

# Spin micromechanics in the physics of plasticity

R B Morgunov

DOI: 10.1070/PU2004v047n02ABEH001683

## Contents

<b>1. Introduction</b>	<b>125</b>
<b>2. Plastic properties of solids in a magnetic field</b>	<b>126</b>
2.1 Conditions for observation of magnetoplastic processes; 2.2 Criteria of spin dependence of magnetosensitive processes; 2.3 Thermodynamic and kinetic aspects of magnetoplasticity	
<b>3. Magnetoplastic effects in microwave fields</b>	<b>136</b>
3.1 Plasticity of crystals as an indicator of EPR of structural defects; 3.2 Effect of optical, X-ray, and gamma-ray radiation on spin-dependent processes in plastic deformation; 3.3 Physical ideas about the effect of defect spins on crystal plasticity	
<b>4. Magnetic field effect in the optical and electrical properties of crystals with defects</b>	<b>141</b>
4.1 Detecting EPR in nonequilibrium defects by changes in the optical and electrical properties of crystals; 4.2 Changes in the optical and electrical properties of real crystals in permanent and pulsed magnetic fields; 4.3 Using rf and optical spectroscopy in MPE studies	
<b>5. Final remarks</b>	<b>143</b>
<b>References</b>	<b>145</b>

**Abstract.** The effect of the spin states of structural defects on the mechanical properties of a crystal is the subject of spin micromechanics, a discipline that emerged at the junction of solid state physics, spin chemistry, and plasticity physics. The main reason for considering the electron spin when discussing elementary processes in plastically deformed crystals is the solid experimental evidence of recent years that the multiplicity of excited short-lived defect pairs affects the way in which dislocations (plastic deformation carriers) move in various non-magnetically ordered crystals. Because the contribution of defect spin states to mechanical properties can basically be found from magnetic field effects on plasticity, the systematization and analysis of recent experimental data on such effects are given the main attention in this review. In interpreting these effects, analogies between the elementary events of a dislocation overcoming an obstacle and the earlier studied spin-dependent processes (charge transfer, light emission, intermolecular chemical bond formation) are employed.

“It always seems to me remarkable that our first understanding of the ductility of metals in terms of atomic movements came after the discovery of the neutron.”

*Sir Nevill Francis Mott, Nobel Lecture, 8 December 1977 [1]*

## 1. Introduction

The development of the physics of plasticity and strength of solids is determined by the extent to which we understand the elementary processes of plastic deformation in terms of the fundamental principles and laws of the microworld. On the path to this goal, the initial continuous macro- and mesoscopic models of structural defects were replaced by ideas about individual atomic events that occur in the movements of dislocations (the elementary carriers of plastic deformation). Later it was found that one needs to study the electronic processes and their effect on the mechanical properties of solids. In recent years, it has been established that the problem of the effect of electron spins localized at the defects of the crystal lattice on the plastic and many other properties of crystals plays a very important role. The use of electron and nuclear spins acting as probes and labels, which provide an idea about the microscopic processes that occur in various media, was made possible thanks to the development of the physical foundations and techniques of magnetic resonance. Along with the ‘passive’ methods used in observing magnetic resonance, there is intensive development of fundamental ideas about the ways of controlling elementary physical and chemical processes in solids by reorienting the particle spins in a magnetic field. Proof of this can be seen in the rapid development of spintronics, the science of controlling electric currents in semiconductors and heterostructures by ‘switching’ the orientation of electron and nuclear spins in magnetic and electric fields [2]. An important contribution to the

R B Morgunov Institute of Solid State Physics,  
Russian Academy of Sciences,  
142432 Chernogolovka, Moscow Region, Russian Federation  
Tel. (7-095) 993 27 55  
E-mail: morgunov@issp.ac.ru

Received 26 May 2003

*Uspekhi Fizicheskikh Nauk* 174 (2) 131–153 (2004)

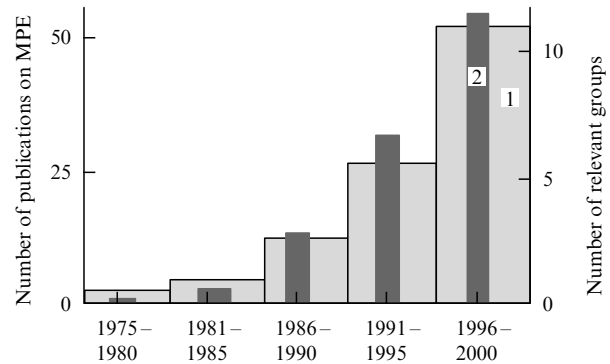
Translated by E Yankovsky; edited by A M Semikhatov

development of the foundations of spintronics has been made by the group of scientists headed by Academician B P Zakharchenya (A F Ioffe Physicotechnical Institute of the Russian Academy of Sciences) [3].

The following fact constitutes the main obstacle in building real ‘spin’ devices and in developing applications based on spin-dependent effects. In a constant magnetic field with an induction  $B_0 \sim 1$  T, the amount of energy transferred to a paramagnetic particle is very small and amounts to  $U_M \approx gS_e\mu_B B_0 \sim 10^{-4}$  eV (here,  $g \approx 2$  is the electron  $g$  factor,  $S_e$  the electron spin, and  $\mu_B$  the Bohr magneton), which is roughly a hundred times smaller than the *mean* energy of thermal fluctuations,  $kT \sim 3 \times 10^{-2}$  eV, at a temperature  $T$  close to room temperature. This implies that the expected size of the effect that the magnetic field has on a system of spins in thermodynamic *equilibrium* cannot exceed  $\sim U_M/kT \sim 0.1\%$ , i.e., is too small to conveniently use spins in applications. At the same time, numerous observations of changes in the macroscopic characteristics, including plastic characteristics, of *nonequilibrium* spin systems, changes that amount to 10–100% at room temperature, make it impossible to consider a magnetic field with an induction of the order of 1 T weak. The present review discusses the experimental data on the stages of spin-dependent interaction of defects that pass so *fast* that thermal fluctuations have no time to destroy the correlation of spins in short-lived pairs of paramagnetic particles. Such situations have been thoroughly studied in the physics of nonequilibrium spin-dependent processes that occur in the structural defects of crystals [4–10], as well as in spin chemistry<sup>1</sup> [11–22].

