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Mechanochemical reactions between structural defects in magnetic fields

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An influence of steady, pulse and microwave magnetic fields on mechanochemical reactions between structural defects in doped ionic crystals has been studied. The effects of dislocation depinning, dislocation mobility increase, macroplastic unhardening and magnetoresonant softening in magnetic fields have been revealed. It is shown that the magnetosensitive spin-dependent reactions between structural defects is the reason of magnetoplastic effects in nonmagnetic crystals. It means that the electron and nuclear spin states of the paramagnetic defects play an important role in the formation of mechanical properties of crystals in magnetic fields and without them.

1. Introduction

The initial stage of any mechanochemical reactions is plastic deformation and fracture of solid reagents. It's well known that dynamics and atomic mechanisms of plastic flow are controlled by generation and interaction of various structural defects—dislocations, slip bands, twins, grain boundaries, impurity atoms, interstitials, vacancies, their complexies, etc. (Fig. 1). It is easy to show that the strain rate of dislocation plastic flow $\dot{\varepsilon}$ is proportional to the rate constant K of the mechanochemical reaction of dislocations depinning from local obstacles

$$\dot{\varepsilon} = \sum_{\mathrm{N}} A\dot{S}_N = \sum_{\mathrm{N}} A\dot{n}/aC = \alpha K$$

where S_{N}—is the area swept by N-th dislocation, $n = aS_{\mathrm{N}}C$—is the number of interaction acts between dislocation and local obstacles in slip plane; a—is the lattice constant, C—is the bulk concentration of local obstacles, A and α—are geometric constants. Hence one can determine the rate constant of chemical reaction between dislocation and local obstacles by strain rate measuring.

The conventional way of strength and plasticity control is doping, work hardening and heat treatment. But strength of solids is a result of electromagnetic interaction of electrons and ions. Therefore there is another way—influence of electromagnetic, photonic and radiation fields on mechanical properties of solids. These means may be considered as a direct way of material strength changing in contrast to indirect traditional processing. These new kinds of material treatment have been studied intensively for more than 30 years, but their mechanisms are not clear enough.

2. Magnetoplastic effects

The influence of a magnetic field (MF) on plastic properties of solids is commonly called magnetoplastic effects (MPE). In the last decade MPE have been observed in very different nonmagnetic materials (ionic, covalent and molecular crystals, polymers, metals and alloys) [1–3]. The MPE were revealed in a wide range of strain and have been studied by various techniques—internal friction, individual dislocations mobility, macroplastic deformation diagram, micro- and nanohardness measurement. Steady, pulse, alternative and microwave magnetic fields of induction B from several mT up to 30 T were used. The strong *in situ* effect of steady MF (B $\sim$ 1 T) on yield stress [4] and work hardening rate [5] of ionic single crystals were observed (Fig. 2). Fig. 3 gives some examples of MF *post factum* effects. Microhardness of different materials decreased and resulted from the influence of MF pulse ($B \sim 30$ T, duration $t_{\mathrm{B}} \sim 0.1$ ms), but then it increased slowly to the original value during the period up to tens of hours [6–8].

3. Interpretation of magnetoplastic effects

Now there is no doubt that a weak MF (about 1 T or less) can change greatly mechanical characteristics of nonmagnetic solids under some conditions. The most important of them is: a material must contain paramagnetic structural defects, which must be far away from thermodynamic equilibrium. The question is—what is the physical nature of numerous magnetoplastic effects which were found in the last several years? The main difficulty of MPE interpretation is a very small energy which MF delivers to any paramagnetic object in magnetodisordered matter. For example, Zeeman energy $U_{\mathrm{m}} \sim \mu_{\mathrm{B}}B$ of electron or any other particle with magnetic moment of about Bohr magneton μ_{B} is only of $\sim$0.01 of mean thermal fluctuation energy

