$ in alkali halide crystals. The ion lattice is formed by (110) planes. Two (110) half-planes form a dislocation. A (001) cleavage plane is perpendicular to this dislocation.

geometry of an edge dislocation. Such a dislocation can be created by introduction of two additional {110} half-planes or one {100} half-plane. The edges of extra {110} half-planes are located at different levels.[6] Figure 2 shows a rectilinear edge dislocation in the structure of NaCl with the vector $\Delta l = [001]$ and the Burgers vector $\mathbf{b} = (a/2)[1\bar{1}0]$. The ionic lattice is represented by a set of $(1\bar{1}0)$ planes. The cleavage plane (001) is perpendicular to a dislocation. The distribution of ions in the core of a dislocation gliding in the $\{1\bar{1}0\}\langle 1\bar{1}0\rangle$ system and the energy of a core in NaCl were first calculated in Ref. 10. The boundaries of extra half-planes from which a dislocation is composed represent a chain of dipoles; if the alternation of charges in this chain is not disturbed, the dislocation is not charged. The periodicity may be disturbed by jogs, i.e., short parts of an edge dislocation, by means of which it is transferred to neighboring parallel slip planes.[11,12] There are two types of jogs. The first corresponds to a discontinuity in both half-planes which are used to represent a dislocation. The height of such a jog is $a\sqrt{2}/2$. Since such a jog (known as a complete jog) induces two reversals of opposite charges, it remains neutral. The second type of jog corresponds to a discontinuity in just one half-plane and is known as a half-jog and its height is $a\sqrt{2}/4$. Figures 3a and 3b show the distributions of ions in two neighboring (100) planes where dislocations have a half-jog. The plane of the figure is parallel to (100). The slip plane is perpendicular to the $[1\bar{1}0]$ direction. It also has a discontin-

uity (traces of slip planes AB and CD). The dislocation line is perpendicular to the plane of the figure and the direction of slip is $[1\bar{1}0]$. It is clear from Fig. 3a that a "defect" appears at some specific point on a dislocation and this defect can be called a "nascent" vacancy (represented by a shaded square). In the neighboring (100) plane (Fig. 3b) there is a positive ion A opposite this vacancy. The case illustrated in Fig. 3 corresponds to "creation" of an anion vacancy and appearance of a positive charge in the case of the half-jog. Similarly, near a "defect" corresponding to "creation" of a cation vacancy there is a negative charge. The charges of nascent vacancies of both types are equal and opposite in sign; we shall assume that these charges are $\pm q$. The addition of an ion with opposite sign to a half-jog alters the sign of its charge, i.e., the nature of the nascent vacancy so that

$$\pm q \mp e = \mp q.$$

Hence, it follows that the charge of a half-jog is $\pm e/2$, i.e., it is half the electron charge. Jogs on edge dislocations in alkali halide crystals may appear because of thermal activation or as a result of intersection of dislocations. The possible types of jogs formed as a result of intersection of dislocations are discussed in Ref. 13. An excess of half-jogs of one sign makes a dislocation charged. A dislocation charge may change because of the diffusion of ions to a half-jog. Bassani and Thomson[14] showed that the charge on an edge dislocation in an alkali halide crystal may also be due to an excess of vacan-
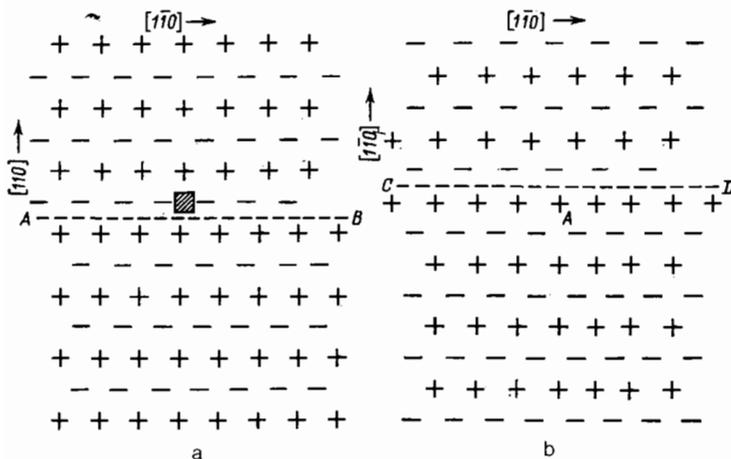
FIG. 3. Distribution of ions in neighboring (100) planes in an alkali halide crystal when an edge dislocation is displaced to a neighboring slip plane via a charged "half-jog."

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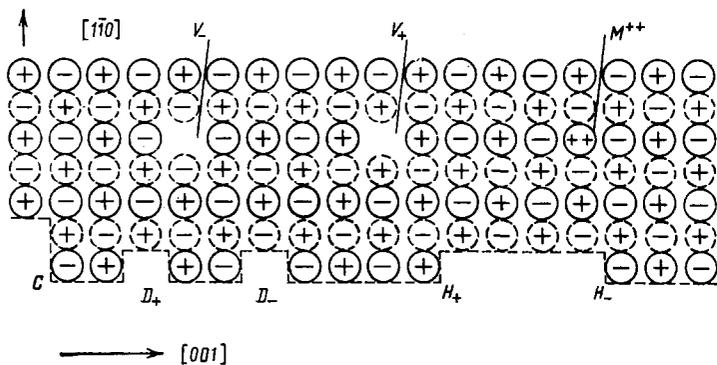
FIG. 4. Fine structure of a (110) extra plane of an edge dislocation with a Burgers vector **b** = (a/2)[110]. The continuous circles are ions in the plane of the figure, whereas the dashed circles lie b/2 below this plane. The defects in the region surrounding a dislocation are also shown.

cies of one sign in the dislocation core. This happens on introduction of divalent impurity atoms into a crystal. Atoms of divalent metals occupy the cation sites in the lattice and retention of neutrality requires formation of one cation vacancy for each impurity ion. In such a doped crystal the number of cation vacancies exceeds the number of anion vacancies by an amount equal to the number of divalent impurities. An excess of cation vacancies in the core of an edge dislocation in a doped crystal determines the charge of the dislocation. This charge changes as a result of a change in the number of charged "defects" in its core. Since the energy of formation of a vacancy in a dislocation core differs from the energy of formation of a pair of independent half-jogs of the same sign, vacancies and half-jogs are regarded as independent types of defect.

Figure 4 shows the projection of a (110) extra plane of an edge dislocation with the Burgers vector **b** = (a/2)[110] onto the plane of the figure. The ions lying in the plane of the figure are identified by continuous circles and the dashed curves identify the ions located at a distance b/2 below the plane of the figure. The defects on a dislocation determine the fine structure of the edge of the extra plane. They include a complete uncharged jog C, positively and negatively charged jogs H_+ and H_-, an anion vacancy D_+ carrying a positive charge, and a cation vacancy D_- carrying a negative charge. This figure shows also defects located far from a dislocation: these are divalent impurity ions M^{++}, and the anion and cation vacancies V_+ and V_-.

2.2. Theoretical models of sessile charged dislocations

The surface of an alkali halide crystal, like an edge dislocation, may also carry an electric charge. Theories of charged dislocations in alkali halide crystals have preceded studies of charges on the crystal surface.

2.2.1. Distribution of a charge on a plane surface of an alkali halide crystal. The distribution of the charge and potential on a plane surface of an alkali halide crystal was first investigated by Lehovec.[15] Lehovec began with the assumption that cation and anion vacancies in a crystal may appear independently of one another and that the energies of their formation are different.[16] The equilibrium number of vacancies of each kind per unit volume of a crystal $n_{1,2}$ can be found from the condition for a minimum of the thermodynamic potential $\mathscr{G}$ and it is permissible to vary it separately with respect to n_1 and n_2. According to Ref. 17, a smaller energy is needed to detach a cation from a lattice site so that an excess of cation vacancies should form and the electrical

neutrality in the bulk of a crystal can be restored by migration of some of the vacancies to the surface of a crystal, i.e., the surface becomes charged. A three-dimensional charged layer appears on the surface. The concentrations of the cation and anion vacancies in such a layer are different. The distribution of the potential in the charged layer can be found by solving the Poisson equation. The problem of finding the potential has a rigorous analytic solution.[15]

I. M. Lifshitz and Ya. E. Geguzin demonstrated[18] that the assumptions used in the calculations of Ref. 15 are incorrect. It is pointless to speak of emergence of vacancies of one type on the surface of a crystal, because this should produce a macroscopic layer of ions of one kind. Moreover, it is not permissible to introduce separately the concepts of activation energies of vacancies of either kind and the thermodynamic potential cannot be varied independently with respect to n_1 and n_2 According to Ref. 18 the number of sites 2N in a lattice is assumed to be an independent internal parameter and allowance is made for the fact that in an ordered structure we have

$$n_1 + N_1 = n_2 + N_2; \qquad (2.1)$$

where $N_{1,2}$ are the numbers of atoms of each kind per unit volume. The thermodynamic potential of the system is

$$\mathscr{G}\,(N_1,\ N_2,\ N) = \mu_0 N - kT \ln w_1 - kT \ln w_2$$
$$- n_1 g_1 - n_2 g_2;$$

here, μ_0 is the chemical potential in a pair of different atoms; $g_{1,2}$ is the characteristic energy of a defect; $k \ln w_{1,2}$ is the contribution of the cation and anion vacancies to the configurational entropy. In the case of a dilute solution ($n_{1,2} \ll N_{1,2}$) the thermodynamic probability is

$$w_{1,\,2} = n_{1,\,2} \ln \frac{n_{1,\,2}}{eN}, \qquad (2.2)$$

where e is the base of natural logarithms. It follows from the condition of equilibrium of the system

$$\left(\frac{\partial \mathscr{G}}{\partial N}\right)_{N_1,\,N_2} = 0 \qquad (2.3)$$

that the expression for the product of the solubilities is

$$\alpha_1(\infty)\,\alpha_2(\infty) = e^{-U/kT} = \alpha_0^2; \qquad (2.4)$$

here,

$$U = \mu_0 - (g_1 + g_2),$$

$$\alpha_1(\infty) = \frac{n_1}{N}, \qquad (2.5)$$

$$\alpha_2(\infty) = \frac{n_2}{N}; \qquad (2.6)$$

and U is the energy of formation of a Schottky pair by removal of one anion and one cation from their normal lattice sites and displacement to new sites on the crystal surface. The solubility product shows that vacancies may be created in pairs so that a charge may not appear on the surface of a crystal. The appearance of a charge on the surface of an alkali halide crystal is due to the fact[18] that in a thin surface layer, of the order of several interatomic distances (we shall call this an intrinsic surface layer), the energy of the interaction between ions is different than in the bulk of the crystal. Consequently, the equilibrium concentration of vacancies of each kind at the surface will differ from the concentration in the bulk. Hence, an electric charge should form on the surface, an electric field should appear, and vacancies should become redistributed in a surface layer of thickness of the order of the Debye screening radius.

The chemical potentials of defects in the bulk are

$$\mu_1(\infty) = \left(\frac{\partial \mathcal{G}}{\partial N_1}\right)_{N, N_2} = kT \ln \alpha_1(\infty) + g_1, \qquad (2.7)$$

$$\mu_2(\infty) = \left(\frac{\partial \mathcal{G}}{\partial N_2}\right)_{N, N_1} = kT \ln \alpha_2(\infty) + g_2. \qquad (2.8)$$

The chemical potentials in an intrinsic surface layer are given by

$$\mu_{1,2} = kT \ln \alpha_{1,2}(x) \pm e\varphi(x) \pm g_{1,2} - \Delta g_{1,2}(x);$$

here, x is the coordinate measured from the surface into the interior of the crystal; $\Delta g_{1,2}(x)$ is the change in the characteristic energy of a defect in an intrinsic surface layer; $\Delta g_{1,2}(x) = 0$ if $x \gg a$; $\varphi(x)$ is the electric potential. The condition of constancy of the chemical potential near the surface and in the bulk of a crystal

$$\mu(x) = \mu(\infty) \qquad (2.9)$$

leads to the following equilibrium value of the vacancy concentration in such an intrinsic surface layer:

$$\alpha_{1,2}(x) = \alpha_0 e^{\pm \chi}(1 + aF_{1,2}^* \delta(x)); \qquad (2.10)$$

here, α_0 is given by Eq. (2.4)

$$\chi = -\frac{e}{kT}(\varphi(x) - \varphi(\infty)),$$

$$\delta(x) = 1, \quad x \leqslant a,$$
$$= 0, \quad x > a.$$

The function $F_{1,2}^*$ is given by

$$aF_{1,2}^* = \int_0^\infty \exp\left(\frac{\Delta g_{1,2}}{kT} - 1\right) dx.$$

A charge distribution established in a crystal is

$$\rho(x) = \frac{2e\alpha_0}{\Omega}\left[\operatorname{sh}\chi + \frac{a}{2}(F_1^* - F_2^*)\right]\delta(x),$$

where $\Omega = a^3$ is the atomic volume. The distribution of the electric potential is found by solving the Poisson equation subject to the following boundary conditions:.

$$\chi(\infty) = 0, \qquad \left(\frac{\partial \chi}{\partial x}\right)_\infty = 0.$$

Calculations indicate that near the surface of a crystal there is a double electric layer and the charge of the intrinsic surface layer is compensated by the charge on the surface.

