Magnetosensitive reactions in ionic crystals during their plastic deformation

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A new method for investigating spin-independent chemical reactions between radical centers at point defects and dislocations in solids is proposed. The method is based on studying the mobility of dislocations in a field of mechanical stresses. The application of a magnetic field with induction $B = 1$ T results in a change in the state of the defects of the crystal lattice in ionic crystals, which can be observed a long time (up to 10^3 s) after switching off the field. Radical reactions were analyzed in which the kinetics of changes in the magnetic field can cause the effect of magnetic "memory" in distorted microregions of the lattice.

Key words: ionic crystals, magnetosensitive reactions, point defects, magnetic "memory" effect.

It is known that ionic crystals of the NaCl type formed from ions with complete electronic shells are diamagnetic.[1] Distortions of the crystal lattice near dislocations and doped centers can result in local rearrangement of the electronic structure and the appearance of electronic levels in the forbidden band.[2] For example, paramagnetic defects in an ionic crystal can be considered by their chemical properties to be free radicals. These defects can be unpaired electrons localized at point defects (doped atoms, vacancies, radiation defects and their complexes) or dislocations. Due to their low concentration, the existence of these radicals in a crystal has a weak effect on the magnetic susceptibility and other volume properties of the specimen as a whole. However, they can play an important role in chemical reactions.

The velocity of motion of a dislocation in a field of external mechanical stresses is likely a convenient function of the response to the state of crystal defects and to chemical processes occurring in the defects. The velocity of motion of dislocations in ionic crystals is mainly limited by their interactions with hindrance points containing dopant atoms. The dislocations play the role of an atomic-scale probe that reacts to the state of these centers. The main reason for delay of dislocations is the field of elastic stresses of point defects.[3] The existence of radicals at dislocations and point defects suggests that along with the elastic interaction of dislocations with point defects, short-range exchange interaction can contribute substantially to the energy of their interaction. This interaction can appear in a quasi-molecule consisting of radicals that belong to a dislocation (R_d) or a

point defect (R_p). This quasi-molecule can be formed in the process of carry-over of the dislocations at a hindrance point, if the distance between radicals R_d and R_p is close to the lattice parameter a. It decomposes due to the action of mechanical stress on the dislocation, which is related to the thermal activation barrier, whose height is determined by the sum of the energies of elastic and exchange interactions. To elucidate the significance of the latter in the delay of dislocations, it is enough to compare the efficiency of its action and the elastic stress field. Taking into account the thermal activated character of overcoming the hindrances by dislocation,[3] the efficiency of the short-range exchange interaction between the dislocations and defects in the bulk is determined by the following correlation

$$j = N_{ex}\exp[E_{ex}/(k_B T)]/N_{fl}\exp[E_{fl}/(k_B T)],$$

where $E_{fl} \approx 0.1$ eV and $E_{ex} \approx 1$ eV are the characteristic energies of the elastic and exchange interactions, N_{fl} and N_{ex} are the numbers of cases in which elastic and exchange interactions between a dislocation and hindrances are established per surface unit. Let us take into account that N_{fl}/N_{ex} is determined by the average distance d between unpaired electrons at the dislocation, which can be estimated from the data on charges at the dislocation,[4] according to which $d \approx 10^2-10^3\ a$. Therefore, $N_{fl}/N_{ex} \approx 10^{-3}$ and $j \approx 1$. Thus, chemical reactions between the radicals at the dislocations and in the bulk crystal can introduce a noticeable contribution to strengthening of the crystal. The state of the radicals at defects can also be estimated from the mobility of the dislocations.

At the same time, the kinetics and yield of the radical reactions under certain conditions are rather sensitive to a static magnetic field (MF) at room temperature.[5,6] In this case, the mechanism of the MF action is unusual. The energy imparted to the crystal by a field with induction $B = 1$ T per radical is equal to $E_m \approx \mu_B g B \approx 10^{-4}$ eV (g is the gyromagnetic factor of an electron and μ_B is the Bohr magneton), which is two orders of magnitude lower than the energy of thermal oscillations $E_h \approx k_B T \approx 10^{-2}$ eV at $T = 300$ K and does not allow one to explain the change in the reaction rates by the action of the energy of the field. This effect can be caused[7-9] by the change in the multiplicity of a radical pair in a MF when two radicals approach to a distance at which the difference in the energies of the singlet (S) and triplet (T) states are comparable with E_m. If the time of the S—T-transition is considerably less than that required to establish a thermal equilibrium in the system, thermal oscillations have no time to affect the probability of the transition. An important condition of the effectiveness of this mechanism is a great number of attempts to form a pair during the period when the radicals exist in the vicinity of each other. It can be expected that this condition is fulfilled for solid-phase reactions better than for liquid-phase reactions due to the lowered mobility of the radicals and the action of mechanical stresses that hold the dislocation to the hindrances.