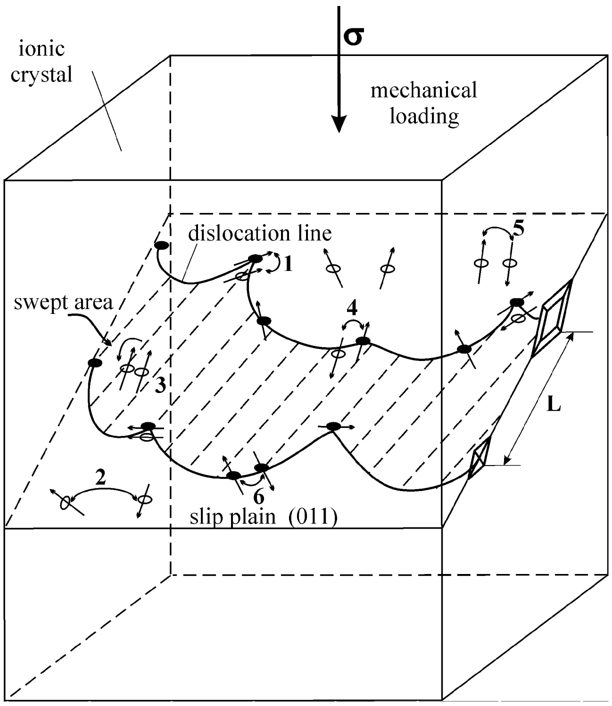


Figure 1 A plastic deformation as solid-state chemical reactions between structural defects: 1, 2 and 3—monomolecular reactions of dislocation depinning from an obstacle, decay of point defects complex and its reorientation accordingly; 4, 5 and 6—bimolecular reactions of capturing of a dislocation by an obstacle, formations of a point defects complex and recombinations of paramagnetic centres in dislocation core accordingly.

$U_T = kT$ at room temperature and thousands times less than local barriers height for dislocations.

Previous to MPE numerous magnetic effects in chemistry were explained in the framework of a well developed theory of spin-dependent processes in non-equilibrium systems [9–11]. In particular MF can change a spin state of radical pairs. This leads to the increase of rate constants of some radical reactions and decreases of others ones. It is well known that paramagnetic defects are generated by plastic flow even in nominally diamagnetic crystals [12, 13]. The most important feature of exchange interaction is the binding energy dependence on spin multiplicity of radical pair (Fig. 4a). A strong bond is formed only in the singlet (S) state when spins of two electrons are antiparallel. As a rule the binding energy is absent (or negative) in triplet (T) state.

One may suppose that covalent bonds between paramagnetic structural defects are arising and broking during plastic deformation. Then, following the theory of spin-dependent reactions MPE is a consequence of MF influence on these processes. Singlet-triplet transitions induced by a MF (e.g. by means Δg—mechanism, as it shown in Fig. 4b) may facilitate dislocation depinning and increase plasticity, as a result. Similar processes can take place in impurity complexes. A dissociation of these complexes enhanced by MF may be another reason of MPE.

If it is true, dislocations with paramagnetic centers in core can overcome paramagnetic obstacles in MF by athermal way without waiting appropriate thermal fluctuation (Fig. 5). Singlet-triplet spin conversion into radical pairs makes it possible. Really, MPE depend on temperature very weakly (if it does at all) in most materials studied [3].

There is a lot of other indirect evidence of this viewpoint. But the direct proof of spin-dependent mechanism of MPE has been absent until recently. The main difficulty in the direct investigation of the role of spin-dependent reactions in plasticity is the low concentration of unpaired spins in dislocation core and in a bulk of diamagnetic crystals. In other words, the number of radicals in these crystals is too small to be registered by a conventional electron spin resonance (ESR) technique. Similar problems have been solved in radical reaction chemistry by the RYDMR technique (Reaction Yield Detected Magnetic Resonance) [10, 11]. The combine effect of the static and microwave magnetic fields on plasticity was theoretically considered in [14] for the first time.