It therefore follows from the theory of Lifshitz and Geguzin that the charge and potential on the surface of an alkali halide crystal are governed not only by the bulk properties, but also by the surface properties.

2.2.2. Model of a dislocation in the form of a charged filament. The first theoretical investigations of charged dislocations were reported by Eshelby et al.[19] A dislocation is regarded in Ref. 19 as an infinite charged filament surrounded by a continuously distributed charge cloud. An infinite value of the potential of the filament itself can be avoided by surrounding it with a cylindrical surface of radius r_0 and the procedure of finding the potential of a dislocation is replaced by the problem of determination of the potential on the surface. The mechanism of formation of a dislocation charge considered in Ref. 19 is similar to the formation of charges on the surface of alkali halide crystals.[15] Eshelby et al. ignored the energy binding defects to a dislocation line so that a dislocation, like a free surface in Ref. 15, is a continuous source or sink of vacancies. In spite of the incorrectness of these assumptions, the paper of Eshelby et al. played a major role in the development of a theory of charged dislocations, becoming a starting point for subsequent theories. Mobile atoms of divalent impurities are considered in Ref. 19 in order to bring the model closer to reality. Conservation of electrical neutrality requires creation of one cation vacancy per each impurity atom, so that $\alpha_1(\infty) = \alpha_2(\infty) + C$, where C is the concentration of divalent impurity atoms. It is shown in Ref. 20 that a doped crystal is described by Eq. (2.4), so that

$$\alpha_1(\infty)(\alpha_1(\infty) - c) = \exp\left(-\frac{g_1 + g_2}{kT}\right) = \alpha_0^2.$$

A compensating charge cloud consists of mobile ion and anion vacancies and of divalent impurity atoms; the density of this cloud is

$$\rho = e(n_M(r) + n_2(r) - n_1(r)), \qquad (2.11)$$

where $n_M(r)$ is the number of impurity atoms per unit volume.

The equilibrium number of defects on a dislocation line in a charge cloud can be determined by minimization of the thermodynamic potential. In general, the thermodynamic potential can be represented by a sum of three terms:.

$$\mathcal{G} = \mathcal{G}_d + \mathcal{G}_c + W; \qquad (2.12)$$

$\mathcal{G}_d$ includes the energy of formation and the entropy term for defects on a dislocation; $\mathcal{G}_c$ applies to a charge cloud; W is the energy of the electrostatic interaction of the dislocation-charge cloud system. The energy W includes the potential energy of the electrostatic interaction between a dislocation W_d and a charge cloud W_c. According to Ref. 19, Eq. (2.12) reduces to $\mathcal{G} = \mathcal{G}_c + W$ and it is found that

$$\mathcal{G}_c = \int_0^R g_{1,2} n_{1,2}(r) \cdot 2\pi r \, dr - kT \ln w_{1,2} - kT \ln w_M.$$

The first term on the right-hand side of $\mathcal{G}_c$ is the energy of formation of defects in the investigated cloud, whereas the second and third are the entropy terms calculated in a dilute

solution approximation [see Eq. (2.2)]. We can reduce W to W_c, which includes the energy of the electrostatic interaction of charge clouds with one another $W_{c,c}$, and with a dislocation line $W_{c,d}$, so that

$$W = W_c = W_{c,c} + W_{c,d} = \int_{r_0}^{R} \rho\varphi(r) \cdot 2\pi r \, dr,$$

where the potential $\varphi(r)$ is due to the cloud and dislocation charges, and R is the radius of a cylinder sufficiently far from a dislocation. Integration is carried out over the whole volume of the cylinder, with the exception of a region of radius r_0 surrounding a dislocation line. The total charge inside this volume is zero. The solution of the variational problem using the electrical neutrality of the system and the condition of conservation of the total number of divalent impurities should make it possible to determine the concentration of vacancies and divalent impurities in a charge cloud.[19] The Poisson equation

$$\nabla^2\varphi = -\frac{\rho}{\varepsilon\varepsilon_0} \qquad (2.13)$$

(ε_0 is the electrical constant of the permittivity of free space and ε is the permittivity of the investigated material) can be reduced to

$$\nabla^2 p = -\sinh p \cdot \Lambda^{-1}, \qquad (2.14)$$

$$p = \frac{e\varphi}{kT}, \qquad \Lambda = \left(\frac{\varepsilon\varepsilon_0 kT}{2\alpha_1(\infty)Ne^2}\right)^{1/2} \qquad (2.15)$$

is the radius of the cloud. Equation (2.14) is expressed in terms of cylindrical coordinates; its exact solution is possible only if $p \ll 1$, i.e., if $\sinh p \approx p$. This solution is

$$p = AK_0\left(\frac{r}{\Lambda}\right) + BI_0\left(\frac{r}{\Lambda}\right);$$

K_0 and I_0 are the modified Bessel functions of the zeroth order and with an imaginary argument. Since I_0 does not have a finite limit at infinity, we shall ignore it. The potential in the charge cloud is

$$\varphi(r) = A\frac{kT}{e}K_0\left(\frac{r}{\Lambda}\right).$$

We can find A using the fact that in the limit $r \to r_0$ the potential becomes equal to the potential of an infinitely long charged filament. We finally have

$$\varphi(r) = \frac{Q_l}{2\pi\varepsilon\varepsilon_0}K_0\left(\frac{r}{\Lambda}\right), \qquad (2.16)$$

where Q_l is the charge per unit length of a dislocation line.

Although the theory of Eshelby et al. was developed only for the case when $e\varphi \ll kT$, which cannot be realized even at room temperature, and although a dislocation was regarded as an infinitely strong vacancy sink, it nevertheless stimulated theoretical and experimental investigations of charged dislocations. There was a considerable resonance to the discovery of the isoelectric points predicted in Ref. 19: these are such temperatures T_i at which the charge Q_l vanishes. The sign of Q_l is reversed at temperature $T > T_i$. The experiments in which the isoelectric points were discovered were first carried out by Davidge.[21] Kosevich, Margvelashvili, and Saralidze[22,23] solved the problem of the distribution of the charge and potential around an edge dislocation in an alkali halide crystal allowing for the energy $W_{1,2}$ of the elas-

tic interaction of cation and anion vacancies with the dislocation. In discussing the appearance of a charge on a dislocation Kosevich et al. used the model of Lifshitz and Geguzin[18] and regarded a dislocation as a special surface near which the energy of formation of defects is different than in the bulk of a crystal. The equilibrium vacancy concentrations are then given by

$$\alpha_{1,2} = \alpha_0\left(\exp\frac{\pm e\varphi - W_{1,2}}{kT}\right)[1 + aF_{1,2}^*\delta(r - r_0)].$$

The dimensionless function $F_{1,2}^*$ has the same meaning as in Eq. (2.10), i.e., it is related to a change in the characteristic energy of vacancies on a surface of radius r_0 surrounding a dislocation. In the determination of $W_{1,2}$ a vacancy is regarded as a dilatation center causing an inelastic change in the volume of the medium. The energy of the elastic interaction of such a defect with an edge dislocation is[24]

$$W_{1,2} = \frac{A_{1,2}\sin\psi}{r}, \qquad A_{1,2} = -\Delta V_{1,2}\frac{Gb(1+\nu)}{3\pi(1-\nu)};$$

here, ψ is the angle measured from the Burgers vector in a plane perpendicular to the dislocation line; r is the distance from the dislocation axis to the point under consideration; G is the shear modulus; ν is the Poisson ratio; $\Delta V_{1,2}$ is the change in the volume of the medium at the location of a vacancy. The solution of the Poisson equation subject to the conditions $e\varphi \ll kT$ and $W_{1,2} \ll kT$ shows that inclusion of the elastic interaction results in a redistribution of the charge in the bulk and in a disturbance of the axially symmetric distribution of the potential. Similar results were obtained by Kolomiĭtsev[25] who also demonstrated that at short distances from the axis of an edge dislocation (up to ~ 30 Å) the distributions of the potential and charge are affected significantly by a modulus effect due to the difference between the elastic moduli of the defects and the matrix.[26]

2.2.3. Allowance for the fine structure of a charged dislocation. The relationship between the fine structure of an edge dislocation and its charge[11,12,14] was developed further by Whitworth.[27,28] It was assumed in Ref. 27 that the dislocation charge is due to charged jogs and vacancies (Fig. 4) which for the sake of brevity we shall call defects on a dislocation. As in Ref. 19, the charge cloud is assumed to consist of mobile cation and anion vacancies as well as mobile divalent impurity atoms. The following characteristic parameters were introduced by Whitworth in calculations of the charge and potential of a dislocation line: $\gamma_{1,2}$—the number of negatively and positively charged jogs per unit length of a dislocation; $\beta_{1,2}$—the number of negatively and positively charged vacancies per unit length of a dislocation; $\Gamma = 1/a$—the number of atomic planes per unit length; $\pm q$—the charge of a jog or a vacancy; J—the energy of formation of a pair of jogs of opposite signs; g_1—the energy of formation of a cation vacancy due to a change in the charge of a negative jog; g_2—the energy of formation of an anion vacancy because of a change in the charge of a positive jog; $g_1 + g_2$—the energy of formation of a Schottky pair in the bulk of a crystal; B_1—the energy of association of a dislocation and a cation vacancy; B_2—the energy of association of a dislocation and an anion vacancy; $\mathscr{L} = (g_1 + g_2) - (B_1 + B_2)$—the energy of formation of a Schottky pair on a dislocation line. In this model, dislocations are no longer regarded as infinite sources or sinks of

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vacancies. In the expression for the thermodynamic potential of Eq. (2.12) the term $\mathscr{G}_c$ is of the same form as in Ref. 19. In the definition of $\mathscr{G}_d$ it is assumed that jogs and vacancies are distributed uniformly along a dislocation and that their contribution to the configurational entropy can be written down in the approximation of a dilute solution, so that

$$\mathscr{G}_d = \frac{1}{2} J (\gamma_1 + \gamma_2) + (g_{1,2} - B_{1,2}) \beta_{1,2}$$
$$- kT\gamma_{1,2} \ln \frac{e\Gamma}{\gamma_{1,2}} - kT\gamma_{1,2} \ln 2 - kT \frac{e\Gamma}{\beta_{1,2}}.$$

The energy is $W = W_c + W_d$, where W_c is defined in the same way as in Ref. 19, whereas $W_d = Q_l \Phi_0$ is the potential energy of a charged dislocation due to the interaction of its charges with one another and with the charge cloud. Here, Φ_0 is the potential of a dislocation line and

$$Q_l = \frac{1}{2} e (\gamma_2 - \gamma_1) + e (\beta_2 - \beta_1). \qquad (2.17)$$

Whitworth[27] found $\gamma_{1,2}$ and $\beta_{1,2}$ by solving the variational problem for the thermodynamic potential and substituting the results in Eq. (2.17), which gives

$$Q_l = 2e\Gamma \left\{ e^{-J/2kT} \operatorname{sh} \left[\frac{(\Delta g/2) - e\Phi_0}{kT} - \frac{1}{2} \eta \right] \right.$$
$$\left. + e^{-L/2kT} \operatorname{sh} \left[\frac{(\Delta B/2) - e\Phi_0}{kT} - \eta \right] \right\}; \qquad (2.18)$$

here,

$$\Delta g = g_2 - g_1, \quad \Delta B = B_2 - B_1, \quad \eta = \ln \frac{\alpha_1 (\infty)}{\alpha_0}.$$

The first term in the above expression for Q_l is due to charged jogs and the second is due to vacancies on a dislocation. We can find Φ_0 by surrounding a dislocation with a surface of radius r_1 selected so that $l \ll r_1 \ll \Lambda$, where l is the distance between neighboring defects on a dislocation. If $r < r_1$, an electric field is established solely by the charges on a dislocation line, whereas for $r > r_1$ we have to allow also for the influence of the charge cloud. The potential Φ_0 differs from the potential considered in Ref. 19 by a correction which allows for the discrete nature of the distribution of charges on a dislocation line, i.e.,

$$\Phi_0 = \frac{Q_l}{2\pi\varepsilon\varepsilon_0} K_0 \left(\frac{r_1}{\Lambda} \right) + (\psi_2 - \psi_1);$$

here, ψ_1 is the potential of the surface surrounding a dislocation, calculated on the assumption that the dislocation line includes 2M charges distributed uniformly with an average linear density Q_l. If $x \gg r_1$, then

$$\psi_1 = \frac{Q_l}{2\pi\varepsilon\varepsilon_0} \ln \frac{2Ml}{r_1}. \qquad (2.19)$$

