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Kinematics of Dislocations in NaCl Crystals with Different Impurities

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Abstract

Kinematics of the magnetoplastic effect on the example of NaCl crystals is experimentally and theoretically studied. Specific features of dislocation motion under magnetic field with or without additional mechanical load in crystals doped with different types of impurities are considered. It is found that even small addition of Ni impurities to the NaCl(Ca) crystal leads to paradoxically strong increase of dislocation mobility. On the other hand, the NaCl(Ca+Pb) crystal, instead of plasticizing under the magnetic field, demonstrates rather strong strengthening. The atomic scale mechanisms of the phenomenon are discussed in detail on the basis of the results of macroscopic experiments.

Keywords: Dislocations; Point defects; Plasticity; Magnetoplasticity

1. INTRODUCTION

The dislocation motion in most crystalline materials determines their plastic properties. The magnetoplastic effect (MPE) in non-magnetic crystals, in its main manifestation, is the movement of dislocations in a magnetic field in the absence of additional external influences. The essence of this phenomenon, discovered by our group [1] (see also reviews [2–6]), is the spin-dependent transformation of the structure of impurity defects in a magnetic field, which is similar to the magnetic influence on the rate of chemical

reactions and other spin-dependent effects [7–11]. In our case, the magnetic transformation of impurity atoms in dislocation cores leads to a change in the pinning force on the dislocations. The sensitivity of MPE to the structure of the impurities, up to a change in its sign, is a reason to study the kinematics of dislocations in NaCl crystals doped with different types of impurities. And this requires a certain strategy of experimental and theoretical steps that allow us to get closer to understanding the observed physical processes. Below we will illustrate by a number of examples how such a strategy could look like.

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2. METHODS

The studies were carried out on NaCl single crystals with various types and concentrations of impurities. Crystals with one- and two-component impurity systems were studied. At the Leningrad Optical-Mechanical Association (LOMO), using the Kyropoulos method, single crystals of NaCl(Ca) with an impurity of calcium (10 ppm) were grown, as well as crystals containing the same amount of calcium and an additional 2 ppm of nickel — for brevity we will denote them NaCl(Ca+Ni). Single crystals of NaCl(Ca+Pb) were obtained by the Stockbarger method at the Institute of Physics and Optics of Hungary. They contained 1 ppm ($\text{Pb}^{(1)}$) and 10 ppm ($\text{Pb}^{(2)}$) of lead. The concentration of Ca impurity in them was 0.5 ppm.

The samples were cleaved along $\{100\}$ cleavage planes in the form of parallelepipeds with approximate dimensions of $3 \times 3 \times (7-8)$ mm, after which they were annealed and chemically polished. Immediately before the experiment, fresh dislocations were introduced into them with a light shock. It was verified that dislocations created in this way are straight directed along the $\langle 100 \rangle$ [2,6]. The initial and final positions of dislocations were recorded by chemical etching (Fig. 1). Dislocation mobility was characterized by measuring the mean path l of individual edge dislocations (in some cases paths were normalized by the mean distances $1/\sqrt{\rho}$ between dislocations: $l \rightarrow l\sqrt{\rho}$). Averaging was carried out over 50–200 measured paths.

Magnetic exposure was carried out in a constant field $B = 0.2-0.7$ T created by an electromagnet. The sample

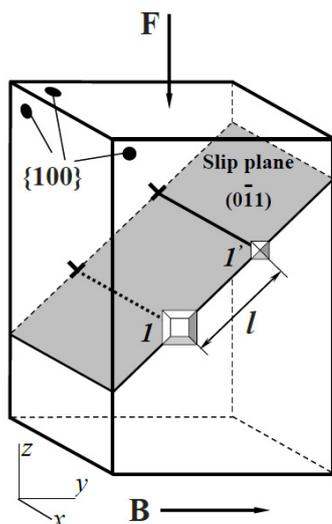


Fig. 1. Schematic diagram of the sample with $\{100\}$ surfaces and the orientations of the magnetic field (\mathbf{B}) and mechanical loading (\mathbf{F}) with respect to the sample. An example of the displacement l of the edge dislocation parallel to the $[100]$ direction in the $(0\bar{1}1)$ slip plane is shown. Initial (I) and final (I') positions of the dislocation are fixed by the etch pits at the surface.