4. Spin-dependent nature of magnetoplastic effects

An experimental examination of this conception was realized by an original technique like RYDMR. The plasticity of ionic crystals under the action of steady and microwave magnetic fields was studied by three

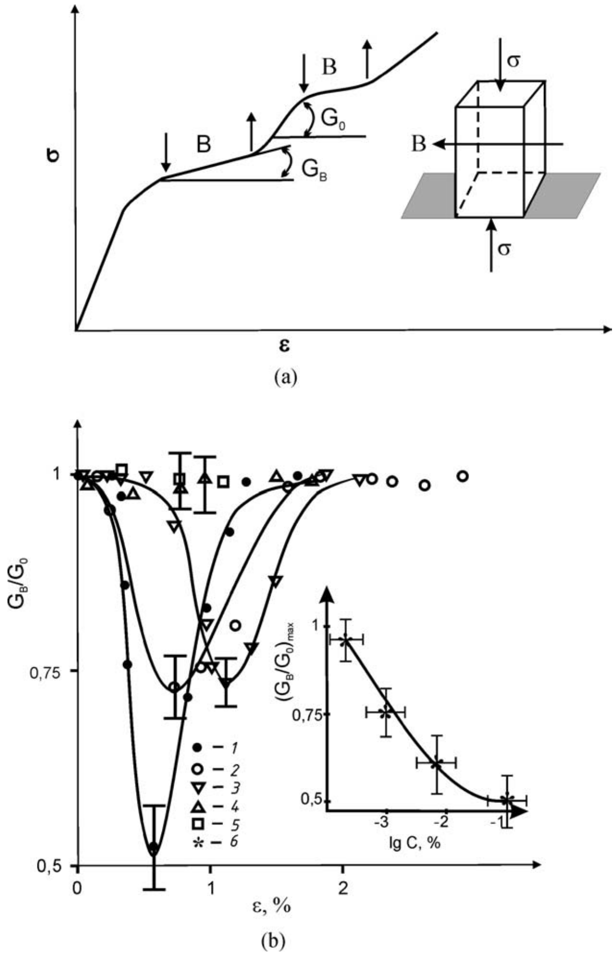


Figure 2 Change of work hardening rate at a macrodeforming of ionic crystals in constant MF ($B = 0.7$ T) in function of the achieved strain ε. $T = 293$ K. 1: NaCl:Ca (0.1 %); 2: KCl:Ca (0.03 %); 3: LiF:Mg (0.03 %); 4: KCl:Pb (0.03 %); 5: KCl:Mn (0.03 %); 6: NaCl:Ca (concentration dependence).