Although the various processes of breakage and formation of new chemical bonds during plastic deformation of solids have been known for a long time, the possibility of affecting the mechanical properties of crystals through electron spins localized on structural defects has been considered only recently. The reason is that *a priori*, the processes that occur in the system consisting of the spins of the defects were considered equilibrium, i.e., in the time that it takes an elementary plasticity process (e.g., the detachment of a dislocation from a stopper) to be completed, the electron spins are able to come into equilibrium with the crystal lattice. Therefore, it was assumed that the contribution provided by the exchange interactions is small compared to that provided by the elastic and electrostatic interactions, which determine the mobility of dislocations. In most cases within such an approach, one did not even need to know the atomic dynamics of dislocations. The discovery and study of the photoplastic effect (the effect of light on plastic deformation) [23–25], magnetoplastic effects (MPEs) in metals at low temperatures [26–30] and in superconducting junctions [31, 32], the effect of electron drag of conduction electrons exerted by dislocations [33, 34], and the electroplastic effect in metals [35] — all this formed the foundations of the physics of electron processes of plasticity and the prerequisites for the development of these ideas on the basis of electron-spin processes affecting plasticity.

Rigorous experimental proof of the effect of spin-dependent processes on the plastic deformation of ionic crystals in magnetic fields [36–41] and the increasing number of publications in this area of research (Fig. 1) have



**Figure 1.** Time distribution of the number of publications on MPE in Russian scientific journals (1), and the number of research groups studying MPE types for which  $U_M/kT \leq 1$  (2).

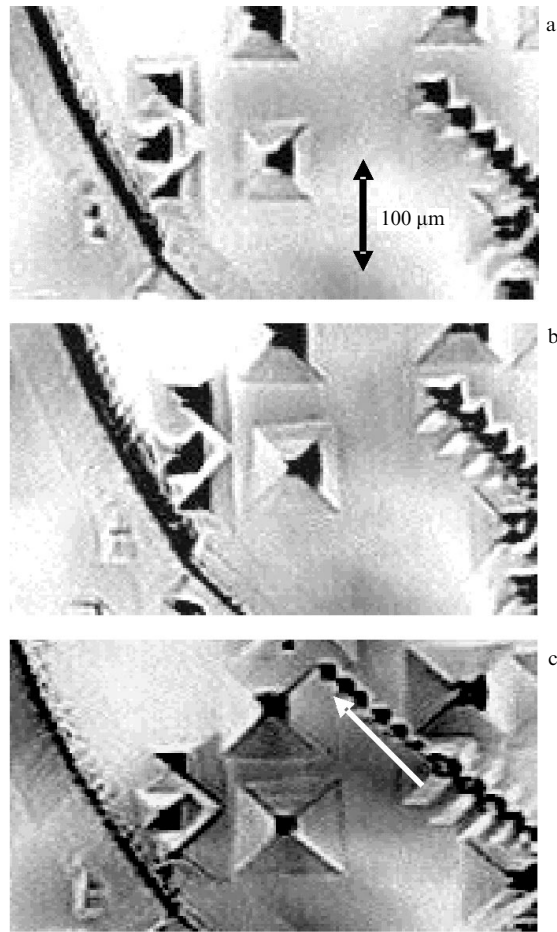
led to the formation of a new area of research in the physics of plasticity, spin micromechanics, whose goal is to extract new knowledge about microscopic spin-dependent processes that affect the mechanical properties of solids. Hence, the central part of this review is concerned with effects that induce changes in the properties of nonequilibrium defects and the plasticity characteristics of diamagnetic crystals in magnetic fields amounting to approximately 10% and greater at the temperatures and values of  $B_0$  such that the inequality  $U_M/kT \ll 1$  is satisfied for a long-lived (i.e., longer than the spin–lattice relaxation time) equilibrium paramagnetic defect in the crystal. Although the magnetic field may serve as an instrument for identifying spin-dependent processes, a detailed analysis of the results of many studies makes it possible to reveal a discrepancy between the experimental data and the main principles of the physics of spin-dependent phenomena, as well as the presence (and even predominance) of other driving forces of magnetically stimulated effects. Hence, another goal of the present review is to critically analyze the experimental data on the magnetic field effect in the plasticity and spin-dependent processes in the subsystem of structural defects.

## 2. Plastic properties of solids in a magnetic field

### 2.1 Conditions for observation of magnetoplastic processes

Many spin-dependent interactions between paramagnetic defects in ionic crystals have been discovered at temperatures close to that of liquid helium, and a detailed theory of how the magnetic field affects such processes has been developed in many cases [42–46]. At the Institute of Solid State Physics of the Russian Academy of Sciences (RAS), Korovkin [47] discovered the effect of the magnetic field with the magnetic induction  $B_0 = 3$  T on the photoplastic effect in gamma-ray irradiated NaCl crystals at  $T < 4$  K. To interpret the optically stimulated MPE, he employed the idea about the reorientation of the spins of the electrons transferred by dislocations at the instant of their interaction with paramagnetic F-centers (vacancy + electron). The mutual orientation of a transferred electron and an F-center then influences the probability of the electron attaching itself to the F-center, i.e., the process of formation of an  $F'$ -center, which is a formidable obstacle for dislocations. Because the predictions of the model are well-supported by the results of experiments, this work can be considered the first convincing proof of the fact that at

<sup>1</sup> Spin chemistry is a section of chemical physics that studies elementary spin-dependent processes of breakage and formation of interatomic bonds and the effect of such processes on chemical reactions [22].



**Figure 2.** Surface of a NaCl:Eu crystal after first etching (a), after second etching (b), and after placement in a magnetic field with  $B = 15$  T and third etching (c).

$U_M/kT \sim 1$ , spin-dependent processes may affect plasticity by transforming the structure of obstacles for dislocations (stoppers).