stood freely on a non-magnetic stand between the poles of the electromagnet, the diameter of which significantly exceeded the dimensions of the sample. The orientation of the sample was, as a rule, chosen so that the dislocations under study were orthogonal to the magnetic induction vector. As was found out earlier, it is in this orientation that the maximum values of dislocation paths are observed. Mechanical loading was applied by means of a triangular or trapezoidal uniaxial compression pulse with an amplitude of shear stresses $\tau_m = 0-0.3$ MPa.

Four experimental schemes were used:

- (i) the crystal was kept in a constant magnetic field without mechanical loading;
- (ii) the sample was subjected to a mechanical pulse in a zero magnetic field;
- (iii) the crystal was simultaneously subjected to mechanical loading and a magnetic field;
- (iv) the sample rotated in the magnetic field with frequency ν .

3. RESULTS AND DISCUSSION

As mentioned above, an elementary act of magnetoplasticity includes a spin-dependent transformation of pinning centers formed by impurity atoms in the dislocation core, that is the process occurring in the systems of atomic size. In particular, MPE turns out to be sensitive to the atomic structure of dislocation cores [12]. And this micro-effect is to be studied only by its indirect macroscopic manifestation, which is in our case the magnitude of dislocation displacements recorded on the surface and amounting to tens and hundreds of microns. With such a significant disparity, understanding the measurement results, based mostly on common sense and physical intuition, often does not go beyond semi-qualitative interpretations and hypotheses that require new experimental tests. Sometimes the first natural assumptions turn out to be very far from the truth. Below we discuss in detail several experimental mysteries and their very non-trivial solutions concerning the atomic scale mechanisms of magnetoplasticity in NaCl(Ca), NaCl(Ca+Ni) and NaCl(Ca+Pb) crystals.

As can be seen from Fig. 2, in the absence of external mechanical loading the crystals of both NaCl(Ca) and NaCl(Ca+Ni) placed in a constant magnetic field demonstrate high dislocation mobility. Moreover, contrary to “common sense”, the addition of Ni impurity, leading to an increase in dislocation pinning, does not reduce, but increases this mobility. It is essential that in these crystals linear dependences of the mean dislocation path l on the square of the magnetic induction B^2 , typical for the MPE, are observed. So far, judging from the difference in the slopes of the two $l(B^2)$ plots, one can state at least at a verbal level that a small addition of Ni impurity to a

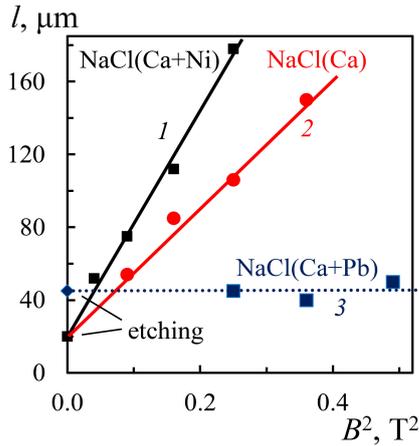


Fig. 2. Dependences of the mean dislocation path l on the square of magnetic induction B for the crystals with the different impurities: 1 – NaCl(Ca+Ni), 2 – NaCl(Ca), 3 – NaCl(Ca+Pb⁽²⁾). Magnetic exposure time is 5 min.

NaCl(Ca) crystal considerably increases its magnetosensitivity. Below we will have to deal with this paradox.