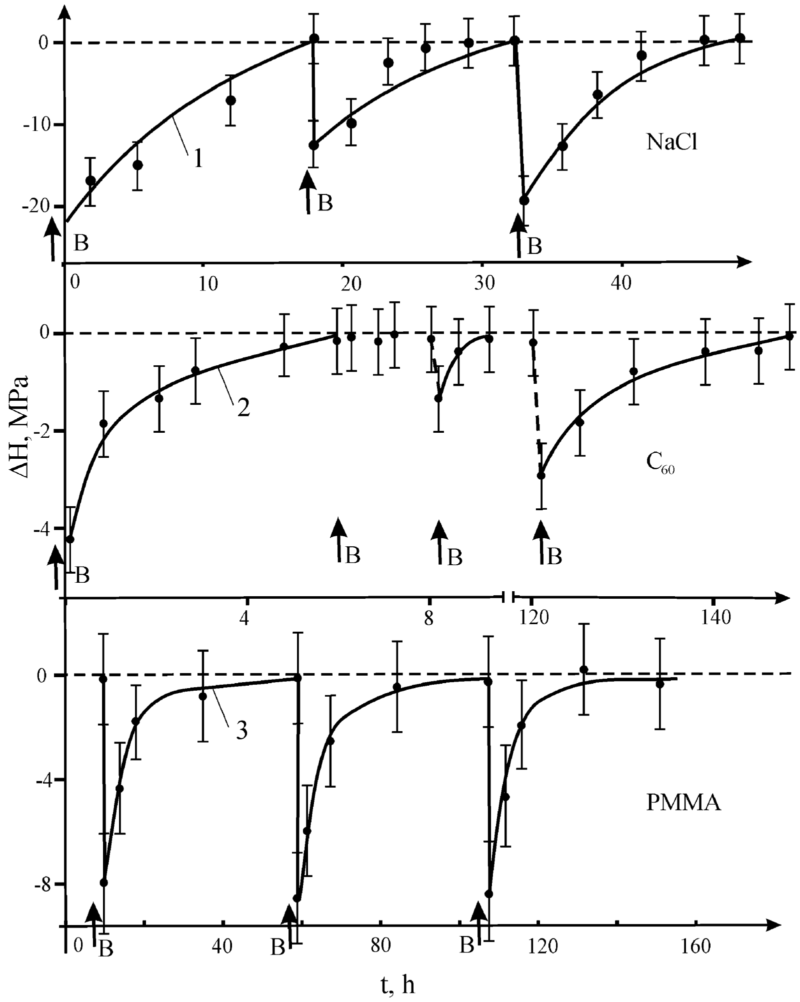


Figure 3 Dependence of microhardness H change on time t after treatment by pulse MF ($B = 24$ T, pulse duration $t_B = 10^{-4}$ s) in monocrystals NaCl (1); C_{60} (2) and PMMA (3). Values H before exposure in MF are shown by a dot line, and the moments of switch MF—by arrows. $T = 293$ K.

well known techniques: (i) a dislocations displacement measuring by double chemical etching; (ii) strain-stress diagrams recording for samples located in crossed static and microwave magnetic field; and (iii) the microhardness measuring of samples after their exposure in the magnetic fields [15–17]. NaCl single crystals doped with Ca (1000 ppm) or Eu (100 ppm) were studied in the experiments. They were annealed at 800–900 K

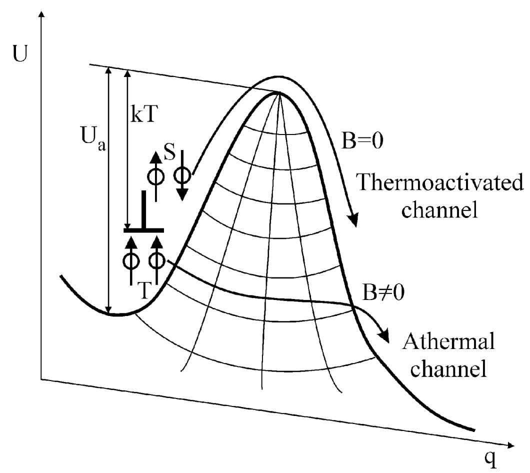


Figure 4 The change of way of overcoming obstacle by dislocation due to singed-triplet transition in magnetic field.