The first to observe an MPE in an *ionic crystal* (in 1985) in the case where  $U_M/kT \ll 1$  was the group headed by Al'shits [48] at the Institute of Crystallography of RAS. The effect amounted to a displacement of newly introduced edge dislocations in NaCl crystals placed in a permanent magnet or an electromagnet with the induction  $B_0 < 1$  T in the absence of a mechanical load. A similar effect was reproduced by a group headed by Y Tanimoto in a magnetic field with the induction 15 T in NaCl:Eu crystals (Fig. 2). The emergence of dislocations at their initial (flat pits) and final (sharp pits) positions was revealed through chemical etching (see Fig. 2). The main characteristic features of the MPEs were the quadratic dependence of the dislocation path lengths on the magnetic field [49], a weak temperature dependence [50], and a selectivity with respect to the type of impurity in the crystal [51]. We note that even earlier there were reports of changes in the dislocation path lengths [52] and in the microhardness [53] of ionic crystals placed in a magnetic field. It was assumed, however, that the MPE can be explained by the action of the vortex electric field on the charged edge dislocations. Clearly, a permanent magnetic field with  $B_0 \sim 1$  T being switched on for  $t = 0.1 - 1$  s leads to the electric field strength  $\sim B_0 d/t \sim 0.1 \text{ V m}^{-1}$  ( $d \sim 10^{-2}$  m is

the size of the sample). Because much higher electric fields (of the order  $10^6 \text{ V m}^{-1}$ ) are needed to initiate the displacement of dislocations [54], one is forced to discard the hypothesis that the vortex field affects the mobility of dislocations. Simple estimates also show that the Lorentz force acting on moving charge dislocations and the magnetostriction effects cannot influence the displacement of dislocations, since they are smaller by five to seven orders of magnitude than the values needed to unpin dislocations from stoppers. It can be assumed that the reason the dislocation moves lies in the action of external mechanical stresses, which always exist in crystals, while the role of the magnetic field is reduced to weakening the interaction of dislocations and obstacles [55]. Because only structural defects may carry a magnetic moment in ionic crystals, it was proposed in Refs [50] and [56] to explain the MPE using the idea that the magnetic field affects the course of the 'short' stages of spin-dependent reactions involving defects. Later, many other magnetoplastic effects were discovered in ionic crystals (NaCl, LiF, KCl, CsI, and KBr); effects detected by the variations in the rate of macroplastic flow [57], creep [58, 59], yield point [60, 61], microhardness [53, 62], the kinetics of the electric polarization of the deformed sample caused by displacement of charged dislocations [63, 64], and internal friction [65–68]. All these data obtained by several independent groups of researchers irrevocably pointed to an unusual (at first glance) new class of MPEs.

One of the first proofs that there is an MPE *in semiconductors* was provided in Ref. [69], where the authors attempted to use the idea of the interaction between conduction electrons and dislocations in order to interpret the increase in dislocation mobility and the decrease in the duration of stabilization of internal friction caused by a magnetic field. Lately, the number of works devoted to the effect of a magnetic field with  $B_0 \sim 1$  T on dislocation mobility in silicon single crystals has increased dramatically. It was found in Ref. [70] that the exposure of Czochralski-grown silicon crystals to a magnetic field with  $B_0 = 1$  T leads to a twofold increase in the dislocation path lengths under subsequent loading compared to the results of control experiments in which there was no magnetic field. The effect of a magnetic field on the acoustic emission of a silicon single crystal through which an electric current is sent was reported in Ref. [71], measurements of the activation parameters and the rate constants of the detachment of dislocations from local stoppers were performed in Refs [72, 73].

The necessary conditions for monitoring the type and amount of impurity in crystals and studying the motion of individual (noninteracting) dislocations were carefully prepared in Ref. [74]. The fact that a magnetic field affects the dislocation mobility in Si was corroborated in Ref. [74]. Moreover, the range of loads within which the MPE is the strongest was also established there, which contributed to creating the necessary conditions for excellent reproducibility. It was found that the main parameter of plasticity that changes in a magnetic field is the value of the starting stress. We note that the results of investigations of the effect of a magnetic field on acoustic emission obtained in Ref. [71] are in good agreement with the results in Ref. [75], where the effect of a magnetic field on the mobility of individual dislocations was discovered in Si under conditions of the electroplastic effect (i.e., conditions in which an electric current stimulating the displacement of dislocations in the sample is sent through the sample).

It was shown in Ref. [74] that an MPE is observed only in silicon crystals containing oxygen. No MPE was observed in oxygen-free samples prepared by zone melting. This suggests that MPEs may also manifest themselves in other solids where silicon–oxygen chemical bonds are present, whose breakage is a spin-dependent process, and may, at least in principle, affect the plasticity of crystals placed in a magnetic field. This standpoint is corroborated by the results in Refs [76] and [77], reporting a twofold increase of microhardness in the electric conduction of silicate glass in a magnetic field with  $B_0 = 0.5$  T and a decrease of magnetic susceptibility and intensity of the IR transmission spectra of the samples. The recognition of the fact that a magnetic field is capable of affecting not the equilibrium state of glass but the vitrification process made it possible to achieve stable reproducibility of the observed effects in Refs [76, 77] and to propose a hypothesis concerning the effect of a magnetic field on the spin-dependent processes of breakage and formation of silicon–oxygen bonds.

A displacement of dislocations in InSb crystals caused by a magnetic field with an induction up to 0.9 T in the absence of a mechanical load was discovered in Ref. [78]. In InSb placed in a magnetic field, in contrast to the data in Ref. [50] obtained for ionic crystals, the dislocation path lengths increase with temperature. The authors of Ref. [79] reported strong sensitivity of the size of the MPE in InSb to the conditions in which ingots of the same impurity composition are grown. The possibility of enhancing the MPE by increasing the temperature suggests that thermal fluctuations play an important role in the formation of magnetoplasticity of InSb, while the sensitivity to the way in which the crystals are grown and the thermal history may mean that for the MPE to manifest itself, there must be metastable defects in the crystal. These features bring the effect discovered in Refs [78, 79] closer to one of the MPE types observed in ionic crystals (see Sections 2.3.1 and 2.3.2). To explain the detected effects, the authors of Refs [78, 79] use the theory of spin-dependent processes. However, there is still no rigorous proof of the validity of this hypothesis for InSb.