Let us now consider the dependence of the mean dislocation path l on B^2 for the NaCl(Ca+Pb⁽²⁾) crystals, illustrated in Fig. 2. In these crystals, the mean dislocation path l is completely independent of the magnetic field, remaining at the background level, determined by manipulations with the samples. At first glance, it is unsurprising: there is little calcium in this crystal (0.5 ppm), and lead is presumably not magnetically sensitive. Fortunately, this assumption can be easily verified by measuring dislocation paths in these crystals under simultaneous application of magnetic field and mechanical loads. Experiments have shown that we are dealing not with the lack of effect, but with magnetic strengthening of these crystals. It turned out that in a magnetic field there is a decrease in the mobility of dislocations compared to their behavior under the same load without a magnetic field. Apparently, under magnetic field action the pinning centers due to Pb impurity acquire a structure corresponding to an increase in the pinning force on dislocations.

Fig. 3 shows the dependence of the dislocation mean path on the applied mechanical load τ_m for NaCl(Ca+Pb^(1,2)) crystals. Here τ_m is the maximum resolved shear stress achieved during uniaxial mechanical compression of the crystal in a magnetic field of 0.3 T or in its absence. Plot 1 in this figure, which corresponds only to mechanical loading at $B = 0$, shows that for both Pb concentrations, the mobility of dislocations is approximately the same. But an application of even a low magnetic field of 0.3 T sharply reduces the dislocation mobility in crystals with a minimum Pb concentration (1 ppm) and completely eliminates it when the Pb concentration increases to 10 ppm.

Let us now try to answer the question why the slopes of the straight lines for NaCl(Ca) and NaCl(Ca+Ni) in

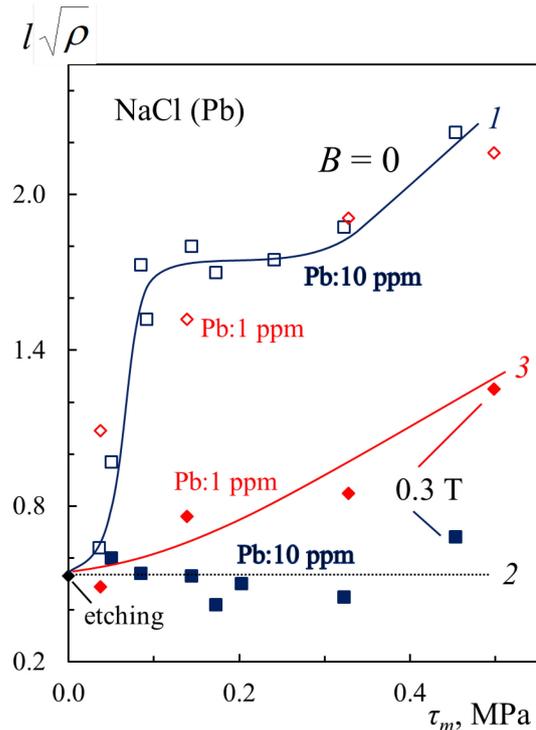


Fig. 3. Dependences of the normalized mean dislocation path $l\sqrt{\rho}$ on the amplitude τ_m of a trapezoidal stress pulse ($t_{\text{pulse}} = 5$ min, the durations of the leading and trailing pulse edges are 0.1 s and 1.0 s, respectively) in a magnetic field for NaCl(Ca+Pb) crystals with the two Pb concentrations: 1 ppm (red points) and 10 ppm (blue points). Plots correspond to 1 – $B = 0$; 2, 3 – $B = 0.3$ T. Point \blacklozenge – etching level.

Fig. 2 differ so noticeably with such a small amount of Ni impurity (2 ppm) against the background of a five times higher Ca concentration (10 ppm), and why does the mean dislocation path increase in NaCl(Ca+Ni). To resolve this paradox, we will have to compare the corresponding loading curves $l(\tau_m)$ for these crystals at $B = 0$. As we will see, this approach will allow us to estimate the total pinning force on dislocations in NaCl(Ca) and NaCl(Ca+Ni).