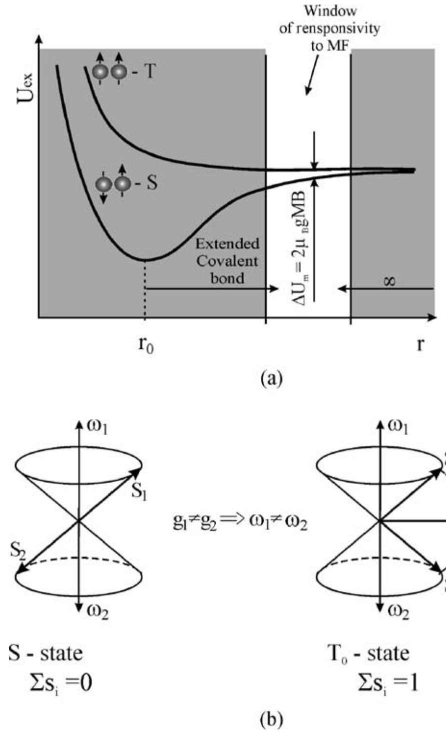
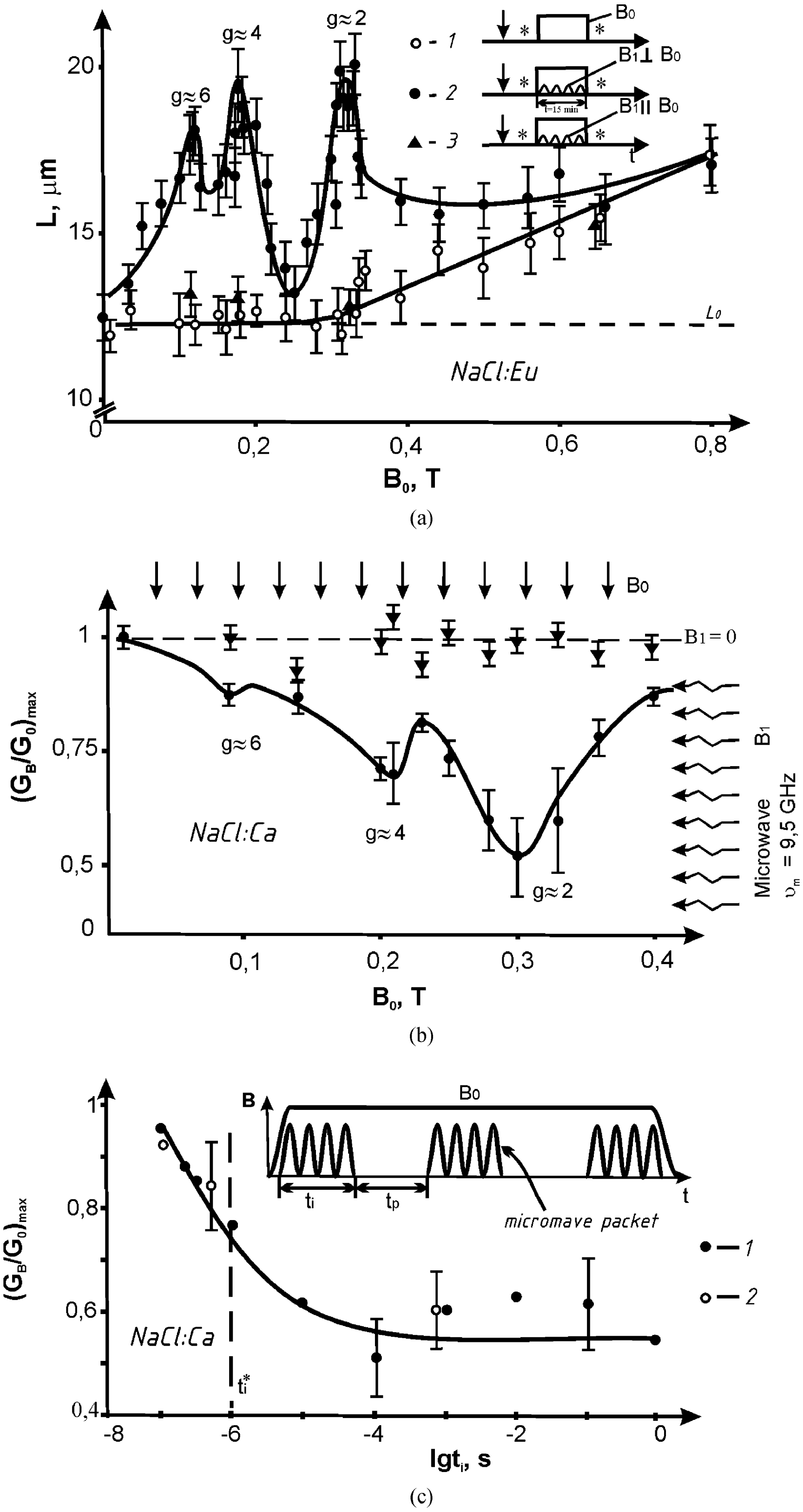


Figure 5 Spin conversion of radial pair in an exterior magnetic field: (a) change of multiplicity in excited short-lived radical pair; (b) the Δg-mechanism of spin conversion in a radical pair. ω_1 and ω_2—are frequencies of the Larmor precession of paramagnetic centres with g-factors g_1 and g_2 accordingly.