Thus, the measurement of the mobility of dislocations or the plastic properties of crystals determined by the mobility can be used for obtaining information on the state of radicals, the kinetics of radical reactions, and the effect of MF on the kinetics. The purpose of the present work is to observe radical reactions in crystals whose sensitivity to MF results in alleviated slipping of dislocations, as well as to study the activation parameters and specific features of the kinetics of these reactions in MF.

Experimental

Changes in the velocity and in the value of the plastic deformation of crystals a short time (from 20 to 200 s) after switching on MF were monitored using an induction detector on a two-coordinate recorder.

Results and Discussion

The rate of the $R_d + R_p$ reaction, which depends linearly on the frequency of collisions of the radicals at the moving dislocation with point defects f, was determined from the relative velocity of the plastic deformation of the crystal $\dot{\varepsilon}$ or the mean velocity of individual dislocations v. This approach is based on the Orovan correlation $\dot{\varepsilon} = b\rho v$ and evident equality $f = CbaL\gamma v$ (b and L are the mean values of the Burgers vector and dislocation lengths, ρ is their density, γ is the concentra-

tion of the radicals on the line of dislocations, C is the volume concentration of point defects, and a is the lattice parameter).

In the first (1) series of experiments, crystals were deformed linearly by mechanical stress of uniaxial compression increasing with time t: $\sigma = kt$. The process of crystal deformation lasted from $3 \cdot 10^2$ to $2 \cdot 10^3$ s.

In NaCl and KCl crystals doped with Ca^{2+} and in LiF crystals doped with Mg^{2+}, Ca^{2+}, and other cations, weakening of the crystal was observed in MF. This effect is manifested as a decrease in the yield point by 10—20% when the crystals are deformed in MF and as a decrease in the strengthening coefficient $d\sigma/d\varepsilon$ when MF is switched on after attainment of the yield point. The latter could be seen in the fact that at the instant when the field was switched on, the slope of the diagram $\varepsilon(\sigma)$ increased compared to the slope of the region of the diagram 20—200 s before MF was switched on. During the whole period of the MF action on the crystal, the slope continued to increase and returned to its initial value (in the absence of MF) only after MF was switched off (Fig. 1), i.e., the weakening is reversible. Switching on MF during the deformation of crystals doped with Pb^{2+} or Mn^{2+} did not result in weakening of the crystals within the experimental accuracy.
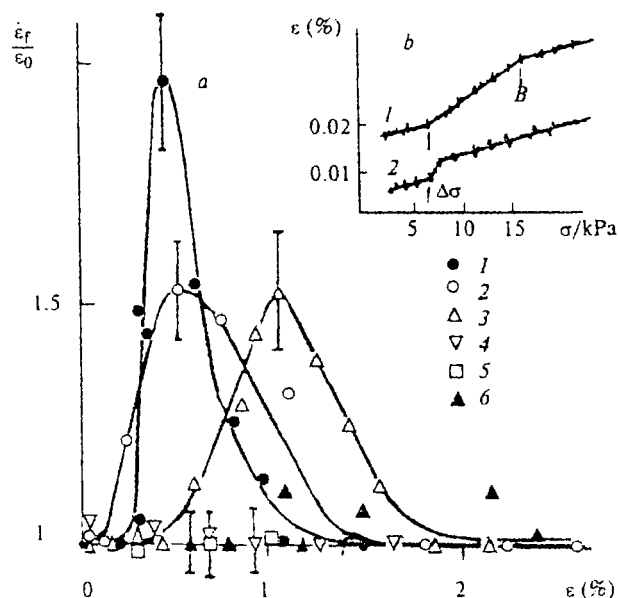