In determination of ψ_2 it is assumed that the radius r_1 tends to zero and the charges on a dislocation are distributed discretely. It is assumed that ψ_2 amounts to $(\psi_{2max} + \psi_{2min})/2$; here, ψ_{2min} is the potential at the center of a gap of length $2l$ between discrete charges, so that

$$\psi_{2min} = \frac{Q_l}{2\pi\varepsilon\varepsilon_0} \sum_{n=1}^{M} \frac{1}{n}. \qquad (2.20)$$

In determination of ψ_{2max} a test charge q is placed at a point

between two neighboring charges on a dislocation line. In the case of a uniform distribution of charges the system should relax i.e. each of the charges should shift by $l/2$, so that

$$\psi_{2max} = \frac{Q_l}{2\pi\varepsilon\varepsilon_0} \left(\sum_{n=1}^{2M} \frac{2}{n} - \sum_{n=1}^{M} \frac{1}{n} \right). \qquad (2.21)$$

Using Eqs. (2.20) and (2.21), we can find ψ_2, which in the case of large values of M can be written in the form

$$\psi_2 = \frac{Q_l}{2\pi\varepsilon\varepsilon_0} (\ln M + \ln 2 + C), \qquad (2.22)$$

where $C = 0.5772$ is the Euler constant. Using Eqs. (2.19) and (2.22) subject to the condition $r \ll \Lambda$, we find that

$$\Phi_0 = \frac{Q_l}{2\pi\varepsilon\varepsilon_0} \left(K_0 \left(\frac{q}{\Lambda Q_l} \right) + C \right). \qquad (2.23)$$

The values of Q_l and Φ_0 can be obtained by solving graphically Eqs. (2.18) and (2.23) and assuming specific values of J, g_1, g_2, B_1, B_2, η, and Λ. An estimate of Φ_0 obtained by means of Eq. (2.18) from the experimental data on Q_l given in Ref. 29 for NaCl at room temperature $[\alpha(\infty) = 5 \times 10^{-5}, Q_l = -2 \times 10^{-11} \text{ C} \cdot \text{m}^{-1}]$,[29] on the assumption that Q_l is entirely due to cation vacancies and that $B_1 = 6.4 \times 10^{-20} J$ (Ref. 14) and $\Gamma = 3.55 \times 10^9 \text{ m}^{-1}$, gives $\Phi_0 = 0.24$ V. Consequently, the condition $e\Phi_0 \ll kT$ necessary for linearization of Eq. (2.13) is not satisfied.

A more general form of a charge cloud was considered by Whitworth in Ref. 28 and the difference from Ref. 27 was that, in addition to mobile cation vacancies, the author allowed also for immobile divalent impurities, which can be in the free state or can form electric dipoles with cation vacancies. The fine structure of a dislocation is represented by one of the types of a charged defect on dislocations that interact with one another. In the treatment given in Ref. 28 Whitworth allowed for the pair electrostatic interaction of defects. The model proposed in Ref. 28 makes it possible to consider not only ionic crystals, but also semiconductors. Let us assume that n_0 is the total number of divalent impurities per unit volume and that it is the same both in the charge cloud and outside; $n_1(\infty)$ is the number of cation vacancies per unit volume far from the cloud; $\tilde{n}_M(\infty)$ and $[n_0 - \tilde{n}_M(\infty)]$ are, respectively, the numbers of free impurities and dipoles. The following parameters are used in the description of the charge cloud:

$\tilde{n}_M$ is the number of impurities in the free state;

$[n_0 - \tilde{n}_M(r)]$ is the number of dipoles per unit volume;

$n_1(r)$ is the number of mobile cation vacancies per unit volume found by solving the variational problem[19] and described by

$$n_1(r) = n_1(\infty) e^{-\varphi(r)/kT}. \qquad (2.24)$$

It follows from the condition of electrical neutrality that

$$n_1(\infty) = \tilde{n}_M(\infty). \qquad (2.25)$$

The concentrations of associated and free defects are related by the law of mass action,[20] from which it follows

$$\frac{n_1(r) \tilde{n}_M(r)}{n_0 - \tilde{n}_M(r)} = \frac{n_1(\infty) \tilde{n}_M(\infty)}{n_0 - \tilde{n}_M(\infty)}. \qquad (2.26)$$

Using Eqs. (2.24), (2.25), and (2.26), Whitworth[28] de-

scribes n_M by

$$n_M = \frac{n_1(\infty)\exp(-e\varphi(r)/kT)}{1+h[\exp(-e\varphi(r)/kT)-1]}. \qquad (2.27)$$

The density of charges in a cloud

$$\rho = e(\tilde{n}_M(r)-n_1(r))$$

is modified after allowance for Eq. (2.27) to

$$\rho = en_1(\infty)\left\{\frac{\exp(-e\varphi(r)/kT)}{1+h[\exp(-e\varphi(r)/kT)-1]}-\exp\frac{e\varphi(r)}{kT}\right\}; \qquad (2.28)$$

here, $h = \tilde{n}_M(\infty)/n_0$.

The potential inside the cloud can be found without linearization of the Poisson equation

$$\frac{d^2p}{dr^2}+\frac{1}{r}\frac{dp}{dr}=\frac{1}{\Lambda^2(2-h)}\left[e^p-\frac{e^{-p}}{1+h(e^{-p}-1)}\right] \qquad (2.29)$$

by numerical methods using two boundary conditions. The first boundary condition is written down in the form of the Gauss theorem:

$$\lim_{r\to 0}\left(r\frac{dp}{dr}\right)=\frac{eQ_l}{2\pi\varepsilon\varepsilon_0 kT}, \qquad (2.30)$$

and allowance is made for the fact that in the limit $r\to 0$ the potential is created simply by the dislocation charges. When the processes inside the cloud are considered, a dislocation is regarded as a charged filament. The second condition follows from the fact that for $p\ll 1$ and $r\to\infty$ the solution of Eq. (2.29) becomes $p=AK_0(r/\Lambda)$. Introducing a dimensionless variable $s=\ln(r/\Lambda)$, Whitworth[28] reduces Eq. (2.29) to the form

$$\frac{d^2p}{ds^2}=e^{2s}\frac{1}{2-h}\left[e^p-\frac{e^{-p}}{1+h(e^{-p}-1)}\right], \qquad (2.31)$$

and the boundary condition of Eq. (2.30) now becomes

$$\lim_{s\to-\infty}\frac{dp}{ds}=-\frac{eQ_l}{2\pi\varepsilon\varepsilon_0 kT}=-H, \qquad (2.32)$$

so that in the limit $s\to-\infty$ the $p(s)$ curves have asymptotes, the slopes of which are the same for different values of h if the temperature of a sample is constant. The value of s_0 from which the boundary condition of Eq. (2.32) begins to be satisfied depends on h. Equation (2.29) is solved by the "chasing" method.[30]

In an analysis of a dislocation it is assumed[30] that it contains only one type of charged defect. We shall assume that M is the number of such defects per unit length of a dislocation. In the extrinsic conduction range the value of M represents the number of cation vacancies or negatively charged jogs; in the extrinsic conduction range it represents the number of anion vacancies or positively charged jogs. Since defects on a dislocation interact in pairs, we can introduce a quantity $j=1,2,3,\dots$, so that ja gives the distance between the defects in a pair. Let us assume that m_j is the number of interacting pairs of defects with a given value of j. The number of ways of distributing defects in such pairs is[31]

$$w=\frac{M!}{\Pi_j m_j!}. \qquad (2.33)$$

The function

$$f=\frac{M}{N}=\sum_{j=1}^{\infty}m_j\left(\sum_{j=1}^{\infty}jm_j\right)^{-1} \qquad (2.34)$$

gives the fraction of positions on a dislocation occupied by defects; here, N is the total number of sites per unit length of a dislocation. Knowing f, we can find the dislocation charge

$$Q_l=\frac{q}{a}f. \qquad (2.35)$$

The equilibrium value of f can be deduced from the condition of constancy of the chemical potential at a dislocation μ_d and in the bulk of a crystal $\mu_1(\infty)$:

$$\mu_d=\left(\frac{\partial\mathscr{G}_M}{\partial M}\right)_{n_l(r)}; \qquad (2.36)$$

here, $\mathscr{G}_M$ includes the M-dependent terms of the thermodynamic potential in Eq. (2.12). These terms are $\mathscr{G}_d$, W_d, and the energy $W_{c,d}$ of the electrostatic interaction between a charge cloud and a dislocation.

We shall assume that $\mathscr{G}_d$ is the characteristic energy of one defect; then, using Eq. (2.33), we find that in the case of large values of M

$$\mathscr{G}_d=Mg_d-kTM\ln\frac{M}{e}+KT\sum_{j=0}^{\infty}m_j\ln\frac{m_j}{e}. \qquad (2.37)$$

Here, W_d includes the energy of the electrostatic interaction of charges on a dislocation with one another $W_{d,d}$ and with a charge cloud $W_{d,c}$:

$$W_d=W_{d,d}+W_{d,c}.$$

In determination of W_d it is assumed first that defects are distributed uniformly on a dislocation and the corresponding energy W_u is found; next, a correction ΔW for the pair of interaction of defects is introduced, so that

$$W_d=W_u+\Delta W;$$

here,

$$W_u=\frac{1}{2}Mq(\varphi_d+\varphi_c(0)). \qquad (2.38)$$

The potential φ_d is created by the dislocation charges and $\varphi_c(0)$ by the cloud charge. It follows from the Green reciprocity theorem,[32] that

$$W_{c,d}=W_{d,c}=\frac{1}{2}Mq\varphi_c(0),$$

so that we obtain

$$W_u+W_{c,d}=\frac{1}{2}Mq\varphi_d+Mq\varphi_c(0). \qquad (2.39)$$

According to Whitworth,[28] the energy ΔW represents the pair interaction

$$W_p=\sum_{j=1}^{\infty}\frac{q^2 m_j}{4\pi\varepsilon\varepsilon_0 a\cdot j}$$

without allowance for the self-energy of the defects

$$W_0=\frac{Mq^2}{4\pi\varepsilon\varepsilon_0 l};$$

here, $l=a/f$ is the distance between neighboring defects on a dislocation, so that

$$\Delta W=\frac{q^2}{4\pi\varepsilon\varepsilon_0 a}\left(\sum_{j=1}^{\infty}\frac{m_j}{j}-Mf\right). \qquad (2.40)$$

Introducing

$$\mathscr{G}_M = \mathscr{G}_M^{(1)} + \mathscr{G}_M^{(2)}, \tag{2.41}$$

where $\mathscr{G}_M^{(1)}$ is given by the right-hand side of Eq. (2.39) and $\mathscr{G}_M^{(2)}$ is the sum of the right-hand sides of Eqs. (2.37) and (2.40), we obtain

$$\mu_d = \left(\frac{\partial \mathscr{G}_M^{(1)}}{\partial M}\right)_{n_i(r)} + \left(\frac{\partial \mathscr{G}_M^{(2)}}{\partial M}\right)_{n_i(r)}. \tag{2.42}$$

We can find $(\partial \mathscr{G}_M^{(1)}/\partial M)_{n_i(r)}$ if we obtain the expressions for φ_d and $\varphi_c(0)$ in Eq. (2.39). Here, φ_d is asssumed to be the potential created by the dislocation charges on a surface of sufficiently small radius, so that the condition of Eq. (2.32) for the potential in the charge cloud is satisfied; in this case the $p(s)$ curve has an asymptote with a slope H. We can then represent φ_d in the form of a sum of the potential of an infinitely long charged filament φ_f and the correction $\Delta \varphi_d$ for the discrete distribution of charges on a dislocation. We can define $\Delta \varphi_d$ as the difference between the potentials described by Eqs. (2.20) and (2.19), so that

$$\varphi_d = \frac{qf}{2\pi\varepsilon\varepsilon_0 a} \ln \frac{Rf}{2a} + C; \tag{2.43}$$

here, R is the radius of a surface sufficiently far from a charge cloud for which we are calculating the potential. The potential of the charge cloud on the dislocation line $\varphi_c(0)$ can also be replaced by the potential on a surface of radius r_0. It can be regarded as the difference between the potential $\varphi(r_0)$ obtained by solving the Poisson equation [Eq. (2.31)] and the potential of a dislocation line represented by a charged filament, so that

$$\varphi_c(0) = \varphi(r_0) - \frac{Ql}{2\pi\varepsilon\varepsilon_0} \ln \frac{R}{r_0}. \tag{2.44}$$

Using Eqs. (2.43) and (2.44), we find that simple transformations yield

$$\frac{\partial \mathscr{G}_M^{(1)}}{\partial M} = \frac{p_0 qkT}{e}; \tag{2.45}$$

here,

$$p_0 = H \ln \frac{\Delta f}{a} + P,$$

where

$$\frac{P}{H} = \left(s_0 + C - \ln 2 + \frac{1}{2}\right) + \frac{p(s_0)}{H}.$$

The following quantities adopted earlier are used in the above expression:

$$s_0 = \ln \frac{r_0}{\Lambda}, \quad p(s_0) = \frac{e\varphi(r_0)}{kT}.$$

The ratio P/H considered as a function of H was plotted graphically by Whitworth[28] for different values of h. The slope H depends on f [see Eqs. (2.32) and (2.35)], so that p_0 is a complex function of f. The second term in the expression for μ_d [Eq. (2.42)] can be found if we determine the equilibrium number of pairs m_j. With this in mind we separate from the right-hand sides of Eqs. (2.37) and (2.40) the terms dependent on m_j and solve the variational problem using two additional conditions which require constancy of the number of sites and of the number of defects on a dislocation.