Some MPEs have been discovered in *solids with a molecular type of bond*. In polymers, in addition to changes in the yield point and creep kinetics occurring after a long-lasting action of the magnetic field that causes reorientation of magnetically anisotropic macromolecules [80], MPEs have been discovered when the samples were subjected to a pulsed magnetic field with  $B = 25$  T and the pulse length 10–100  $\mu$ s, in which the role of molecular reorientation is certainly insignificant [81, 82]. It was established in Ref. [82] that the size of the MPE is determined by the rotational mobility and the electric polarization of the side sections of macromolecules. Such an MPE in a pulsed magnetic field has been observed in the fullerite  $C_{60}$ , where a certain relationship between the MPE and an orientational phase transition has been observed (see Refs [83, 84]), as well as the effect of a permanent magnetic field with an induction of the order 1 T on the diffraction spectra of neutrons (such spectra characterize the rotational mobility of molecules) [85] and on the creep rate [86]. The reversibility of the changes caused by a magnetic field suggests that the driving force of the above MPE in molecular crystals and polymers may be not the effect of the magnetic field on spin-dependent processes but the change in the correlations of rotation of large ensembles of nonuniformly charged molecules or their side groups.

MPEs in *metals* are of interest from the standpoint of applications. The effect of a magnetic field on the plasticity of

ferromagnets and the MPE in high-purity metals (mentioned in Section 1) at liquid helium temperatures is not considered here, because the magnetic field does not satisfy the condition  $U_M/kT \ll 1$  in such substances. Of significant practical interest for the type of MPEs discussed here is the electroplastic effect in metals, which at present has no thorough explanation and cannot be reduced to the heating of the samples by an electric current [35]. Today, the effect of an electric current with a density of the order  $10^2 - 10^3$  A mm<sup>-2</sup> on the plasticity of metals is widely used in metal working. The often-mentioned reasons for the loss of strength of deformed metals when an electric current is sent through them are the scattering of electrons at the crystal surface, dynamic pinch effect, nonuniform thermal expansion, and scattering of conduction electrons by impurity atoms and dislocations [35]. However, even all of these reasons taken together do not explain the sign and size of the electroplastic effect in real experiments.

The authors of Ref. [87] suggested taking into account that a local magnetic field is generated by the electric current passing through the metal; as in ionic crystals, this field is capable of changing the kinetics of spin-dependent reactions involving the defects. An indirect indication of this is provided by the athermal nature of the electroplastic effect in Zn [88] and Ti [89, 90] and by the results of experiments in which there was no electric current, while the change in plasticity of Zn and Al was discovered only in a permanent magnetic field at  $T = 300$  K [91, 92]. The quadratic dependence of the dislocation path lengths on the magnetic field induction, the linear dependence on the time of exposure of the crystals to the magnetic field [88, 89], and other indications of an MPE discovered in Zn and Al make it identical to the effect of softening of ion crystals in magnetic fields [50]. The effect of a pulsed magnetic field (with the pulse length 0.1 ms and pulse amplitude approximately 0.3 T) on the external friction of a crystalline binary alloy of oxygen and tin at room temperature was discovered in Ref. [93]. The researchers observed residual variation of plasticity after exposure of the crystals to the magnetic field and the effect of impurity dislocation atmospheres on the size and sign of the MPE. This does not allow explaining the discovered MPE by trivial factors, such as magnetostriction, Foucault currents, and thermomagnetic phenomena.

All these data lead us to the following conclusions:

(1) MPEs are reliably detected as changes in the characteristics of plasticity by roughly 10–100% caused by a magnetic field that satisfies the condition  $U_M/kT \ll 1$ . The methods used to study MPEs (about 10 standard types) cover a broad range of relative deformations ( $10^{-7} < \epsilon < 10^{-1}$ ) and are characterized by the extent to which they are close to the macroscopic processes occurring in the magnetic field;

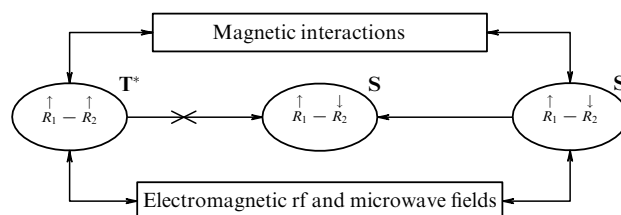
(2) MPEs have been discovered in ionic, ion–covalent, covalent, molecular, and metallic solids. In some cases, the phenomenological features of MPEs in crystals of different types coincide, which makes it possible to divide all the MPEs into several groups according to the following criteria: (a) the variation of plasticity occurs only when the crystals are deformed in a magnetic field. The presence of a field before or after the deformation process does not alter the mechanical properties of the crystals [48–51]. Usually, these effects are weakly sensitive to temperature and strongly sensitive to the type of impurity in the crystal; (b) the plasticity of the crystals may be changed if they are subjected to a magnetic field prior to deformation, i.e., residual changes induced by the magnetic

field are preserved [53, 62, 65–68, 76, 77, 83, 84]. Such MPEs usually require special ways of growing the crystals; and (c) an external exciting factor, such as light [47], electric current [71, 75], or ultrasound [93, 94], is needed in addition to the magnetic field.