One should keep in mind that under the conditions of our experiments, the mean paths of dislocations in Fig. 2 and forced displacements under action of external mechanical loads in Fig. 3 are $l \sim 10\text{--}100 \mu\text{m}$. This is of the same order of magnitude as the average distance between dislocations in the crystals under study. Therefore, when moving under the action of a time-dependent external stress $\tau(t)$, a freshly introduced dislocation must overcome in addition to the total pinning force τ_p of impurity defects also the spatially variable internal stress $\tau_i(x)$ of nearby old (immobile) dislocations. However, in the latter case we do not necessarily deal with “overcoming”. Indeed, when fresh dislocations are introduced, they scatter down the slopes of the internal stress relief, stopping at points where the driving stress is compensated by the “dry friction” of pinning: $\tau_i(x_0) = \tau_p$, where x_0 is the position of

the dislocation at the equilibrium point. This is the position of the dislocation on the slope of the relief at the start before the pulse $\tau(t)$ is turned on. Under loading conditions, the dislocation will continue to descend along the relief and reach its lowest point, where $\tau_i = 0$, when the pulse amplitude $\tau_m = \tau_p$. With a further increase in amplitude, an upward movement begins along the next slope of the relief. In this case, the position of the dislocation at each moment of time is now determined by the following balance of three forces:

$$\tau(t) = \tau_p + \tau_i(x). \quad (1)$$

This is a typical quasi-static mode of movement, when the dislocation velocity depends only on the loading rate, and the resulting path is completely determined by the amplitude τ_m of the mechanical pulse [13]. It is not surprising that plot *l* in Fig. 3 is insensitive to the pulse shape. According to our data, it is also independent of the pulse duration and depends only on its amplitude [14]. Of course, possible non-stationary movements of dislocations from unstable positions down the relief remain outside the scope of quasi-statics. But such movements usually make a small contribution to the mean path *l*.

In the quasi-static approximation, with amplitude $\tau_m < \tau_p$, there will be no upward movements at all. In the interval $\tau_p < \tau_m < 2\tau_p$ there will be a monotonic increase in the range to a position in the relief corresponding to the driving force $\tau_i < 2\tau_p - \tau_p = \tau_p$. When the pulse is turned off, the dislocation will stop, since the driving force $\tau_i < \tau_p$ is not large enough to move it down. With a further increase in amplitude $\tau_m > 2\tau_p$, turning off the pulse will capture the dislocation at the point, where the driving force $\tau_i > \tau_p$, so it will move back down to the position where $\tau_i = \tau_p$, which corresponds to the position it occupied at $\tau_m = 2\tau_p$. Such return movements correspond to saturation on the experimental plot $l(\tau_m)$, that is to the horizontal plateau. A similar characteristic plateau is observed in plot *l* for the NaCl(Ca+Pb⁽²⁾) crystal at $\tau_m \approx 0.1$ MPa, which corresponds to $\tau_p \approx 0.05$ MPa. Unfortunately, for another NaCl(Ca+Pb⁽¹⁾) crystal in Fig. 3 we do not have enough experimental points to localize the beginning of the step. But such data are available for a crystal pair NaCl(Ca) and NaCl(Ca+Ni) [15].

The corresponding mean path plots $l(\tau_m)$ for these crystals are shown in Fig. 4, where characteristic plateaus are also observed. For the crystals with the addition of Ni, the plateau stress is twice higher than that for the NaCl(Ca) crystal, wherefrom one finds

$$\tau_p^{\text{Ca}} = 0.05 \text{ MPa}, \quad \tau_p^{\text{Ni}} = 0.1 \text{ MPa}. \quad (2)$$

Thus, these data indicate that, despite the relatively small amount of Ni, this impurity appears to significantly anchor dislocations. It follows that after introducing fresh