The solution gives the expression

$$m_j = A \exp\left(-\mathscr{H}j - \frac{Q}{j}\right); \tag{2.46}$$

we have here

$$Q = \frac{q^2}{4\pi\varepsilon\varepsilon_0 kTa},$$

where A and $\mathscr{H}$ are constants. Using Eq. (2.46), we obtain

$$\left(\frac{\partial \mathscr{G}_M^{(2)}}{\partial M}\right)_{n_i(r)} = g_d + kT \ln \zeta; \tag{2.47}$$

here,

$$\ln \zeta = -\ln \sum_{j=1}^{\infty} \exp\left(-\mathscr{H}j - \frac{Q}{j}\right) - 2fQ$$

is a function of f. Therefore, using Eqs. (2.45) and (2.47) Whitworth[29] obtained

$$\mu_d = \frac{qp_0 kT}{e} + g_d + kT \ln \zeta.$$

The condition for equilibrium of such a system is

$$\frac{\mu_1(\infty) - g_d}{kT} = \ln \zeta + \frac{qp_0}{e}$$

or, using Eqs. (2.7) and (2.8),

$$p_0 \frac{q}{e} = -\ln \zeta + \left(\frac{\Delta g}{kT} + \ln \alpha_i(\infty)\right); \tag{2.48}$$

here, $\Delta g = g_i - g_d$ is the energy of association of a defect on a dislocation. If we know Δg, we can use Eq. (2.48) to find graphically (using the dependences of p_0 and $\ln \zeta$ on f) the equililbrium value of f corresponding to a specific concentration $\alpha_i(\infty)$ at a given temperature. The procedure which can be used to find f is described in Ref. 28. It is interesting to compare the value of f found by this method with the value obtained ignoring the electrostatic interaction of defects on a dislocation. Adopting the scheme described above, Whitworth used Δg as a parameter and found the corresponding values of f for three NaCl crystals with different total concentrations c of divalent impurities, different concentrations of free vacancies $\alpha_i(\infty)$, and different values of h (Ref. 28). The properties of these crystals are listed in Table I. The calculations were made for $Q = 16.5$, corresponding to a charge $q = e$ at room temperature. Figure 5 shows the dependence of f on Δg for these crystals on a semilogarithmic scale. The dashed curve is plotted for a crystal B without allowance for the interaction between defects on a dislocation. We can see that inclusion of the electrostatic interaction plays an important role in the estimate of f and, consequently, in determination of Q_l.

Seitz[11] and Bassani and Thomson[14] were the first to point out the possibility that a charge can appear at an edge dislocation in an alkali halide crystal and they attributed this charge to jogs and vacancies on a dislocation. Initially the theory of charged dislocations was developing parallel to the theory of charges on the surface of alkali halide crystals. Lehovec[15] explained the appearance of a charge on the surface of a crystal by a difference between the energies of formation of cation and anion vacancies in the bulk of a crystal. Eshelby et al.[19] used the model of Lehovec[15] and developed the first theory of charged dislocations in which a disloca-

TABLE I. Properties of crystals represented by curves in Fig. 5, determined at $T = 293$ K (extrinsic conduction region).

Crystal	A	B	C
Total concentration of divalent impurities c	$2 \cdot 10^{-7}$	$2 \cdot 10^{-5}$	10^{-4}
Concentration of free cation vacancies $\alpha(\infty)$	$2 \cdot 10^{-9}$	$2 \cdot 10^{-8}$	10^{-7}
Fraction of free impurities in the bulk h	10^{-2}	10^{-3}	10^{-3}
Ratio Λ of the radius of a charge cloud to the lattice constant	550	174	78

tion was regarded as a charged filament. Lifshitz and Geguzin[18] corrected the model of Lehovec[15] and demonstrated that the charge on the surface of an alkali halide crystal is not only due to the bulk properties of such a crystal, but also due to the properties of the surface itself. Kosevich, Margvelashvili, and Saralidze[22,23] pointed out the possibility that the ideas of Lifshitz and Geguzin[18] can be applied to edge dislocations in alkali halide crystals. Finally, Whitworth[27] obtained an expression for the charge on an edge dislocation and related the charge to the characteristic energies of defects on a dislocation. Over a period of thirty years there has been a move from a charged filament to the fine structure of a dislocation, leading to the development of a model of a sessile charged dislocation.

2.3. Influence of an electric field on elementary plastic deformation events. Characteristics of motion of charged dislocations

2.3.1. Forces acting on a dislocation. Koehler,[33] Mott, and Nabarro[34,35] introduced the concept of a force acting on a dislocation. This makes it possible to describe the motion of a dislocation as that of an extended mechanical object. A distinction is made between a self-interaction force which appears as a result of a change in the length or shape of a dislocation, a force due to the interaction of a dislocation with other dislocations, and the force which appears on application of an external mechanical load. According to the Peach-Koehler expression, the force per unit length of a dislocation is $\mathbf{F} = [(\hat{\tau}\mathbf{b})\Delta\mathbf{l}]$, where $\hat{\tau}$ is the stress tensor.
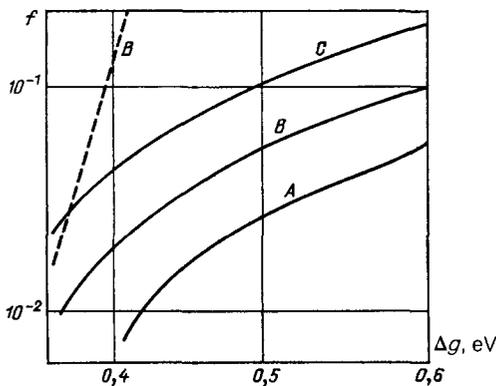
FIG. 5. Dependence of the fraction of positions on a dislocation line occupied by defects on the energy of their association f (Δg), plotted for three samples, with properties listed in Table I. The dashed line is the dependence calculated for the crystal B ignoring the pair interaction between defects.

Hence, the force acting on a dislocation in its slip plane is

$$F = ((\hat{\tau}\mathbf{b})\,\mathbf{n})\,[\Delta\mathbf{l},\,\mathbf{n}], \qquad (2.49)$$

where

$$\mathbf{n} = \frac{[\mathbf{b}\,\Delta\mathbf{l}]}{|\,\mathbf{b}\,\Delta\mathbf{l}\,|}$$

is a unit vector along the normal to the slip plane. A dislocation in an alkali halide crystal experiences forces also due to the presence of an electric charge. If there is an electric field in a crystal, then a dislocation moving in its slip plane experiences a force[36]

$$\mathbf{F} = ([Q_l\,\Delta\mathbf{l},\,\mathbf{E}]\,\mathbf{n})\,[\Delta\mathbf{l}\,\mathbf{n}]. \qquad (2.50)$$

The action of an electric field is not equivalent to the influence of a mechanical load, because the field influences not only the dislocation but also the charge cloud surrounding it as well as the charged pinning centers, causing reorientation of the latter and altering their coupling to the dislocation.

2.3.2. Influence of an electric field on the yield stress of an alkali halide crystal. A mechanical stress close to the yield stress of an alkali halide crystal can be created by an electric field of intensity amounting to several tens of megavolts per meter. Studies of the effects of such high fields meet with major experimental difficulties, so that it is usual to study the simultaneous effect of a mechanical load and an electric field.

We shall consider a crystal split along the $\{100\}$ cleavage planes (Fig. 1) and assume that an electric field is created along the [010] direction and also that a mechanical load is applied along the [001] axis. Edge dislocations with the Burgers vectors $(a/2)[011]$ and $(a/2)[01\bar{1}]$ located in (011) and $(01\bar{1})$ planes, experience forces due to the mechanical load and the electric field. The resultant force differs for dislocations with different mechanical signs and it can be written in the form[37]

$$\mathbf{F} = \mathbf{b}\tau^* \pm \frac{Q_l\mathbf{E}}{\sqrt{2}}; \qquad (2.51)$$

here, τ^* is the effective stress which ensures thermally activated overcoming of obstacles in the presence of an electric field. The velocity of thermally activated motion of a dislocation governed by these obstacles is[38]

$$v = Ae^{-\mathscr{G}(F)/kT}, \qquad (2.52)$$

where A is a constant at a given temperature and $\mathscr{G}(F)$ is the value of the thermodynamic potential associated with overcoming of an obstacle. Since the field affects the starting stress, for example by its effect on the dislocation-pinning

centers, it follows that

$$\tau^* = \tau_0^* + \Delta\tau,$$

where τ_0^* is the starting stress observed only under the influence of a mechanical load. The force needed to overcome an obstacle and to initiate translational motion of a dislocation in the absence of an electric field is

$$\mathbf{F}_0 = \mathbf{b}\tau_0^*,$$

whereas the additional force acting on dislocations of different mechanical signs in the presence of a field is

$$\Delta\mathbf{F} = \mathbf{b}\,\Delta\tau \pm \frac{Q_l E}{\sqrt{2}}. \tag{2.53}$$

In the presence of an electric field the thermodynamic potential $\mathcal{G}\,(F_0 + \Delta F)$ can be expanded as a Taylor series. Substituting this series in Eq. (2.52) we find that the velocity v depends on a number of parameters associated with $\mathcal{G}'(F_0)$, $\mathcal{G}''(F_0)$, etc. We then have

$$\mathcal{G}'(F_0) = -\frac{m^* kT}{F_0};$$

m^* can be found in experiments applying loads in steps or in studies of creep.[38] If we confine ourselves to the linear terms of the expansion, we can describe the velocity of dislocations of different mechanical signs in the presence of an electric field by the expression

$$v = v_0 \exp\left[\frac{m^*}{b\tau_0^*}\left(b\,\Delta\tau \pm \frac{Q_l E}{\sqrt{2}}\right)\right], \tag{2.54}$$

where v_0 is the velocity in the absence of a field. Clearly, v is a function of just one controlled parameter m^*. The rate of deformation (strain rate) in the absence of an electric field, on condition that only the edge dislocations are in motion, amounts to $\dot{\varepsilon}_0 = \frac{1}{2}Kbv_0$, where K is the dislocation density. If the numbers of dislocations of opposite mechanical signs are the same and equal to $K/2$, the rate of deformation in an electric field can be represented by

$$\dot{\varepsilon} = \frac{1}{2}Kbv_0 e^{m^*\,\Delta\tau/\tau_0^*} \,\mathrm{ch}\,\frac{m^* Q_l E}{b\tau_0^* \sqrt{2}}. \tag{2.55}$$

It follows from Eq. (2.55) that if the rate of deformation is note maintained at $\dot{\varepsilon} = \dot{\varepsilon}_0$, the yield stress in an electric field decreases by

$$\Delta\tau = -\frac{\tau_0^*}{m}\ln\mathrm{ch}\,\frac{m^* Q_l E}{b\tau_0^* \sqrt{2}}. \tag{2.56}$$

It follows from Eq. (2.56) that in weak electric fields obeying the inequality $E \ll b\tau_0^*\sqrt{2}/m^* Q_l$, the change in the yield stress is

$$\Delta\tau = -\frac{1}{4}\frac{m^* Q_l^2 E^2}{\tau_0^* b^2}, \tag{2.57}$$

i.e., the yield stress varies proportionally to the square of the electric field intensity. In high fields, we have

$$\Delta\tau = \frac{\tau_0^*}{m^*}\ln 2 - \frac{Q_l E}{\sqrt{2}\,b}, \tag{2.58}$$

i.e., the yield stress decreases linearly on increase in E.