Fig. 1. *a*. Dependences of the velocity of plastic deformation $\dot{\varepsilon}_f$ (normalized to the flow velocity in a switched-off field $\dot{\varepsilon}_0$) in static MF with $B = 0.7$ T on the total deformation ε of crystals: *1*, NaCl—Ca^{2+} (0.1%); *2*, KCl—Ca^{2+} (0.03%); *3*, LiF—Me^{2+} (0.01%, lines of slipping dislocations $L \perp B$); *4*, KCl—Mn^{2+} (0.01%); *5*, KCl—Pb^{2+} (0.03%); *6*, LiF—Me^{2+} (0.01%, $L \| B$). *b*. The fragment of the $\varepsilon(\sigma)$ diagram during the action of MF (*1*) and at the instant of jumpwise mechanical loading (*2*).
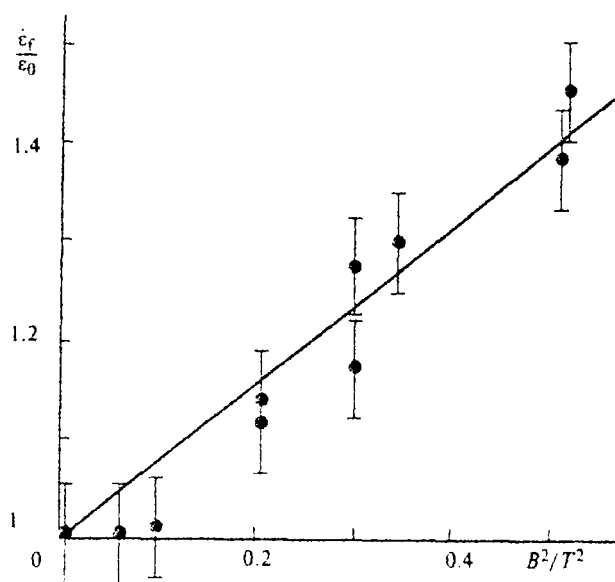
Fig. 2. Dependence of weakening of crystals in MF on the induction B.

Fig. 3. Dependences of the maximum value of weakening of NaCl (*I*) and KCl (*2*) crystals in static MF with $B = 0.7$ T on the concentration (%) of dopant Ca^{2+} in the crystal and the dependence of the dislocation charge density on the concentration (%) of dopant Ca^{2+} in KCl crystals at $B = 0$ (*3*).

A jumpwise increase in the mechanical load of the sample during deformation $\Delta\sigma = 30—40$ kPa resulted in an increase in $\dot\varepsilon$ comparable with the increase in $\dot\varepsilon$ in MF in the first 10 s after the increase in the load. With further loading, the former slope was established (see Fig. 1). Thus, the effect observed differs from that occurring in mechanical loading by the fact that the MF action on the crystal does not cease immediately after MF is switched off, but lasts for a long time. Since at $\sigma > \sigma_s$ switching off MF resulted in an increase in the velocity of the plastic flow $\dot\varepsilon_f$ compared to the velocity before switching on MF $\dot\varepsilon_0$, the $\dot\varepsilon_f/\dot\varepsilon_0$ ratio was considered as the numerical value of the effect. Weakening of the crystal usually reached a maximum immediately after the yield point and faded at $\varepsilon > 1—2\%$ (see Fig. 1). Sometimes it appeared at high deformations, but its character was irregular and irreproducible.

In these experiments, the dependence of the effect on B turned out to be close to the square function (Fig. 2). Weakening of the crystal increased up to the solubility limit ($C \approx 0.1\%$) as the concentration of the Ca^{2+} ions increased. In the crystals where weakening was observed, its value ($\dot\varepsilon_f/\dot\varepsilon_0$) correlated with the linear density of the dislocation charge q measured in KCl according to analysis of the dislocation electrical polarization[4] (Fig. 3).