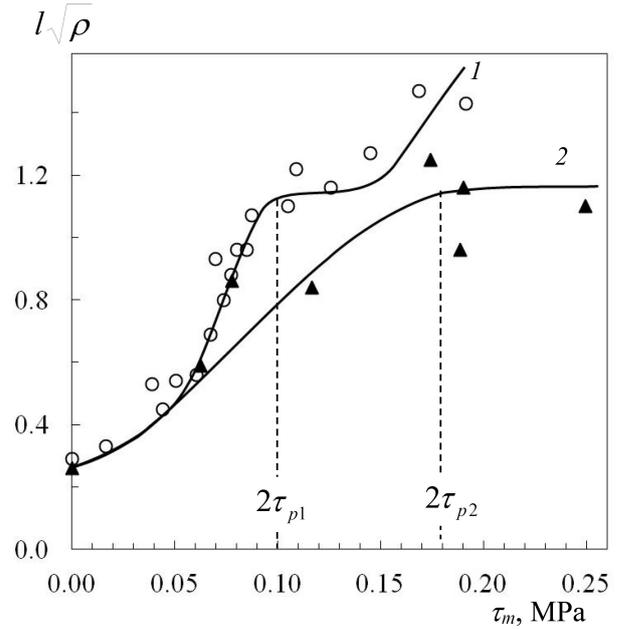


Fig. 4. Dependences of the normalized mean dislocation path $l\sqrt{\rho}$ on the amplitude τ_m of a triangular mechanical loading pulse (in terms of the resolved shear stresses) for the NaCl(Ca) (1) and NaCl(Ca+Ni) (2) crystals. The durations of the leading and trailing pulse edges are 0.1 s and 1.0 s, respectively.

dislocations into these crystals, their starting positions x_0 turn out to be considerably different: in samples with nickel, dislocations stop at positions with higher internal stresses. And therefore, after the magnetic transformation of the corresponding pinning centers in these crystals, a deeper relaxation of internal stresses should follow, that is the mean dislocation path should be noticeably greater as compared with crystals doped by Ca.

It is worth to note that these considerations do not lead to any conclusions concerning the relationship between the magnetoactivities of Ni and Ca impurity centers, which are characterized by the times t_{dp} of dislocation depinning from them. These characteristics can be determined from other experiments. To solve this problem, it is necessary to measure the mean paths *l* in samples rotating in a magnetic field, depending on the rotation frequency ν . At low frequencies, the spins of radical electron pairs, precessing around the direction of the magnetic field, must have time to complete their evolution and change their spin state, for example, from singlet ($S=0$) to triplet ($S=1$) similarly to the model of Buchachenko [16]. So, in this case, the dislocation paths should not differ from the paths in static experiments. But at a certain threshold frequency ν_c , orientation chaos must occur: the spin evolution will no longer follow the rapidly changing direction of the field. So the dependence $l(\nu)$ should have the form of a diffuse step, which should sharply decrease above a certain critical frequency ν_c . In this case, the depinning time t_{dp} is estimated as

$$t_{dp} \approx k / \nu_c, \quad (3)$$

where $k \sim 10^{-2} - 10^{-3}$ is a parameter that varies slightly from crystal to crystal.

The described expectations are fully justified in the experiment [17]. Fig. 5a shows such steps for the crystals of our interest. The critical frequency for NaCl(Ca+Ni) is approximately 7 times higher than that for crystals without nickel. Accordingly, from Eq. (3) one finds

$$t_{dp}^{Ca} / t_{dp}^{Ni} \approx 7. \quad (4)$$

After this assessment, it can be argued that the nickel impurity not only firmly pins a dislocation in the absence of a magnetic field, but also quickly releases it as a magnetic field is switched on. The combination of these two properties of the Ni impurity could well compensate the low concentration of this impurity compared to the Ca impurity.

Here, one should mention that analogous experiments showed that critical frequencies ν_c depend only on the impurity type, but not on its concentration C (Fig. 5b) [18]. However, the step height depends quite definitely on the concentration ($l \propto 1/\sqrt{C}$) which is in accordance with other independent experiments [2,6].

4. CONCLUDING REMARKS

In conclusion, we should note that there is another important difference between these pinning centers, which acts in the same direction and does not require experimental verification. It is well known that both impurities enter the NaCl ionic crystal in the form of divalent ions Ca^{2+} and Ni^{2+} . The first of them is not magnetically active, since spins of its electrons are paired. Its obvious role in magnetoplasticity of NaCl(Ca) crystals (see Fig. 2 and Fig. 5) has a simple interpretation [2,6]: when the Ca^{2+} pinning centers enter the dislocation core, some of them can capture electrons, becoming paramagnetic Ca^+ ions. Such electron with the electron from neighboring Cl^- ion form a radical pair which changes its spin state under the magnetic field with subsequent transformation of the pinning center structure. This is a supposed type of elementary act of magnetoplasticity [16, 19].