2.3.3. Influence of a charge cloud on a vibrating dislocation. In an analysis of the influence of a charge cloud on a vibrating dislocation it is usual to consider above-barrier motion of dislocations in place of the thermally activated mechanism of overcoming of obstacles. Two limiting cases can be distinguished: a charge cloud in motion and a cloud at rest. In the case of a cloud at rest a dislocation which is displaced experiences a restoring force F_b due to elastic and electrostatic interactions of a dislocation with the cloud. When only the electrostatic interaction is allowed for, it is found that

$$F_b = -Q_l\frac{d\varphi_c}{d\zeta} \quad (\zeta \text{ is the displacement of a dislocation}).$$

This force can be estimated from

$$F_b = -K_F\left(\frac{\zeta}{\Lambda}\right)\frac{Q_l^2}{2\pi\varepsilon\varepsilon_0\Lambda};$$

here $K_F(\zeta/\Lambda)$ is a dimensionless parameter. If $\zeta \ll \Lambda$ and $K_F = K_0\zeta/\Lambda$, then K_0 lies within the range 1.8–4 (Ref. 9), so that F_b is proportional to the displacement:

$$F_b = -L\zeta, \quad L = K_0\frac{Q_l^2}{2\pi\varepsilon\varepsilon_0\Lambda^2}. \tag{2.59}$$

We shall consider a dislocation segment lying in the (x,y) plane and pinned at points $\pm l/2$. We shall assume that this segment experiences an alternating stress $\tau = \tau_0 e^{i\omega t}$, where ω is the angular frequency of this stress. The differential equation describing the motion of such a segment is

$$A\frac{\partial^2\zeta}{\partial t^2} + B\frac{\partial\zeta}{\partial t} - T\frac{\partial^2\zeta}{\partial y^2} + L\zeta = b\tau_0 e^{i\omega t}. \tag{2.60}$$

The first term on the right-hand side of Eq. (2.60) represents the force of inertia ($A = \pi\rho b^2$ is the effective mass per unit length); the second is the friction, and the third is an approximate expression for the self-interaction force

$$T = \frac{Gb^2}{\pi(1-\nu)},$$

whereas the fourth term is the force exerted by the charge cloud. In the kilohertz range the frequency of oscillations of the external force is low compared with the resonance frequency of the segment, so that the inertial term can be ignored.[39] Assuming, for the sake of simplicity, that the friction force vanishes, we obtain the following solution of the above equation:

$$\zeta = \frac{\tau b}{L}\left[1 - \frac{\mathrm{ch}\,(\gamma y)}{\mathrm{ch}\,(\gamma l/2)}\right], \quad \gamma = \left(\frac{L}{T}\right)^{1/2}. \tag{2.61}$$

It follows from Eq. (2.61) that if $\frac{1}{2}\gamma l \ll 1$, i.e., in the case of low values of l, a dislocation bends like an elastic filament and its maximum displacement is $\zeta(0) = \tau b l^2/8T$. If $\frac{1}{2}\gamma l \gg 1$, i.e., when l is large, we find that $\zeta = \tau b/L$, and the charge cloud plays the dominant role in limiting the vibrational motion of a charged dislocation. The influence of a cloud at rest can be investigated by the methods of internal friction at low amplitudes of the relative strain ε_0 at room temperature.[40]

A mobile cloud follows a dislocation and the associated diffusion processes result in energy dissipation. The deceleration in the case of an electrostatic interaction of a dislocation with a charge cloud moving by diffusion was first considered by Brown.[41] The value of the electrical potential φ_c necessary to find the force acting on a dislocation can be found by simultaneous solution of the Poisson equation (2.13) and of the diffusion equation

$$\frac{\partial n}{\partial t} - \nabla \left(D\nabla n + n \frac{qD}{kT} \nabla\varphi_c \right) = 0, \tag{2.62}$$

which is derived using the Nernst-Einstein relationship between the diffusion coefficient D and the conductivity σ. However, the Brown solution is strictly speaking valid only in the case of low frequencies ω of vibrations of a dislocation segment. In the more general case the influence of a charge cloud can be discussed on the basis of the treatment proposed by Tanibayashi.[42] It is assumed in Ref. 42 that a cloud consists of two types of charged defects of opposite sign. The relaxation time of the cloud is

$$\theta = \frac{\Lambda^2}{D}, \quad D = \frac{2D_1 D_2}{D_1 + D_2},$$

where D_1 and D_2 are the diffusion coefficients of defects of each type. The cloud creates a force which depends on the displacement and velocity of a vibrating dislocation. If $\omega\theta \gg 1$, the cloud can be regarded as immobile and the force exerted by it can be divided into two components, one of which is proportional to the displacement

$$F_b = \frac{Q_l^2 \zeta}{8\pi\varepsilon\varepsilon_0\Lambda^2} \ln(2\omega\theta), \tag{2.63}$$

and the other to the velocity of a vibrating dislocation

$$F_m = -\frac{Q_l^2 v_-}{16\pi\varepsilon\varepsilon_0\Lambda^2\omega}. \tag{2.64}$$

The restoring force F_b depends on the frequency. However, according to Ref. 9, the value of F_b for a cloud at rest should be independent of ω [see Eq. (2.59)]. The general expression for the force exerted by a charge cloud on a vibrating dislocation[42] can be used to find the damping decrement δ. The influence of a cloud on the damping in alkali halide crystals was considered by Robinson and Tallon.[43-45] However, the equation of a vibrating dislocation segment was solved in Refs. 43–45 using expressions similar to Eqs. (2.63) and (2.64), which are valid only if $\omega\theta \gg 1$. According to Ref. 42, a charge cloud has the strongest influence on the damping in the presence of long dislocation loops. The frequency dependence $\delta(\omega)$ is predicted to have an asymmetric maximum at a frequency $\omega_m \approx \dfrac{D}{\Lambda^2}$.

It therefore follows that a charge cloud plays a role in limiting the vibrational motion of charged dislocations. A study of the influence of such a cloud can be made by the internal friction method if dislocations are not detached from weak pinning centers. The temperature dependence of the damping should reveal isoelectric points in respect of variation of δ caused by disappearance of the interaction of dislocations with a charge cloud.

2.3.4. Transport of charge by moving dislocations. Dynamic methods are used in experimental investigations of the dislocation charge and its transport by moving dislocations. A charge carried by a moving dislocation changes because a dislocation "sweeps through" vacancies. This idea of sweeping out of vacancies by a moving dislocation was put forward by Pratt.[46] Experimental data on reduction in the charge due to stopping of a dislocation showed that the transported charge is not in equilibrium. A rigorous theory describing this nonequilibrium charge is not yet available. Phenomenological models are based on two mechanisms of charge transport by moving dislocations. According to Ref.
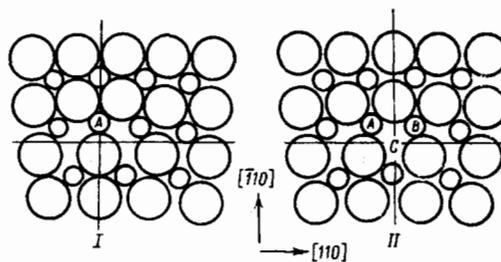
FIG. 6. Distribution of ions in (001) planes which are normal to the line of a moving edge dislocation in NaCl. The state labeled II represents the dislocation that shifted by $b/2$. The positions A and B identify cation vacancies.

47, a moving dislocation captures cation vacancies encountered in its path and it may also capture vacancies which are components of impurity-vacancy dipoles or even more complex aggregates when their positions relative to a moving dislocation are favorable. On the other hand, divalent impurity ions, dipoles, and dipole aggregates with appropriate positions relative to a traveling dislocation may act as vacancy "traps." Two symmetric configurations in a (001) plane, perpendicular to an edge dislocation with the Burgers vector $(1/2)[110]$ in an NaCl crystal, are shown in Fig. 6, which is taken from Ref. 47. The large circles are the Goldschmidt radii of the chlorine ions, whereas the smaller circles represent the sodium ions. The ion positions are based on the calculations reported in Ref. 10. A vacancy at a point A is bound to a dislocation. A shift by $b/2$ transforms the configuration shown on the left (I) to the one on the right (II). The smallest potential energy in the configuration II corresponds either to a vacancy at the position A or to an ion at a position C when the sites A and B are vacant. In the former case the position A remains vacant and the distribution of ions is no longer symmetric. Further displacement to the right leaves the vacancy behind the dislocation. The transport of the vacancy requires the displacement of an ion from B to A when the dislocation is moving to the right. Such a jump must be thermally activated. Therefore, at low temperatures a dislocation cannot carry charge. In the second case in the configuration II a positive ion is at the symmetric position C and the positions A and B are vacant. Further motion of dislocation to the right transfers an ion from C to A and this restores the configuration I and a vacancy again appears in a dislocation core. This process does not require thermal activation so that in the configuration II a dislocation can carry a charge at any temperature. Of these two possible configurations the one encountered in practice is that which has a lower potential energy.

It follows from qualitative considerations of the energy[48] that the maximum charge Q_l^{max} acquired by a dislocation in the course of its motion corresponds to one vacancy per two positive sites, i.e., it is half the self-evident limit of one vacancy per one site.

The second mechanism of charge transport by a moving dislocation allows not only for the capture of vacancies, but also for their diffusion,[49,50] i.e., it postulates thermal activation. The nature of the temperature dependence of the transported charge is governed not only by the diffusion parameters, but also by the velocity of the dislocation itself. The dynamic equilibrium charge carried by a moving dislocation is limited by the processes of emission and absorption of va-

cancies and, according to Ref. 49, is

$$Q_l = \frac{Q_0 + Q_\infty (v/v_0)}{1 + (v/v_0)}, \quad Q_0 = \frac{en_t}{w_t}, \quad Q_\infty = \frac{en_l}{w_l}, \quad v_0 = \frac{w_t}{w_l}.$$

(2.65)

Here, n_t is the number of vacancies which are deposited per unit length of a dislocation per unit time as a result of their diffusion out of the bulk of a sample; n_l is the number of vacancies swept through by a dislocation of unit length per unit path; w_t is the probability that a dislocation loses a vacancy as a result of thermal activation; w_l is the probability that a vacancy is lost from a dislocation because of capture by traps which are encountered by a dislocation in the course of its motion At low velocities ($v \ll v_0$) vacancies manage to migrate toward a dislocation from the bulk and the dominant mechanism of vacancy loss is spontaneous emission. At high velocities the motion of a dislocation changes from thermally activated to viscous, the efficiency of sweeping out vacancies decreases strongly, and the quantity Q_l tends to a temperature-independent limit Q_0. The mechanism of charge transport acting in this range of velocities does not require thermal activation. The nature of this mechanism is still the subject of discussion. The quantitites n_t, n_l, w_t, and w_l in Eq. (2.65) are not known so that the proposed model cannot be used to obtain quantitative estimates. However, the very idea of a diffusion mechanism of charge transport by a moving dislocation is valuable. The proposed model explains satisfactorily the experimental dependences of the charge carried by a dislocation on its velocity and on temperature.[49]

The model of diffusion transport of charge by a moving dislocation has been developed further by Hungarian physicists.[51,52] The transport of vacancies in the elastic and electric fields of a dislocation is considered in Ref. 51. A charged dislocation is regarded as a series of uniformly distributed charges.[27] A computer calculation method developed by the authors of Ref. 27 made it possible to calculate the influence of various factors on the charge carried by a dislocation. They investigated the establishment of a dynamic equilibrium charge in the process of motion of an initially uncharged dislocation. It was found that when a dislocation charge is formed, vacancies collect at points close to the dislocation line. On the other hand, according to Refs. 53 and 54, some of the transported charge is not bound to the dislocation core. A moving dislocation not only transports charges inside its core, but also drags (by its elastic field) vacancies and sets them in directional drift motion which is called the vacancy wind. The problem of vacancy drift is still a matter of discussion.[9]

A charge swept out by a dislocation is not initially surrounded by a cloud of charged defects of the opposite sign. A charge cloud forms as a result of diffusion of charged particles in the electric field of a dislocation and the main carriers are mobile cation vacancies. The time required to establish a charge equilibrium is $t = \varepsilon \varepsilon_0 / \sigma$.

2.4. Direct and converse dislocation piezoelectric effects. Electroacoustic loop

The polarization in an elastic field is known as the direct piezoelectric effect:

$$\mathscr{P}_i = d_{ijk} \tau_{jk}.$$

(2.66)

The strain in an electric field is known as the converse piezoelectric effect:

$$\varepsilon_{ij} = d_{ijk} E_k;$$

(2.67)

d_{ijk} is the piezoelectric modulus.[55] The piezoelectric effects do not occur in centrosymmetric crystals, which include alkali halides. If alkali halides contain mobile dislocations, then in elastic and electric fields they exhibit phenomena which are known as the direct and converse dislocation piezoelectric effects. Motion of charged dislocations in an elastic field results in an additional polarization

$$\Delta \mathscr{P}_i = \Delta d_{imn} \tau_{mn}.$$

(2.68)

By analogy with Eq. (2.66), this is called the direct dislocation piezoelectric effect. A dislocation piezoelectric modulus Δd_{imn} can be expressed in terms of the characteristics of a dislocation. Motion of dislocations in an elastic field also causes dislocation strains and, consequently, makes an additional contribution to the elastic compliance. A dislocation strain which appears in an electric field is proportional to the intensity of this field:

$$\Delta \varepsilon_{kl} = \Delta d'_{klj} E_j.$$

(2.69)

This is known as the converse dislocation piezoelectric effect. In general, the piezoelectric moduli describing the direct and converse effects are different. Displacement of charged dislocations induces also an additional polarization and, consequently, makes an additional contribution to the electric susceptibility.