Thus, it is established that MF has an effect on the macroplastic flow of ionic crystals. The reason for the weakening of the crystals is a decrease in the effective cross section of the interaction of the dislocations with some types of hindrances. The narrow interval of defor-
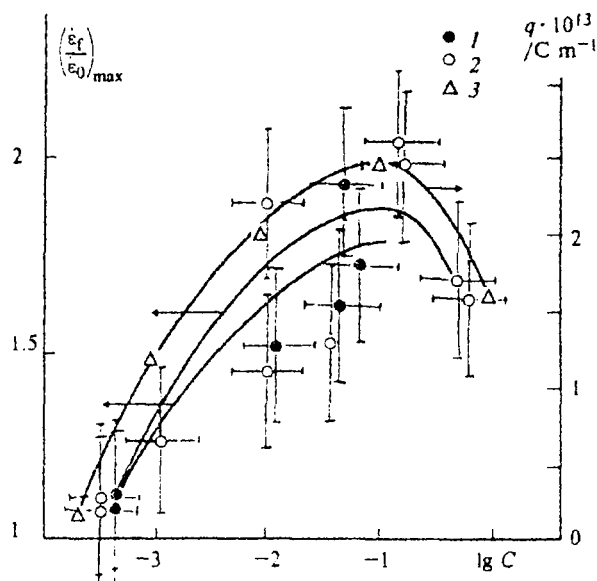
mations within which the effect can be detected testifies that MF facilitates overcoming only a portion of the hindrances, which are substantial at the initial stage of the plastic flow. Apparently, these hindrances are point defects, mainly of doped origin. The dislocations appearing at $\varepsilon > 1—2\%$, which play a more significant role in delaying slipping dislocations than doped centers, are not likely sensitive to MF, as can be seen from Fig. 1.

In the second (*2*) series of experiments, the value of the average path of individual dislocations in the field of a calibrated pulse of mechanical compression stresses that was the same in all experiments (amplitude 0.1 MPa, duration 6 s, front 10 ms) was chosen as an indicator and a measure of the effect of MF on the state of ionic crystals. The crystals were exposed to MF, and dislocations were introduced in different orders in experiments of types *2* and *3*. The results of measuring the paths in these experiments (l_2 and l_3) were compared with the results of the control experiments of type *I* (l_1) (Fig. 4). Since MF was absent during loading, the possible effect of MF on the interaction of dislocations with hindrances was excluded. In experiments of the third (*3*) type, fresh dislocations were introduced, then the specimen was placed in the electromagnet and exposed to the field for time t_1 (from several s to several h), and the position of the dislocations was fixed by the first etching. After switching off the field and a pause of t_2 (also from several s to several h), the crystal was mechanically loaded (t_p), and the specimen was etched once more. The average path of the dislocations l was determined by averaging $3 \cdot 10^2—10^3$ paths of individual
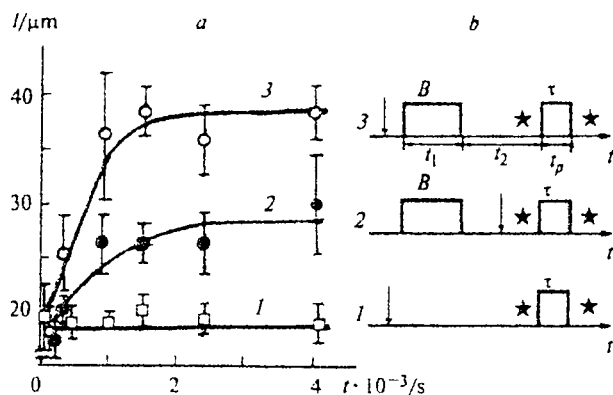
Fig. 4. *a*. Dependence of the average path lengths of edge dislocations on time of exposure of crystals to static MF with $B = 1$ T in experiments of different types (*1—3*). *b*. Schematic representation of the order of procedures in time (*t*) in experiments of different types (*1—3*) (instants of introduction of dislocations are designated by arrows, ★ indicate instants of etching, *B* is the induction of MF, and τ are mechanical stresses).
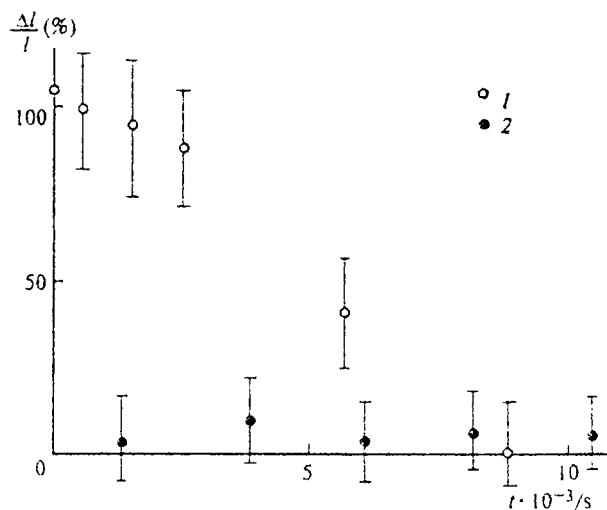