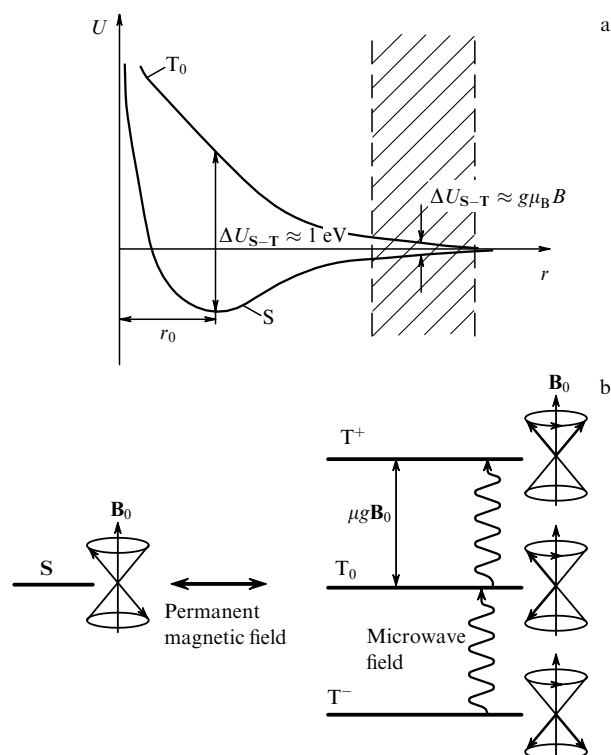
## 2.2 Criteria of spin dependence of magnetosensitive processes

Further analysis of the experimental data on MPEs requires working out criteria that would use the features established through experiments to confirm or discard the ‘spin’ origin of one or another magnetoplastic effect. For this, one can use the huge body of ideas accumulated in the physics of structural defects [4–10], the fine methods used to study spin dynamics in semiconductors and the fundamental information gathered in the studies of the optical orientation of electron spins [3, 95], and the ideas of spin chemistry [11–22]. The important role that spin chemistry plays in the problem discussed in the present review stems from the deep analogy between processes of transformation of chemical bonds and many processes in solid state physics, such as elementary acts of plastic deformation, the interaction between paramagnetic structural defects, and the recombination of electron–hole pairs initiated by photoexcitation and passage of electric current. In Russia, the section of spin chemistry that studies the effect of a magnetic field on the course of chemical reactions is represented by groups of scientists (to name a few) headed by A L Buchachenko (Institute of Chemical Physics of RAS, Moscow), Yu N Molin (Institute of Kinetics and Combustion of the Siberian Branch of RAS, Novosibirsk), R Z Sagdeev (International Tomography Center of the Siberian Branch of RAS, Novosibirsk), and E L Frankevich (Institute of Energy-related Aspects of Chemical Physics of RAS, Moscow). Groups of scientists at centers in other countries are headed by Y Tanimoto (IMS, Japan), H Paul (Physicochemical Institute, Switzerland), K MacLauchlan and P Hore (Oxford, Great Britain), J Norris and M Forbs (USA), and others. A large international conference, titled “Spin and Magnetic Field Effects in Chemistry and Related Phenomena”, is held every two years. The reports at such conferences deal with the discoveries of new effects of magnetic fields on chemical reactions and the physical properties of condensed media (see <http://www.chem.unc.edu/conferences/SCM2003/index.html>).

Researchers in spin chemistry have discovered many effects of magnetic fields with  $B_0 < 1$  T on light-stimulated reactions (and many other reactions as well) at room temperature (see the reviews and monographs [11–22]). A generalizing diagram demonstrating the possibility of magnetic fields affecting chemical reactions is given in Fig. 3, where a pair of particles of spin  $S_e = 1/2$  each (these may be structural defects, excitons, radicals, etc.) is shown in three different spin states [11]. The intermediate states of these pairs, states that emerge in chemical reactions and breakage and formation of interatomic bonds in the course of dislocation motion, aggregation of a paramagnetic impurity, generation of charge carriers by light, and many other processes, may be either triplet states ( $T_0^*$ ) with zero projection of spin on the direction of the magnetic field and with the total spin  $S_e = 1$ , or a singlet state ( $S^*$ ) with the total spin  $S_e = 0$ . (If the field is permanent and there is no hyperfine coupling, transitions involving  $T^\pm$  states are forbidden, but they can still be initiated by the magnetic field of the atomic nuclei. We see in what follows that this is an indication of the



**Figure 3.** Diagram illustrating the transformation of a pair of particles with spins initiated by a permanent magnetic field and a microwave field from an excited triplet state ( $T^*$ ) to an excited singlet state ( $S^*$ ); the transformation produces a stable reaction product in a stable singlet state  $S$  [22].



**Figure 4.** (a) Diagram representing the dependence of the exchange energy of a pair of radicals,  $U$ , on the distance  $r$  between the paramagnetic parts of a complex in the single  $S$  and triplet  $T_0$  states. The region within which a weak magnetic field is capable of mixing the excited states  $S^*$  and  $T_0^*$  is indicated by the hatched area, and  $r_0$  is the equilibrium distance between the partners in the pair [16]. (b) Mutual arrangement of spins in a pair of particles that are in states of different multiplicities ( $S$ ,  $T_0$ ,  $T^-$ ,  $T^+$ ), and the corresponding energy levels of the pair in a permanent magnetic field [16].

possibility of nuclear spins affecting plasticity.) *A magnetic field is capable of changing the spin state (initiate  $S^* \leftrightarrow T_0^*$  transitions) only in pairs for which the energy difference between the singlet and triplet states,  $U_S - U_T$ , is comparable to  $U_M$  (the hatched area in Fig. 4a). In the stable state of the pair, with  $U_S - U_T \gg U_M$ , there is no way in which a weak magnetic field can affect the pair. Because the energies  $U_S$  and  $U_T$  are functions of the distance  $r$  between the particles, paramagnetic defects must be capable of moving closer to each other or away from each other, thus changing  $U_S - U_T$  and making it comparable to  $U_M$ , at least sometimes.*