The relationship between the electrical and elastic properties of alkali halide crystals containing mobile charged dislocations can be represented by an electroacoustic loop shown in Fig. 7. We can see that in the presence of charged dislocations an electric field not only induces a polarization, but also a strain in alkali halide crystals. In turn, an elastic field not only deforms, but also polarizes a crystal. In the absence of dislocations the elastic properties of alkali halide crystals are unrelated to the electrical properties.

The contribution of mobile charged dislocations to the electric susceptibility χ_{ij}, to the elastic compliance S_{klmn}, and to the dislocation piezoelectric moduli Δd_{imn} and $\Delta d'_{klj}$ were first calculated theoretically by Brantley and Bauer.[36] These authors considered the condition of equilibrium of a dislocation segment pinned at its ends and subjected to an
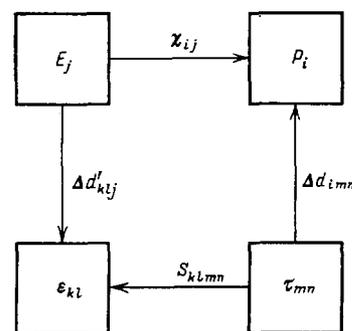
FIG. 7. Electroacoustic loop of an ionic crystal containing mobile charged dislocations. Here, Δd_{imn} and $\Delta d'_{klj}$ are the coefficients representing the direct and converse dislocation piezoelectric effects.

elastic or electric force, but they ignored the influence of a charge cloud. The self-interaction force was considered in the approximation of linear tension and was assumed to be equal to T/R, where R is the radius of curvature of the dislocation segment. In the presence of an elastic field applied along the [100] axis the contribution of dislocations to the elastic compliance is[36]

$$\Delta S_{1111} = \frac{Kb^2l^2}{48T}.$$

The direct and converse dislocation piezoelectric moduli are the same. When an electric field is applied along the [001] direction, it is found that

$$\Delta d'_{311} = K\frac{Q_l l^2 b}{24\sqrt{2}\,T}$$

and the contribution of dislocations to the electric susceptibility is

$$\Delta\chi_{33} = \frac{KQ_l^2 l^2}{24T\varepsilon_0}.$$

In another paper[56] Bauer and Brantley considered dynamic effects on application of acoustic and alternating electric fields. As in Ref. 36, they assumed that the dislocation segments were of equal length and ignored the influence of a charge cloud. The differential equation describing the forced vibrations of a dislocation segment on application of an electric field $F = Q_l E_0 \exp(i\omega t)$ can be written in the form given by Eq. (2.60) ignoring the restoring force $F_b = -L\zeta$. Having determined ζ, we can now find the dislocation polarization $\Delta\mathscr{P}_k$ and the correction to the electric susceptibility due to dislocations. According to Ref. 56,

$$\Delta\chi_{33} = \Delta\chi_{33}^{(1)} + i\,\Delta\chi_{33}^{(2)}.$$

The quantity

$$\Delta\chi_{33}^{(1)} = \frac{8Q_l^2}{\varepsilon_0}\frac{K(\omega_0^2-\omega^2)A}{\pi^2 A^2(\omega_0^2-\omega^2)^2 + B^2\omega^2}$$

determines the contribution to the electric susceptibility and

$$\Delta\chi_{33}^{(2)} = \frac{8Q_l^2 BK\omega}{\pi^2\varepsilon_0 A^2(\omega_0^2-\omega^2)^2 + B^2\omega^2}$$

gives the contribution to the dielectric losses; here, $\omega_0 = (\pi/l)(T/A)^{1/2}$ is the resonance frequency of vibrations of a dislocation segment. If a sample is subjected not only to an alternating electric field, but also to an acoustic field of the same frequency, additional contributions are made to $\Delta\chi_{ij}^{(1)}$ and $\Delta\chi_{ij}^{(2)}$ and they depend on the phase shift between these two fields.

The solution in the case when only an acoustic field is acting was obtained by Koehler[57] and by Granato and Lücke[39] who calculated the contribution of dislocations to the elastic compliance defect $\Delta S_{klmn}/S_{klmn}$ and to the damping decrement δ. The expression for the dislocation piezoelectric modulus was obtained by Robinson[58]:

$$\Delta d_{311} = \frac{\sqrt{2}\,S_{1111}Q_l}{4b}\left(\frac{\Delta S_{1111}}{S_{1111}} - i\delta\right). \tag{2.70}$$

The application of an alternating electric field to the same sample makes additional contributions to δ and $\Delta S_{1111}/S_{1111}$ and this contribution depends on the phase shift between the electric and acoustic fields. Calculations of the

direct and converse dislocation piezoelectric moduli allowing for the influence of a charge cloud were reported in Refs. 59 and 60. The differential equations describing vibrations of a dislocation segment in alternating acoustic and electric fields were supplemented by a force exerted by a charge cloud. In the case of an electric field an allowance was made for its direct influence on the charges in a cloud consisting of one[59] and two types of charged defects of the opposite signs.[60] This effect displaces charges in an electric field and alters the force exerted by the cloud on a dislocation. The result is that at frequencies $\omega \ll (D_1 + D_2)/\Lambda^2$, when the charge cloud is mobile, the dislocation piezoelectric moduli Δd and $\Delta d'$ are different. The effects predicted in Refs. 59 and 60 will require new experimental investigations of the direct and converse dislocation piezoelectric effects at various frequencies and in a wide range of temperatures.

3. EXPERIMENTAL DATA ON THE BEHAVIOR OF CHARGED DISLOCATIONS AND THEIR INFLUENCE ON THE PROPERTIES OF ALKALI HALIDE CRYSTALS

Reviews of experimental investigations of charged dislocations in alkali halide crystals carried out up to 1975 can be found in Refs. 7–9. The progress made in the last 10–15 years in theoretical investigations of charged dislocations and the associated effects has stimulated a large number of new experimental studies (Table II). Investigations of charged dislocations in alkali halide crystals have covered a wide range of topics, such as the appearance of a potential difference between different points on a sample on application of a static or an alternating load, the deformation of a sample in an electric field, the influence of an electric field on the mechanical properties associated with the presence of a charge on dislocations (internal friction, defect of the elastic compliance, creep, yield stress, etc.), the influence of an electric field on the motion and multiplication of dislocations in alkali halide crystals deformed by ultrasound, etc.

3.1. Investigations of electrical effects due to application of a mechanical load

Such investigations were begun by A.V. Stepanov[2,3] who established in 1933 an effect (later identified by his name) representing the appearance of an electric charge on the surface of a rocksalt crystal when it was subjected to macroscopic deformation by a uniaxial compressive force. Caffyn and Goodfellow[61] related the Stepanov charge to the properties of dislocations and carried out a series of experiments designed to detect this charge. Later experiments have revealed that the charge can be induced also by other deformation methods (bending, application of a concentrated force, alternating loads) and for different positions of electrodes on a sample.[9] The appearance of a charge on the surface of an alkali halide crystal subjected to macroscopic deformation is explained by the fact that dislocations moving along slip (glide) planes carry their charge to the surface. The subsequent development of the method of uniaxial compression put forward by Stepanov has yielded quantitative data on the charge carried by a dislocation in an alkali halide crystal and on the dependence of such a charge on the applied stress, rate of deformation, numbers of cation and anion vacancies, temperature, etc.[53,54,62,63,65,66] In Refs. 62 and 63 the charge Q_l carried by an edge dislocation was deduced by measuring a current I in a circuit between elec-

TABLE II. Electric charges Q_l (per unit length) carried by dislocations in alkali halide crystals, taken from published data.

Crystal	Concentration of divalent impurities, mol. fraction	T, К	Q_l, C/m	Ref.
LiF	total concentration 10^{-5}	77	$-8,1\cdot10^{-13}$	44
	10^{-5}	298	$-1,1\cdot10^{-12}$	44
	—	room (293 K)	$-1,0\cdot10^{-12}$	63
	Mg^{++}, $7\cdot10^{-5}$	»	$-2,2\cdot10^{-12}$	78
	Mg^{++}, $1\cdot10^{-4}$	»	$-3,1\cdot10^{-12}$	78
	—	»	$+2,2\cdot10^{-12}\ldots+2,9\cdot10^{-12}$	84
	—	300	$-1,2\cdot10^{-11}\ldots-2,1\cdot10^{-11}$	76
	excess of cation vacancies	room	$-3\cdot10^{-14}\ldots-1,3\cdot10^{-10}$	49
NaCl	—	»	$-2\cdot10^{-13}\ldots-1,7\cdot10^{-12}$	44
	—	78	$-1,7\cdot10^{-13}\ldots-3,7\cdot10^{-13}$	110
	Ca^{++}, $2\cdot10^{-5}$	296	$-7\cdot10^{-12}$	115
	Ca^{++}, $2\cdot10^{-5}$	321	$-2,5\cdot10^{-12}$	115
	—	300	$-2\cdot10^{-13}\ldots-1,7\cdot10^{-12}$	76
	—	room	$-2\cdot10^{-11}$	36
	Mn^{++}, $2\cdot10^{-5}$ $-3\cdot10^{-5}$	»	$-2,5\cdot10^{-11}$	106
	Ca^{++} до $4,5\cdot10^{-5}$, Mg^{++} $7\cdot10^{-6}$	»	$-2\cdot10^{-11}\ldots-4\cdot10^{-11}$	27
	Mn^{++}, $1,4\cdot10^{-5}$		До $-1,1\cdot10^{-10}$	48
KCl	—	300	$-1,5\cdot10^{-14}\ldots-2,4\cdot10^{-11}$	76
	—	room	$-1,0\cdot10^{-12}$	116
	total concentration $2\cdot10^{-5}$	»	$-2,7\cdot10^{-12}\ldots-7,5\cdot10^{-12}$	58
	10^{-5}	298	$-3,1\cdot10^{-12}$	43
	Ca^{++}, $1,5\cdot10^{-4}$	room	$-4\cdot10^{-11}\ldots-9,5\cdot10^{-11}$	105
	Ca^{++}, —	»	$-7\cdot10^{-11}$	87
KBr	total concentration 10^{-}	»	$-8\cdot10^{-12}\ldots-2,2\cdot10^{-11}$	75

trodes and by determination of the rate of deformation ε: $Q_l = \sqrt{2}\,bI/S\dot{\varepsilon}$, where S is the electrode area. The current was due to the fact that different numbers of edge dislocations reached the two electrodes. The deformation in Ref. 62 was applied along two systems of crystallographic easy glide planes, whereas in Ref. 63 it was applied along one such system. It was interesting to note a change in the sign of the signal obtained when deformation was applied in one glide system[63] (this change in the sign was attributed earlier to a change in the effective glide or slip systems in the course of active loading of a sample[7]). The change in the sign was observed before reaching the yield stress. After inversion the signal increased, reached its maximum value in the yield plateau, and then decreased rapidly as a result of further loading. This decrease in the signal after passing through the yield plateau could be explained by the dependence of the charge carried by dislocations on the velocity of their motion, which in turn reached its maximum value on the yield plateau.[64] The investigations reported in Refs. 53, 54, 65, and 66 were concerned with a charge carried on the surface of an alkali halide crystal under uniaxial compression conditions. The experiments described in Refs. 53 and 54 were carried out on NaCl crystals with cation or anion impurities. These crystals were deformed using two slip (glide) systems at temperatures between room and 600 °C. The electric charge transported to a side face of a sample was measured with an electrometer. The linear charge density Q_l on a dislocation was deduced from the transport charge and the number of dislocations ΔK, which reached a side face in the course of deformation and ΔK was found from a shear step measured by an interference method. However, the charge calculated by this method for temperatures in excess of 500 °C was higher than the limiting value $Q_l^{\max}$. This was explained in Refs. 53 and 54 by putting forward the idea of a directional drift of vacancies dragged by the elastic field of a

dislocation. Confirmation of this idea would require further experiments. Detailed investigations of inversion of the sign of the signal obtained for NaCl samples with controlled numbers of cation and anion vacancies were reported in Refs. 65 and 66. It was established that during the initial stage of deformation the sign of the charge carried to the surface was opposite to the sign of the charge at dislocations of the investigated crystals. This "minority" signal reached its maximum value for a load corresponding to the yield stress. The strain ε_i corresponding to the point of inversion of the sign of the signal and the magnitude of the signal itself before and after the inversion increased considerably on increase in the deformation rate. One of the possible explanations of the change in the sign of the charge carried to the surface was that initially it was due to the charge on the surface and only after the inversion point it was contributed by dislocations. The final identification of the mechanism responsible for the inversion of the sign of the charge would require further experiments on samples with a controlled state of their surface. Fischbach and Nowick[67] first observed an electric signal when a concentrated load was used. A qualitative analysis indicated[68] that the signal increased considerably as a result of preliminary bending of a sample or introduction of divalent impurities. Further modernization of the method employed[69-71] made it possible to determine the charge carried by an edge dislocation. An indentation method was used in Refs. 49 and 50 to investigate formation of a dynamic equilibrium charge carried by a moving dislocation in LiF crystals. An investigation of the sign of the potential which appeared as a result of indentation showed that dislocations in crystals containing divalent cation impurities were negatively charged, whereas those in crystals containing anion impurities were positively charged. Figure 8 shows the dependence of the charge on the velocity of a dislocation in an LiF crystal with an Mg impurity (10^{-5}
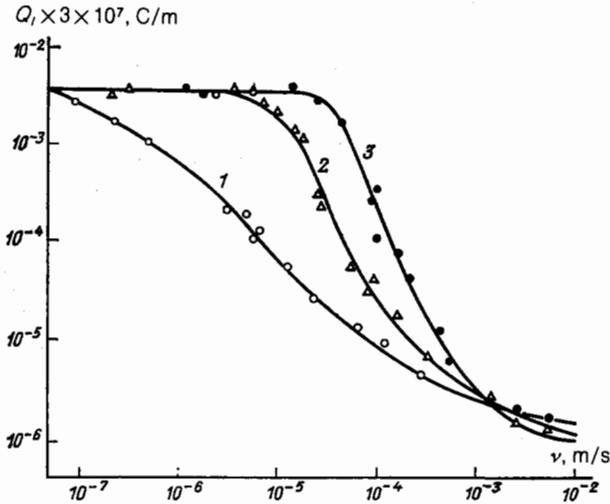
FIG. 8. Dependence of the charge carried by a dislocation in LiF on the velocity of its motion[49]: 1) 20 °C; 2) 100 °C; 3) 150 °C.

molar fraction) at three different temperatures.[49] The dependence of Q_l on the velocity indicated that the mechanism of charge transport was thermally activated. Clearly, at high velocities the charge decreased by several orders of magnitude tending to a velocity-independent limit Q_0. A phenomenological explanation[50] of the dependence $Q_l(v)$ was given by us earlier in Sec. 2.3.3. Identification of the mechanism of transport of the charge Q_0 will require further investigations.