Fig. 5. Dependence of the relative increase in the path length of dislocations caused by preliminary exposure of the crystal to MF on the time between switching off the field and mechanical loading (*1*); path lengths of dislocations in experiments without MF depending on the time between their introduction and loading the specimen (*2*).

dislocations for each specimen. The type *2* experiments differed from the type *3* experiments only by the fact that the dislocations were introduced into the crystal not before, but after treatment in MF. In both series of experiments (types *2* and *3*), the *l* value increased over that of the control experiments (see Fig. 4). Therefore, some elements of the structure "remember" the effect of the MF. For the dislocations introduced after the MF action, the increase in *l* indicates that these elements may be local hindrances. A greater increase in *l* was observed for the dislocations introduced before MF was switched on. The difference in the average paths in the type *2* and *3* experiments characterizes residual changes in the structure and properties of the dislocations that have stayed in MF and indicates that the dislocations also "remember" the MF action. As the exposure to MF increases, the value of $\Delta l = l_3 - l_2$ increases and reaches saturation at $t_1 > 10^3$ s.

The aftereffect of MF was temporary and decayed with a time constant of ~$3 \cdot 10^3$ s when the pause between switching off MF and the mechanical loading increased (Fig. 5). It was established in the control experiments that this relaxation is not related to aging and fixation of the dislocations, because in the specimens that were not subjected to MF the pause between the introduction of the dislocations and the mechanical loading was up to several h and did not result in a noticeable decrease in their mobility (see Fig. 5). It follows from the results obtained in this series that the dislocations and point defects have "memory" about exposure of the crystal to MF, *i.e.*, MF has an effect on the state of both dislocations and point defects in ionic

crystals. The residual MF-induced changes in the state of these objects can be observed even 10^3 s after switching off the field.

The results obtained make it possible to determine the types of reactions whose kinetics can change in MF due to weakening of the crystals. The types of possible reactions occurring in the crystal can be presented in the following form:

$$R_d + R_p = M_1, \tag{1}$$

$$R_{p_1} + R_{p_2} = M_4, \tag{2}$$

$$R_{d_1} + R_{d_2} = M_2, \tag{3}$$

$$R'_p + R''_p = M_5, \tag{4}$$

$$R'_d + R''_d = M_3. \tag{5}$$

where indices 1 and 2 refer to dislocations or point defects, and hash marks designate the radicals that belong to the same defect. Let us consider the conditions of the reactions indicated without MF and the effect of the field on their kinetics. Reactions of types (1) and (3) occur when the dislocations move around in the crystal, *i.e.*, due to its plastic deformation. The mobility of the dislocations is limited by reaction (1) at the initial stage of the deformation (up to $\varepsilon \approx 2\%$)[10] and, according to Fig. 1, this is the reaction that is subject to the effect of MF. To establish the reasons for this effect, it should be taken into account that the effective cross

section of this reaction is determined by two factors: 1) the frequency of collisions between the radicals of the dislocations and point defects f and 2) the binding energy of the radical pairs formed E_{ex}.

The effect of MF on the plasticity of the crystals can cause a change in any of the factors mentioned. In the first case, this is due to a change in the concentration of unpaired radicals in the crystal, and in the second case, due to a change in the binding energy in the $R_d + R_p$ pair caused by the S—T-transitions in MF. Only the second possibility has been *a priori* considered previously.[11,12] According to the results presented in Figs. 4 and 5, which testify that the aftereffect of MF exists, this is not the only possibility. Therefore, new magnetosensitive degrees of freedom of the states of defects in ionic crystals have been discovered.

Thus, a change in the probability of the collision of the R_d and R_p radicals can be caused before the motion of the dislocations by decreasing their concentration. This can occur due to a change in the rates and yields of reactions (2), (4), and (5). Let us estimate the possibilities and characteristic parameters of the kinetics of each of them in MF.