As the paramagnetic particles in a pair in the  $T_0^*$  state move closer, further formation of a stable molecule and a covalent bond between the particles is forbidden according to

the Pauli exclusion principle. A stable molecule in the singlet state  $S$  can be formed only from the  $S^*$  state of the preceding pair (see Fig. 3). But if pairs are created primarily in the  $T_0^*$  state, the orientation of one of the spins in the pair can be changed (in relation to the other spin) by applying a magnetic field. To make the effects by which a magnetic field acts on the interaction of defects and other processes large ( $\sim 10\%$ ), there *must be spin correlation in the pairs*, i.e., there must be a nonequilibrium excessive number of pairs of the same multiplicity. In other words, in accordance with the principle of detailed balance, the mean level population remains unchanged even in the presence of a magnetic field (this is true to within insignificant variations of the order  $U_M/kT \sim 0.1\%$ ). There are many mechanisms of spin reorientation in a magnetic field, and the quantum theory of these mechanisms for pair interactions of particles with spins  $S_e = 1/2$  has been developed in full [12]. We illustrate only one possibility, the  $\Delta g$  mechanism, which has to do with MPEs. The spins of the particles in a pair that is, e.g., in the  $T_0^*$  state precess in an external magnetic field about the direction of  $\mathbf{B}_0$  with a frequency  $\sim gB_0\mu/h$  (Fig. 4b). If the  $g$  factors of the particles differ by  $\Delta g$ , the spin precession frequencies also differ, and the initially triplet pair of particles periodically (with a period  $\tau_{S-T} \sim h/\Delta g B_0\mu$ ) lands in the  $S^*$  state. This opens the possibility of the formation of a stable molecule (or a pair of defects).

Spin relaxation leads to the mixing of states and destroys spin correlations. Hence, if we want the magnetic effects to be large, the pair lifetime  $\tau_{ex}$  in the intermediate state must be much shorter than the spin relaxation time  $\tau_{rel}$ . The effective temperature of such pairs is close to zero (the mean temperature of the sample may be much higher). At the same time, the magnetic field must be able to reorient the spins during the lifetime of the pair (hence, spin-dependent reactions often exhibit threshold dependences of the measured parameters on  $B_0$ ). Thus, the following *inequalities must hold*:  $\tau_{S-T} < \tau_{ex} < \tau_{rel}$ . The role of the magnetic field in spin-dependent processes is similar to that of a railway switch, which is capable, through the use of a very small amount of energy, of changing the path of a freight train weighing hundreds of tons, provided that action is applied at the right moment in time. Because the switching of the course of a reaction in a magnetic field must lead to a macroscopic effect, one more condition must be met: *there must be several alternative courses of the reaction, which branches out at the spin-dependent stage*.

Finally, the initiation by a microwave magnetic field of transitions between Zeeman-split  $T^\pm$  and  $T_0$  levels leads to a change in the intensity of  $S-T_0$  transitions [11–22]. This is possible if the frequency  $\nu$  of the microwave magnetic field satisfies the EPR condition  $g\mu_B B_0 = h\nu$ , which *guarantees that the characteristic under investigation* (e.g., plasticity) *changes in a resonant manner* (Fig. 4b). Thus, many macroscopic properties of crystals that depend on the electron spin orientation may serve as a response to the emergence of an EPR. The respective magnetoresonance phenomena and the method of indirect detection of EPR became known by its generalized abbreviation RYDMR, which stands for reaction yield detected magnetic resonance [11–22]. The main contribution to the development of this area of physics and spin dynamics was provided by the works of E L Frankevich and coworkers.

The set of the above conditions places rather rigorous restrictions on the sensitivity of the macroscopic properties of

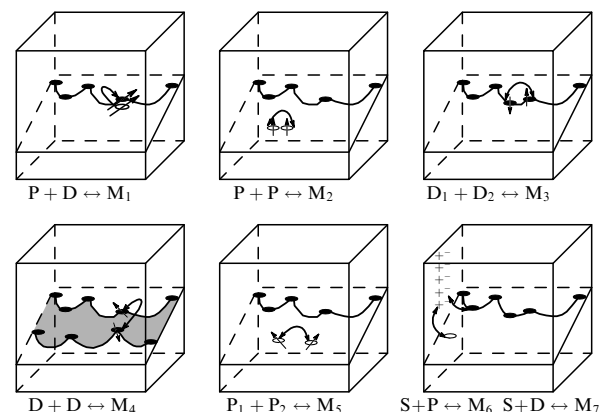
crystals to magnetic fields and dictates a certain set of experiments that allows selecting from among the many MPEs those that are caused by the effect that magnetic fields have on nonequilibrium spin-dependent processes.

### 2.3 Thermodynamic and kinetic aspects of magnetoplasticity

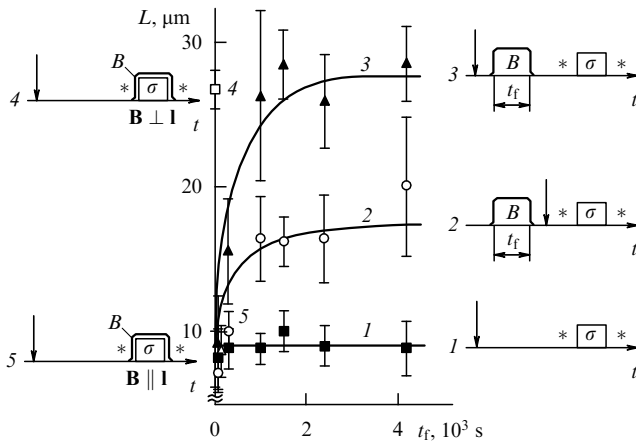
**2.3.1 Types of magnetosensitive defects in crystals.** To establish the reasons for an MPE, one must know at which defects the magnetic moment is localized and which interactions between defects are capable of participating in the formation of the plastic properties of crystals in a magnetic field. In the first MPE models for ionic crystals (before the ‘spin’ hypothesis had been verified by experiment), it was assumed that the magnetic field affects the spin-dependent process of interaction of a dislocation  $D$  and a paramagnetic point defect  $P$  at the moment that they move closer to each other under mechanical stresses (Fig. 5, the upper left figure) and changes the probability of formation of a covalent bond between them [50, 56]. According to [50, 56], the transition of  $P-D$  pairs from the  $S^*$  state to the  $T_0^*$  state, caused by the magnetic field, leads to a situation in which the ‘coupling’ behavior of the pairs is replaced by a ‘decoupling’ behavior, thus decreasing the probability of a dislocation being pinned on a stopper.