The appearance of an electrical signal as a result of cyclic deformation is observed at low[72-75] and ultrasonic[58,76-79] frequencies. In the case of small strains the signal is due to reversible displacements of a charged dislocation relative to a Debye-Hückel cloud. At high vibration amplitudes a dislocation travels a large distance and its charge increases as a result of vacancy capture. Developments of this method have made it possible to estimate quantitatively the dislocation charge. Whitworth et al.[47,48,74] subjected previously bent NaCl samples to tensile-compressive strains at a frequency of 0.04 Hz. When the load was applied along the [100] direction and the voltage was measured between the (001) faces, the charge was described by

$$Q_l = \frac{Ub(C + C_e \eta)}{\sqrt{2}\varepsilon_0^p S}.$$
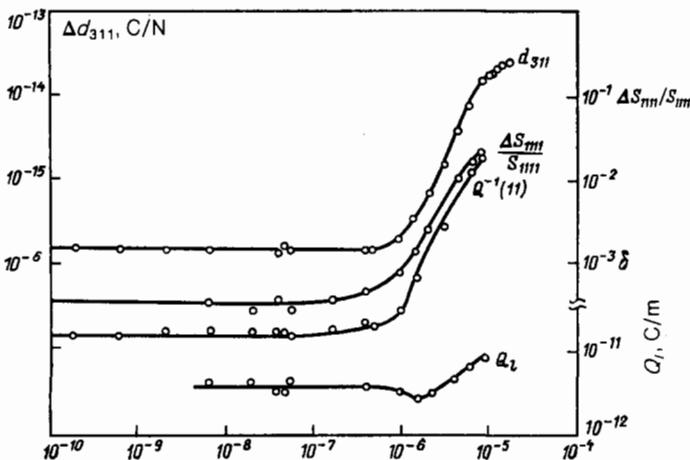
Here, ε_0^p is the plastic strain amplitude equal to the difference between the total and elastic strains; C is the capacitance between the electrodes; C_e is the capacitance of an electrometer; $\eta = (K_1 + K_2)/(K_1 - K_2)$; K is the dislocation density with the required mechanical sign to create bending found from Nye's formula,[80] and $K_1 + K_2$ is the total density of dislocations calculated from the etch figures. It was established that the charge Q_l increased on increase in the load amplitude tending to its maximum limit Q_l^{max} corresponding to one electron charge e per two like ions on a dislocation line. When a sample was subjected for a longer time to the maximum amplitudes employed in Ref. 48, the charge Q_l decreased, i.e., the charge acquired by a moving dislocation was not the equilibrium value. The Whitworth method was used by van Dingenen[75] to investigate an electrical signal developed as a result of vibrations of KBr at low (0.02 Hz) and acoustic frequencies. In the interpretation of the results obtained at different stages of cyclic loading an attempt was made to separate the electrical effects due to displacement of a vibrating dislocation relative to a charge cloud from the effects resulting from an increase in Q_l due to the capture of vacancies by a moving dislocation. Further experiments are needed to investigate the contribution of these two effects to the measured electrical signal at different vibration amplitudes and frequencies. The piezoelectric modulus for the direct Δd and converse $\Delta d'$ dislocation piezoelectric effects, the damping δ, and the elastic compliance defect $\Delta S_{1111}/S_{1111}$, were determined[58,76] for previously bent LiF, NaCl, and KCl samples; the measurements were made at a frequency of 40 kHz and then Eq. (2.70) was used to calculate the dislocation charge Q_l. In the range of amplitudes ε_0 used in these investigations it was found that Δd and $\Delta d'$ were the same. Figure 9 shows the amplitude dependences $\Delta d_{311}(\varepsilon_0)$, $(\Delta S_{1111}/S_{1111})(\varepsilon_0)$, $\delta(\varepsilon_0)$, and $Q_l(\varepsilon_0)$ obtained for a sample of KCl at room temperature. It is clear from this figure that in the absence of an amplitude dependence of the damping the charge carried by a dislocation did not change when ε_0 was increased. Simultaneous studies of the direct and converse dislocation piezoelectric effects, internal friction, and the electric voltage U between electrodes on the surfaces of LiF and NaCl samples, carried out at a frequency of 100 kHz, were made[77-79] using the method of Ref. 81. The direct and converse dislocation piezoelectric effects were observed only for the samples subjected to a

FIG. 9. Amplitude dependences of the dislocation piezoelectric modulus Δd_{311}, of the elastic compliance defect $\Delta S_{1111}/S_{1111}$, of the damping δ, and of the charge Q_l carried by a dislocation in a KCl crystal.[58]

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preliminary plastic deformation by bending and the piezoelectric moduli were the same for the direct and converse effects. The amplitude dependence of the electrical signal $U(\varepsilon_0)$ obtained at low values of ε_0 was a linear function of the strain, so that the charge carried by an edge dislocation subjected to low strains ε_0 was not affected by its motion.[79] The amplitude dependences of the internal friction and of the dislocation piezoelectric modulus were qualitatively similar. The linear dependence $U(\varepsilon_0)$ was retained in a certain range of ε_0, where $\delta(\varepsilon_0)$ already exhibited an amplitude dependence. In spite of the fact that investigations of the amplitude dependences of the damping and of the dislocation piezoelectric modulus reported in Refs. 58 and 76 and in Refs. 77–79 were carried out in the same range of amplitudes ε_0 and although the results were qualitatively similar, the interpretations adopted were different. In Refs. 58 and 76 the authors invoked a model of the interaction of a vibrating dislocation with a charge clout.[43-45] An increase in the damping on increase in ε_0 was attributed to the escape of a vibrating dislocation from a cloud. In the course of vibrations outside a cloud a dislocation "swept through" vacancies encountered in its path and increased the charge. A calculation of the average displacement of a dislocation $\bar{\zeta}$ at an amplitude ε_0 corresponding to the onset of the amplitude dependence $\delta(\varepsilon_0)$ indicated that $\bar{\zeta}$ and the Debye-Hückel cloud radius Λ had similar values. On the other hand, in the model proposed in Ref. 79 use was made of the idea of thermal-fluctuation-induced detachment of edge and screw dislocations from pinning centers[82,83] and an edge dislocation was regarded as a charged string. Additional data are needed to determine under what conditions each of the proposed mechanisms predominates.

3.2. Investigations of dislocation strains in alkali halide crystals subjected to an electric field

The deformation of alkali halide samples due to the motion of charged dislocations in an electric field was first re-

ported by Sproull.[84] When a voltage was applied to the electrodes on two opposite surfaces of a previously bent LiF sample, the sag of the sample changed by an amount measured with a special electromechanical transducer. The strain was found to be an odd function of the electric field, i.e., it was different from electrostriction and was due to displacement of charged dislocations. Translational motion of charged dislocations in an electric field was observed by Shvidkovskiĭ, Tyapunina, and Belozerova[85] who used the selective etching method. Similar experiments were carried out by Zagoruĭko,[86] who detected a change in the direction of motion of an edge dislocation as a result of reversal of the field. Only edge dislocations participated in such motion. There was a threshold field in which motion began. In experiments on NaCl this field was 8×10^5 V/m. A change in the direction of motion of an edge dislocation as a result of repeated switching of the electric field in the experiments of Zagoruĭko[86] is demonstrated in Fig. 10. The motion of edge dislocations along rays of a dislocation rosette emerging from an indentation made in a KCl crystal in an electric field was reported in Ref. 87. Such motion also began when a certain threshold electric field was reached. Assuming that the threshold field causing dislocation motion was equivalent to a mechanical force, the authors of Ref. 87 used the critical shear stress and the threshold field intensity E_{th} to calculate Q_l. The charge found in this way was 58% of the maximum charge Q_l^{max}. A series of investigations[88-91] revealed the motion of dislocation walls of edge dislocations in alkali halide crystals subjected to an electric field. This field was perpendicular to the boundary of a sample. The motion was observed only above room temperature and it began when a certain threshold field was reached.[88,89] The displacement of a dislocation wall depended on the intensity of the electric field and the duration of exposure to this field, which in the experiments of Refs. 88 and 89 amounted to 11–90 h. The experimental results[88-91] did not give a clear answer on the sign of the charge of dislocation walls in alkali
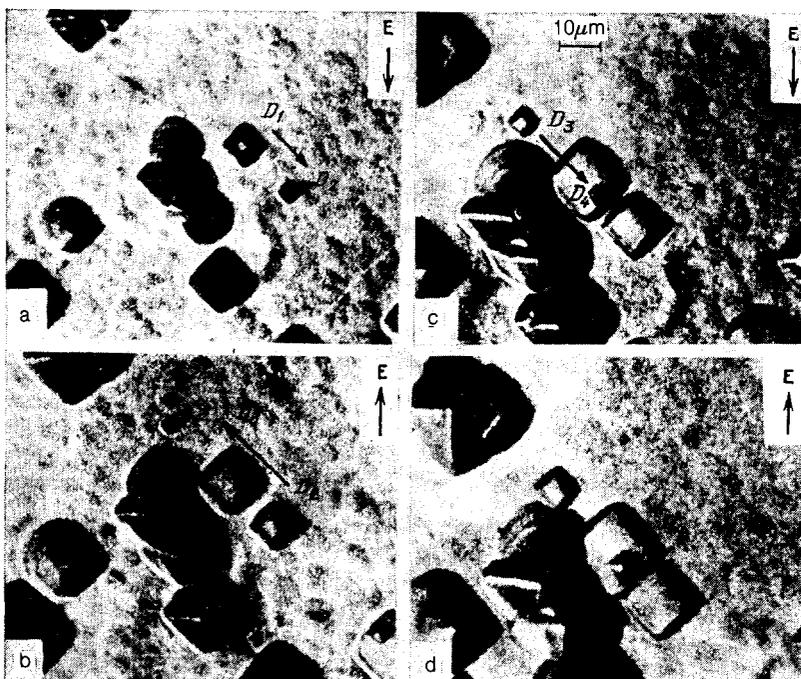
FIG. 10. Changes in the direction of motion of an edge dislocation as a result of reversal of an electric field ($E = 1.5 \times 10^6$ V/m).[86]

halide crystals. According to Refs. 88 and 89, the charge carried by a wall in an alkali halide crystal was negative below 620 °C and positive above 640 °C. According to Ref. 90, a dislocation wall in NaCl was charged negatively at temperatures 500–700 °C. In the study reported in Ref. 91 it was found that dislocation walls in NaCl consisting of edge dislocations were displaced in the direction of the electric field at temperatures 300–440 °C, i.e., they were positively charged. At room temperature it was found that a redistribution of cation vacancies took place near such walls when a sample was subjected to an electric field.[91] This altered the microhardness on both sides of the wall. The microhardness increased in the zone of accumulation of negative charges and decreased in the softening zone located on the other side of a dislocation wall. The abrupt change in the microhardness depended on the density of the electric field and the duration of exposure to this field. In 1966, Driyaev et al.[92,93] discovered vibrations of LiF samples in an alternating electric field. These samples represented single-wave vibrators exhibiting flexural vibrations. Under resonance conditions the vibrations of a sample lagged by $\pi/2$ behind the electric field, i.e., the field was in phase with the effective electric force that excited the crystal. According to Refs. 92 and 93, an alternating electric field induced vibrations of charged dislocation segments. The sag of a dislocation creates microplastic strains and gives rise to an effective force which excites vibrations of the crystal.