1. Type (2) reaction. For the typical concentration of the admixture in the crystal $C \approx 10^{26}$ m^{-3} and the diffusion coefficient of doped atoms in the lattice $D \approx 10^{-22}$ m^2 s^{-1}, the characteristic time necessary to encounter the radicals is $t = C^{-2/3}D \approx 10^5$ s, which is considerably greater than the characteristic time of the process observed in MF (see Figs. 4 and 5). Therefore, changes in the kinetics of this reaction cannot be a reason.

2. Type (5) reactions can occur between the radicals arranged along the dislocation line. Their characteristic time can be close to the measured value, because the diffusion coefficient along the dislocation nucleus D_n exceeds the bulk coefficient by several orders of magnitude. Indeed, according to the published data,[4] charged singularities are located at the dislocations in ionic crystals at an average distance of $z \approx 100$ a along its line and can be associated with radicals with unpaired spin. These singularities, moving along the dislocation line under the action of thermal fluctuations, are capable of approaching each other to distances comparable with a during time $t \approx z^2/2D_n \approx 10^{-1}$ s. In the absence of MF, the encounter of these radicals in $\omega_T = 3/4$ cases results in the formation of a pair in the T-state, and in $\omega_S = 1/4$ cases, of a pair in the S-state. The difference in the binding energies of the pairs in these states results in a difference in the rates of their decomposition under the action of thermal oscillations, *i.e.*, the establishment of a dynamic equilibrium between the paired and free radicals. This equilibrium is violated in MF, because at the instants the radicals encounter one another, the transitions from the S- to T-state occur and, hence, the probabilities ω_T and ω_S change. Increasing the equilibrium concentration of free radicals increases the effective cross section of reaction (1), *i.e.*, strengthens the

crystals. In our experiments, the number of unpaired radicals at dislocations likely decreases in MF, because weakening of the crystals is always observed. This testifies that the binding energy of a pair in the T-state is lower than that of a pair in the S-state. It cannot be ruled out that a change in the type of crystals can result in the opposite sign of the effect in MF.

After MF is switched off, the state of the dislocation is recovered after time $\tau = \upsilon \exp(E_{ex}/k_B T)$, which depends on the binding energy of the radical pair E_{ex} and the frequency of the attempts $\upsilon \approx 10^{11}$ s^{-1}. The data in Fig. 5 give evidence for the decomposition of the pairs and allow one to estimate E_{ex} (~0.9 eV). This value confirms that the radical reactions can contribute substantially to the delay of dislocations. It should be noted that weakening of the crystal in MF, which occurs during the motion of dislocations, can appear during times much shorter than 10^3 s (see Fig. 1). In terms of the model suggested, this can be explained by the fact that the motion of the atoms along the dislocation nucleus intensifies considerably as it moves and, hence, the time between the encounters of the radicals decreases. This results in an increase in the reaction rate.

3. Type (4) reactions can take place inside point defects with complicated configurations containing several dopant atoms, vacancies, *etc.* The data in Fig. 4 testify that the electronic state of the defects can also change in MF due to the increase in the probability of the formation inside the defect of a stable pair of radical electrons, whose spins were not mutually correlated before the crystal was placed in MF. The application of mechanical stresses to a crystal can increase considerably the rate of this reaction, because the point defect falls in the band of mechanical stresses of the nucleus of the moving dislocation. In fact, since the value of these stresses can attain $\sigma \approx 0.1 G$ (G is the modulus of elasticity of the crystal) and the activation volume of the reaction γ is not greater than the volume of the point defect $\gamma \leq 10^{-29}$ m^3, the increase in the reaction rate can attain $\tau/\tau_0 = \exp\gamma\sigma \approx 10^3$ times.

These estimations of the parameters of reactions in ionic crystals testify that the consideration of reactions of types (4) and (5) provides a qualitative explanation for the effects observed in MF. Thus, a new type of magnetosensitive chemical solid-phase reaction is discovered, and the existence of new degrees of freedom of the state of defects in crystals is established. The results obtained are universal and can be applied to analysis of radical reactions in semiconducting, metallic, and polymeric crystals. Finally, the study of the MF effect on spin-dependent reactions in crystals allows one to investigate the nature of many magnetic effects in biological systems.

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