(a)

(b)

(c)

Figure 6 Magnetoresonant softening of NaCl single crystal: (a) a resonant increase of dislocations mobility in NaCl with impurity Eu (100 ppm) after treatment of a sample in crossed constant and microwave MF; (b) a resonant macro softening in monocrystal NaCl with impurity Ca (100 ppm) at the uniaxial deformation in crossed steady and microwave MF. G_B—work hardening rate at a combined effect of microwave and constant MF; G_0—the same at switched—off microwave MF. The sequences of procedures in different experimental series are shown in inserts; and (c) dependence of work hardening rate on microwave packet duration t_i.

and then cooled to 293 K in a copper block immediately before testing. Samples were placed at a crest of standing wave in the resonator H_{102} connected with the microwave generator of power ~0.1 W and permanent frequency $\nu = 9.5$ GHz. The resonator was inserted between the poles of an electromagnet, which produced static magnetic field of induction B_0 up to 0.8 T. This equipment (except the microwave power detector, which was not used in our experiments) is the basis of a standard ESR spectrometer.

In the first series of experiments the combined effect of the static and microwave magnetic fields on the mobility of individual edge dislocations was investigated. The NaCl:Eu crystals after injecting fresh dislocations

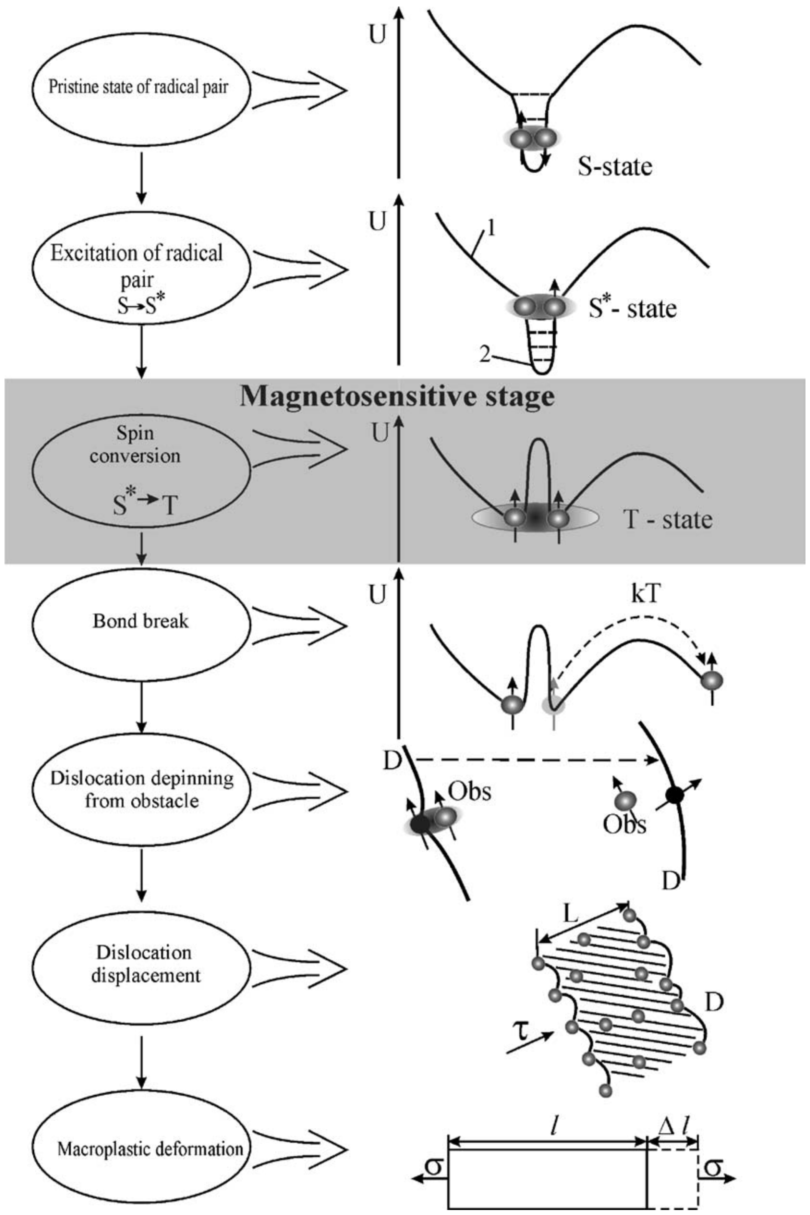


Figure 7 Possible mechanism of MPE due to dislocations depinning enhanced by MF. *D*: dislocation, *L*: displacement, *Obs*: a local obstacle, τ and σ: stresses applied, *l* and Δl: length of a sample and its change during deformation accordingly, 1 and 2—an elastic and exchange part of interaction energy of defects accordingly.

and first chemical etching were positioned in the resonator where they were subjected to crossed magnetic fields action for 15 min. Then, new positions of dislocations were revealed by the second etching to determine mean dislocations displacement L. The double etching procedure itself (in the absence of magnetic fields) led to dislocations displacement $L_0 = 12 \pm 1\ \mu$m. The simultaneous exposure of crystals in the static and microwave magnetic fields (in the configuration $\mathbf{B_1} \perp \mathbf{B_0}$, where $\mathbf{B_1}$ is the induction of a microwave magnetic field) results in L increase at $B_0 = B_{1\mathrm{RES}} = 0.32 \pm 0.03$ T, at $B_0 = B_{2\mathrm{RES}} = 0.18 \pm 0.02$ T, and at $B_0 = B_{3\mathrm{RES}} = 0.12 \pm 0.02$ T (Fig. 6a). Near the peaks the measurements were performed with special care (up to 500 individual measurements of dislocation displacements at each figure