3.3. Simultaneous influence of an electric field and a mechanical load

We shall now consider the experiments in which an electric field was applied simultaneously with a mechanical load. Static,[94] pulse,[95–99] and alternating[100,101] loads have been used. The simultaneous application of a mechanical load and an electric field to a sample produces effects different from those when the load and field are applied consecutively. In addition to a direct effect on charged dislocations, the electric field induces a redistribution of charged jogs and reorients pinning centers which are formed by impurity-vacancy dipoles and by aggregates of dipoles, and it redistributes charged defects at block boundaries and on the surface of a crystal.

The influence of an electric field on the starting stresses and on the distance traveled by dislocations in NaCl samples subjected to uniaxial compression was investigated and reported in Ref. 94. A reduction in the starting stresses and an increase in the mean free path of dislocations were observed when an electric field was applied. A calculation of the charge Q_l from the change in the starting stress, allowing only for the direct effect of an electric field on a charged dislocation, gave values exceeding $Q_l^{\max}$. According to Ref. 94, an electric field acts not only on dislocations, but also on dipole pinning centers causing their reorientation and weakening their coupling to dislocations. The influence of shear stress and electric field pulses on the mobility of edge and screw dislocations in NaCl crystals was also investigated.[95–99] An increase in the mobility of edge dislocations on application of an electric pulse to a sample subjected to a mechanical load was interpreted as the effect of an electric field on the dislocation charge. A strong rise in the mobility of screw dislocations after a preliminary electric field pulse was attributed to a redistribution of charged jogs along a
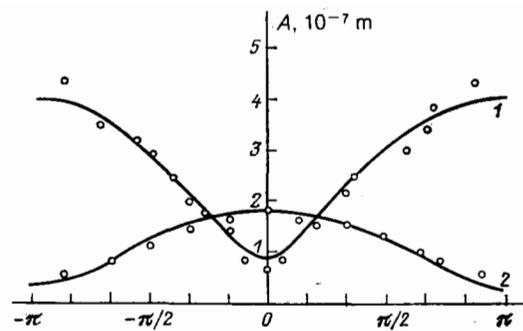
FIG. 11. Dependences of the amplitudes of flexural vibrations of a sample, subjected simultaneously to a mechanical force and an electric field, on the phase shift between the force and the field.[93] Curve 1 represents a sample with positively charged dislocations and curve 2 represents a sample with negative dislocations.

dislocation. The simultaneous effects of an alternating mechanical force, exciting flexural vibrations of an LiF crystal, and of an alternating electric field of the same frequency was studied by Driyaev et al.[93] This study was carried out on crystals of two types with positively and negatively charged dislocations. The amplitude of vibrations of the investigated crystals depended on the phase shift φ between the mechanical and electrical forces. The relevant dependence is shown in Fig. 11. It is clear that in the case of crystals with negatively charged dislocations the amplitude A was maximal for $\varphi = 0$ (curve 1), whereas in the case of positively charged dislocations the amplitude A reached its maximum value for $\varphi = \pi$ (curve 2). The theoretical curve for the amplitude A was obtained by simultaneous solution of the differential equation describing flexural vibrations of a sample and of the equation describing vibrations of a dislocation segment subject to mechanical and electrical forces exerted on such a dislocation regarded as a charged filament.[100] According to Ref. 100,

$$A = K \left(F_{0\tau}^2 + F_{0E}^2 + 2F_{0\tau}F_{0E}\cos\varphi \right)^{1/2};$$

here, $F_{0\tau}$ is the amplitude of mechanical vibrations and F_{0E} is the amplitude of oscillations of the electrical force acting on a crystal via charged dislocations with its direction depending on the sign of the dislocation charge. The values of A calculated using this expression agreed with the experimental curves in Fig. 11. The influence of an electrostatic field on translational motion of edge dislocations along rays of a dislocation rosette in KCl was observed[101] under hf vibration conditions. The main effect of the field was to increase the distance traveled and the number of displaced dislocations. The influence of the field was manifested also when E was parallel to the lines of edge dislocations, but in this case the field should not affect directly the charged dislocation. According to Ref. 101, an electric field acts not only on charged dislocations, but also on dipole pinning centers. At large amplitudes of ultrasonic vibrations an electric field facilitates ultrasonically induced multiplication of dislocations in alkali halide crystals.[102] Figures 12a and 12b show the results of etching of mirror-smooth cleaved faces of two KCl samples which were subjected to the same ultrasonic treatment, but one of these samples was additionally subjected to an electric field (Fig. 12a). A comparison of Figs. 12a and 12b shows that the field activates new sources
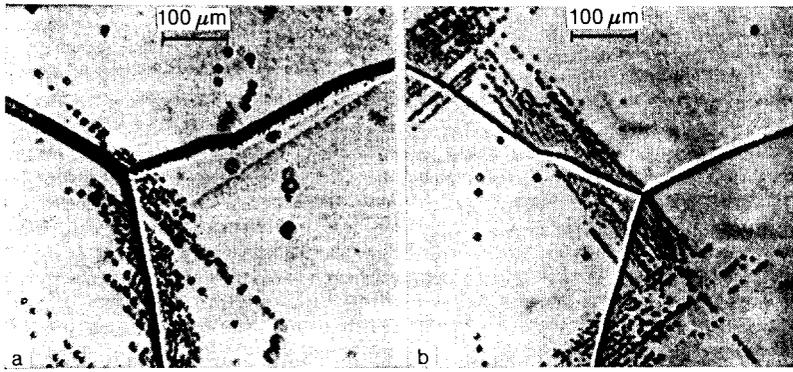
FIG. 12. Influence of an electric field on the deformation of KCl crystals during irradiation with ultrasound. The figure shows the results of etching of the surface of a sample after vibration in an electric field (b) and mirror-smooth cleavage surface of the same sample in the absence of a field but subjected to the same ultrasonic irradiation (a). Here, $\tau_0 = 7.8$ MPa, $f_r = 73$ kHz, and $E = 0.3$ MV/m.

in block boundaries which do not operate in its absence. It was typical that even in the case of those crystals in which the sources at block boundaries did not operate in the absence of an electric field, we found that in the presence of a field the process of plastic deformation began with the operation of such sources. An electric field also activated the sources located near the surface of a crystal. The role of the field was to alter the electrical state of a surface or a block boundary. This resulted in a redistribution of charged defects and increased the probability of appearance of sources of the optimal length $\tilde{L}$, operating under an influence of ultrasound of different frequencies.[103] Further studies of the effects described in the present subsection are desirable in order to obtain information on plasticization of materials under the influence of an electric field.

3.4. Influence of an electric field on mechanical properties of alkali halide crystals

An electric field alters those mechanical properties of alkali halide crystals which are associated with the presence of charged dislocations (creep, yield stress, elastic compliance defect, internal friction, etc.).

The influence of an electric field on the creep curves of alkali halide crystals, i.e., on slow flow of crystals under a constant load, was first reported in Ref. 104. The application of a field accelerated the flow and the creep curves exhibited small deformation jumps. The dislocation density in a sample increased considerably, i.e., an electric field facilitated plastic deformation; additional data would be required to identify the mechanism of this effect. The influence of an electric field on the yield stress of alkali halide crystals subjected to a mechanical load (electroplastic effect) was reported in Refs. 105–108. The application of a field reduced the stress needed to maintain a constant strain. The method gave a quantitative estimate of the dislocation charge Q_l [see Eqs. (2.56)–(2.58)]. According to Ref. 108, the charge was higher than Q_l^{max} and one of the possible reasons for this result could be a change in the electrical state of the surface under the influence of the field. An electric field influences also the damping and the elastic compliance defect of alkali halide crystals. This influence had been observed in the amplitude-independent[109,110,111,113,114] and amplitude-dependent[111,113] regions. The increase in the amplitude-independent damping in an electric field was observed in Ref. 109 in the hertz and kilohertz frequency ranges. It was concluded in Ref. 109 that the field did enhance detachment of dislocations from a compensating cloud of point defects. The influ-

ence of an electrostatic field on the amplitude-independent decrement δ and on the elastic compliance defect $\Delta S_{1111}/S_{1111}$ at amplitudes $\varepsilon_0 \sim 10^{-8}$–$10^{-7}$ at 80 kHz was described in Ref. 110. The application of a field increased both $\delta(t)$ and $(\Delta S_{1111}/S_{1111})(t)$. When the field was switched off, the decrement first increased and then began to fall reaching values close to those observed initially. A model of thermally activated detachment of segments of charged dislocations from Debye–Hückel clouds and subsequent modification of these clouds was used to explain the observed effect. In the absence of a field such charged dislocation segments are assumed to vibrate symmetrically within a charge cloud. When a field is applied, the force exerted by it displaces a segment and its vibrations relative to a cloud become asymmetric. In high fields a dislocation is in a region with a low concentration of defects and this enhances the decrement and the elastic compliance defect. As a result of subsequent modification a cloud assumes a symmetric shape relative to the new position of the dislocation and this reduces the damping. When the field is switched off, a dislocation segment returns to its initial position and exhibits vibrations in a cloud free of defects. Therefore, immediately after the field is switched off the damping increases and then modification of the cloud causes relaxation to the initial state. An amplitude dependence of the damping and of the Young modulus defect $\Delta M/M$ was reported in Ref. 111 for alkali halide crystals subjected to strain of amplitudes ε_0 in the same range as in Ref. 76. An estimate of the displacement of a vibrating dislocation obtained using an expression put forward by Baker[112]

$$\bar{\zeta} = \frac{2\,(\Delta M/M)\,\varepsilon_0}{Kb}$$

demonstrated that $\bar{\zeta}$ was close to the radius of a charge cloud calculated from Eq. (2.15). The amplitude dependence was explained in Ref. 111 by the motion of a vibrating dislocation segment projecting beyond the limits of a cloud. In the presence of an electric field the onset of the amplitude dependences $\delta(\varepsilon_0)$ and $(\Delta M/M)(\varepsilon_0)$ shifted toward lower values of ε_0. The influence of the field on the damping and the modulus defect at amplitudes ε_0 in the region of detachment of dislocations from weak pinning centers was investigated by Belozerova et al.[113,114] Figure 13 shows the influence of the field on the amplitude dependence $\delta(\varepsilon_0)$ of a KCl sample at a frequency 73 kHz taken from Ref. 114. Clearly, the amplitude dependence $\delta(\varepsilon_0)$ for a sample in an electric field began at lower values of ε_0 than for a control sample. We found no
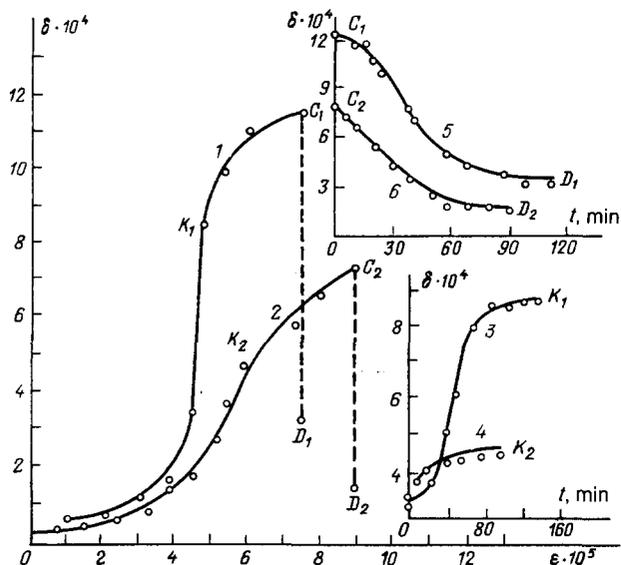
FIG. 13. Influence of an electric field on the amplitude dependence of the damping.[114] Curve 1 represents a sample in an electric field and curve 2 represents a control sample. Curves 3 and 4 demonstrate establishment of steady-state damping at points K_1 and K_2. Reduction of the damping at high values of ε_0 (curves 5 and 6) is due to pinning of dislocations controlled by bulk diffusion in KCl. Here, $f_r = 73$ kHz and $E = 1.6 \times 10^5$ V/m.

published data on the influence of an electric field on the damping in alkali halide crystals in the region where dislocation multiplication was possible. A study of the influence of an electric field on plasticization of crystals containing charged dislocations, which include semiconductor materials, is not only of scientific but also of practical interest. The internal friction provides a convenient and sensitive method for investigations of this influence.

4. CONCLUSIONS

Less than thirty years have passed since the publication of the first results of investigations of charged dislocations. Such investigations are now proceeding on a wide front and they have revealed new information on the influence of charged dislocations on mechanical and electrical properties of alkali halide crystals. Such information is essential in the preparation of materials with precisely specified properties, which are used in many branches of science and technology, and in forecasting the behavior of materials under various test conditions. The authors are grateful to I. A. Yakovlev for his interest and valuable advice.

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