Other objects and possible spin-dependent processes in crystals (see Fig. 5) were proposed in Ref. [96] for discussion, namely, (1)  $D + P \leftrightarrow M_1$  processes involving centers localized at the core of dislocation  $D$  and centers represented by point defects  $P$  in the bulk of the crystal; (2)  $P + P \leftrightarrow M_2$  processes inside a single cluster of point defects; (3)  $D_1 + D_2 \leftrightarrow M_3$  processes involving paramagnetic centers localized at the dislocation core; (4)  $D + D \leftrightarrow M_4$  processes in pairs formed by two dislocations; (5)  $P_1 + P_2 \leftrightarrow M_5$  processes involving different point defects as they move closer to each other or, if they are far away, through distant reactions accompanied by electron tunneling; and (6) processes involving surface states  $S$  and structural defects in the bulk of the crystal,  $S + P \leftrightarrow M_6$  and  $S + D \leftrightarrow M_7$ .

A report in Ref. [97] deals with the case where the crystals are exposed to the magnetic field before fresh (meaning capable of moving) dislocations are introduced into them, i.e., such that reactions with the symbol  $D$  could be excluded



**Figure 5.** Possible pairs of structural defects whose spin state can affect the plasticity of crystals:  $P$ , point defects;  $D$ , dislocations;  $S$ , surface states; and  $M$ , quasimolecules formed by a pair of defects. A dislocation in the slip plane is depicted by a string bent between stoppers by mechanical stresses. The spins of the defects are indicated by arrows.



**Figure 6.** Dependence of the mean path  $L$  of edge dislocations caused by mechanical loading (the same in all experiments) of NaCl crystals on the time  $t_f$  of exposure to a magnetic field with  $B_0 = 1$  T: 1, no magnetic field; 2, dislocations were introduced into the crystals after exposing the crystals to the magnetic field; 3, dislocations were introduced into the crystals before exposing the crystals to the magnetic field; 4, loading the crystals and exposing them to the magnetic field were done simultaneously in the course of 6 s under conditions where the magnetic induction vector  $\mathbf{B}_0$  was perpendicular to the dislocation lines  $\mathbf{l}$ ; and 5, the same as in 4 but with  $\mathbf{B}_0 \parallel \mathbf{l}$ . The inset shows the sequence of procedures in different types of experiment:  $B$ , exposure to the field;  $\sigma$ , mechanical loading; arrows depict the introduction of dislocations; and asterisks depict etching [97].

from the above list. The researchers found that in this case, the dislocation path lengths become large compared to those obtained in control experiments in which there is no magnetic field (Fig. 6, experiments 1 and 2, respectively). The results in Ref. [97] may be considered the first proof of the fact that a magnetic field is capable of affecting not only processes of the  $D + P \leftrightarrow M_1$  type but also other processes (listed above) in which dislocations do not participate. The absence of direct participation of dislocations in a spin-dependent process does not actually mean that the course of such a process has no effect on plasticity. A dislocation may act as a microscopic probe that is sensitive to changes in the structure of clusters of point defects in a magnetic field.

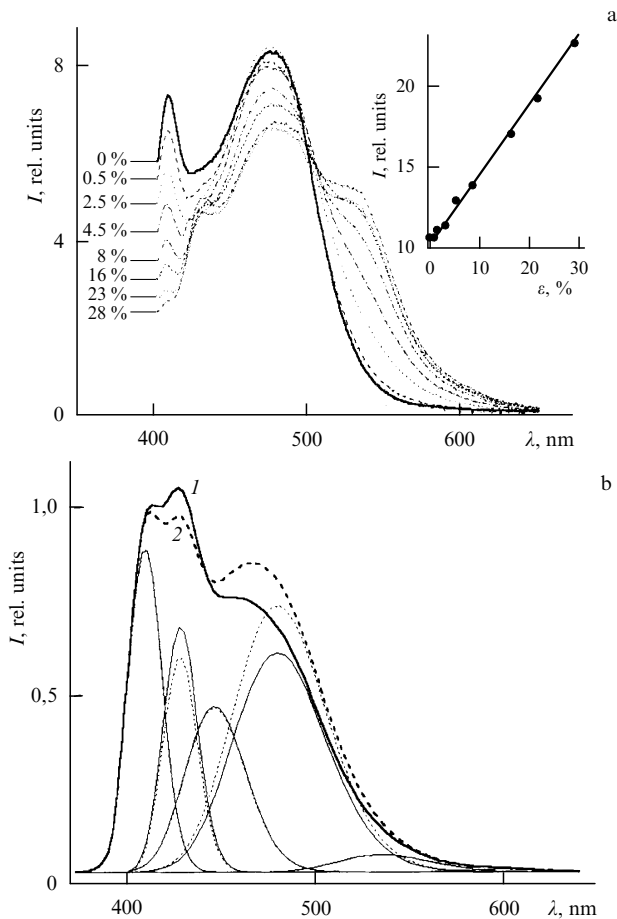
We note that in contrast to the known situations in spin chemistry, in studies of the role that defects play in plasticity, there is much less certainty in and fewer possibilities for correctly identifying paramagnetic particles. The reason is that the structure of most stable defects is unknown, to say nothing of short-lived and metastable clusters. Certain progress in identifying structures and the composition of defects that participate directly in MPEs has been achieved as a result of detecting EPR by changes in the plasticity of crystals (see Section 3.1) and in experiments in which the magnetosensitive dislocation stoppers also served as luminescence centers (see Section 4.3).