As concerns the Ni^{2+} ions, they all are paramagnetic in our NaCl crystals and even give the EPR signal. This occurs due to two unpaired electrons in the $3d$ -shell. The Ni centers also remain paramagnetic in some crystal forming complexes. For example, it is known that the paramagnetic high-spin configuration occurs in such Cl containing complex as tetrachloronickelate $[NiCl_4]^{2-}$. In our context it is important that, in contrast to Ca centers a considerable part of which even on dislocations remains diamagnetic [19], all pinning centers of Ni are

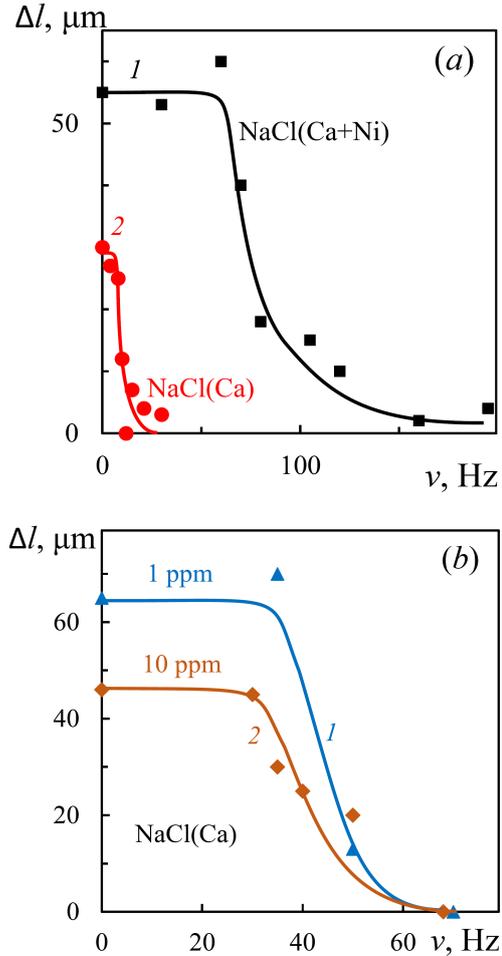


Fig. 5. Dependences of the mean dislocation path l in NaCl crystals with different type and concentration of impurities on the rotation frequency ν of the samples in a magnetic field: (a) 0.3 T, 5 min, 1 – NaCl(Ca+Ni), 2 – NaCl(Ca); (b) 0.5 T, 5 min, NaCl(Ca) with calcium impurity concentration of 1 – 1 ppm and 2 – 10 ppm.

ready to react under the magnetic field. Thus, the difference in the concentrations of the impurities in question ceases to be so significant.

As has been shown, using a suitable set of macroscopic experiments, one can get deep insight into physical mechanisms controlling magnetoplasticity, thus overcoming even such a giant difference in length scales: from an atomic-scale phenomenon and to its macroscopic manifestations. But this requires healthy scepticism, courage in hypotheses and mandatory experimental testing.

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Кинематика дислокаций в кристаллах NaCl с различными примесями

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Аннотация. Кинематика магнитопластического эффекта экспериментально и теоретически исследована на примере кристаллов NaCl. Рассмотрены особенности движения дислокаций в магнитном поле с дополнительной механической нагрузкой или без нее в кристаллах, легированных примесями разного типа. Обнаружено, что даже небольшое добавление примесей Ni в кристалл NaCl(Ca) приводит к парадоксально сильному увеличению подвижности дислокаций. С другой стороны, кристалл NaCl(Ca+Pb) вместо пластификации под действием магнитного поля демонстрирует довольно сильное упрочнение. Механизмы явления атомного масштаба подробно обсуждаются на основе результатов макроскопических экспериментов.

Ключевые слова: дислокации; точечные дефекты; пластичность; магнитопластичность