point). The peaks were not detectable when $\mathbf{B_1} \parallel \mathbf{B_0}$. $B_{1\mathrm{RES}}$ coincides the value calculated from equation $B_0 = h\nu/\mu_\mathrm{B} g$ at $g = 2$ and the frequency $\nu = 9.5$ GHz used in our experiments (g—is the effective factor of spectroscopic splitting). Thus, at certain B_0 values the resonant transitions between spin sublevels of electrons were excited and one of the new routes of the reaction was initiated.

The second series of experiments was carried out to investigate a combined effect of static and microwave fields of frequency $\nu = 9.5$ GHz, applied in a $\mathbf{B_1} \perp \mathbf{B_0}$ configuration, on the macroplastic flow rate in NaCl:Ca crystals. Each sample was deformed to the strain $\varepsilon = 0.5\%$ for 10–15 min in a static continuously applied magnetic field. The microwave field was switched on several times for 20–30 s, i.e. much less than the total loading period. After reaching the yield stress (when multiplication of dislocations takes place) adding the microwave magnetic field to the static field led to a rise in the strain rate $d\varepsilon/dt$ and decrease of work hardening rate $G = d\sigma/d\varepsilon$ (Fig. 6b), which are characteristics of dislocation mobility or the rate of the reaction between dislocations and local obstacles. The increase in strain rate under crossed magnetic fields reached its maximum at the same values of B_0 as in the previous experimental series.

Thus, weakening of crystals under conditions of electron paramagnetic resonance is found, and it is shown experimentally that spin-dependent magnetosensitive reactions in a subsystem of paramagnetic structural defects of ionic crystals make a noticeable contribution to their plastic properties. The kinetics of these reactions can be controlled by a weak static magnetic field and by its proper combination with the microwave magnetic field. The super short stages of evolution of assemblages of structural defects, which play an important role in controlling the mechanical characteristics of materials, are found by modulation of microwave MF (Fig. 6c). The possible mechanism of macroscopic MPE is presented in Fig. 7.

5. Summary

The results obtained can form a basis for both a new highly sensitive technique for the investigation and strong change of paramagnetic structural defects and mechanical properties of nonmagnetic crystals in magnetic fields. The magnetic technique described could be extended over a wide range of materials in which plastic deformation is accompanied by spin-dependent reactions between the defects.

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