**2.3.2 Nonequilibrium nature of defects as the necessary condition for the sensitivity of plastic properties of crystals to a magnetic field.** For processes of the  $D + P \leftrightarrow M_1$  type, the existence of nonequilibrium  $D-P$  pairs can be maintained by the external mechanical stresses that move dislocations along the crystal and control the distance in a pair consisting of a dislocation and a paramagnetic point defect. But the interpretation of the effect of a magnetic field on the structure of defect clusters (i.e., processes of the  $P + P \leftrightarrow M_2$  type, which are responsible for the other part of the discovered MPEs)

first met with serious difficulties in attempts to use the ideas of spin-dependent processes. If we are dealing with point defects that reside in the crystal under conditions of thermodynamic equilibrium long before the crystal was exposed to a magnetic field, then, in view of the ideas expressed in Section 2.2, the magnetic field cannot change the subsystem of point defects to such an extent that the dislocation path lengths change by 50–100% and the enhanced mobility of dislocations remains unchanged in the crystal for several hours or even days [97]. Thus, the problem of identifying magnetosensitive centers and the thermodynamic contradictions are of the same origin. Hence, we must first establish the source of generation of metastable point defects, since only such defects can be affected by the magnetic field. In the first experiments, no great importance was attributed to this fact, with the result that there appeared, for instance, the term ‘magnetic memory’ in relation to crystals [97], which cannot actually be applied to the effect of a magnetic field on the kinetics of the process. Later, it was found that the key issue for MPEs in NaCl crystals is whether the crystals have been thermally treated before the magnetic field is switched on [98–103]. Such treatment initiates the process of aggregation of point defects and the formation of intermediate configurations of clusters sensitive to magnetic fields. Still later, it was shown that there are other ways of exciting point defects into a magnetosensitive state. In gamma-ray irradiated crystals, this is achieved by irradiating them with visible light, which stimulates the ionization of F-centers [104]. The authors of Ref. [105] excited the subsystem of point defects into a magnetosensitive state by applying an alternating electromagnetic field. In Ref. [106], it was discovered that the formation of a fresh cleavage surface in a crystal leads to the formation of an MPE in crystals that had not gone through thermal treatment. This fact agrees well with the known data on variations of microhardness after formation of a fresh cleavage surface [54].

Finally, there has recently been a report about new data on the generation of magnetosensitive defect clusters in the process of ‘cutting’ the precipitates by moving dislocations [107]. The deformation of NaCl:Eu crystals was found to lead to a redistribution of the intensities of the bands in the spectrum of photoluminescence bands of different clusters and precipitates of Eu (Fig. 7a). As a result of the interaction between dislocations and large impurity clusters, there is an increase in the intensity of the luminescence bands with the wavelength  $\lambda = 427$  nm, for which the impurity–vacancy dipole clusters containing only of a few atoms are responsible (see the inset in Fig. 7a). This section of the luminescence spectrum is sensitive to magnetic fields, which increase the rate of transformation of clusters consisting of a few atoms into flat  $\text{EuCl}_2$  precipitates ( $\lambda = 479$  nm), i.e., the magnetic field affects the kinetics of the relaxation process by opening new fast channels for this process (which are closed in the absence of a magnetic field) (Fig. 7b).

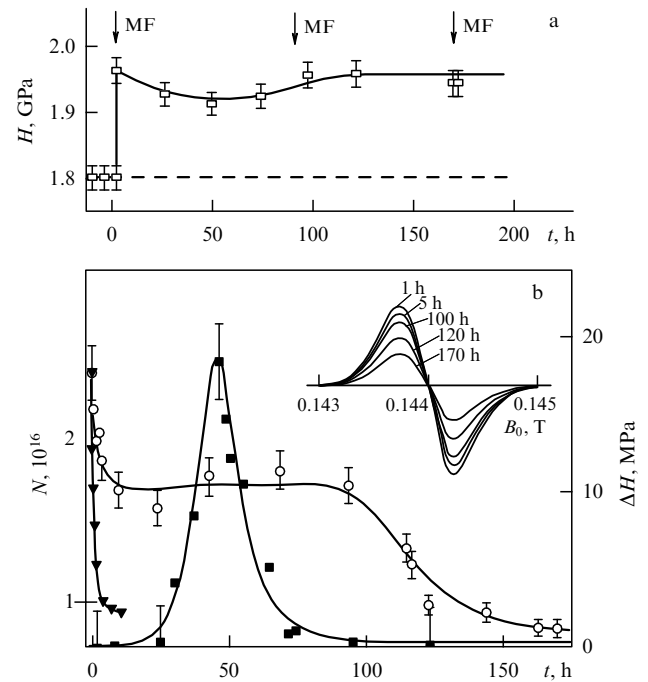
If we remain within the scope of the ideas discussed in Section 2.2, we see that in the absence of a source of energy stimulating continuous generation of nonequilibrium pairs of defects with spins, only a magnetic field of a sufficiently large amplitude and duration is capable of affecting only once the state of the nonequilibrium point defects stored in the crystal and the crystal plasticity. This conclusion has been corroborated in experiments with NaCl:Ca, NaCl:Eu, and ZnS crystals (see Refs [36, 99, 108] and Fig. 8a). Variations in microhardness observed after thermal treatment of the crystal and the emergence of an MPE at the same stage of



**Figure 7.** (a) Photoluminescence spectra of NaCl:Eu (0.1 at.%) crystals stored (for five years at room temperature) after the growth process and subjected to plastic deformation by  $\varepsilon = 0\text{--}28\%$ . The inset shows the dependence on  $\varepsilon$  of the integrated intensity  $I$  of the luminescence band of the impurity–vacancy dipole clusters consisting of only a few atoms ( $\lambda = 427$  nm). (b) Photoluminescence spectra of aged NaCl:Eu crystals subjected to deformation up to  $\varepsilon = 2\%$  prior to (1) and after (2) exposure to a magnetic field. (Decomposition in Gaussian components prior to exposure to the field is depicted by a solid curve and after exposure by a dashed curve.)

aggregation of impurity–vacancy dipoles, when such dipoles form clusters with a small number of atoms (Fig. 8b), are proof that the magnetic field acts not on the equilibrium states but on the *process* of impurity aggregation running in the crystal.

The dislocation paths in NaCl:Ca [68, 96, 97, 99, 109] and in Si [74] are gradually restored after exposure of the crystals to a magnetic field. This fact was first taken as an indication of restoration of the thermodynamic potential of the crystal to its initial state (prior to exposure to a magnetic field) and served as a reason for drawing erroneous conclusions concerning the ‘excitation’ of defects by a magnetic field [109]. Later, it was found that the state that seemed to be restored was actually insensitive to a magnetic field, i.e., the process in the crystal cannot even be interpreted as relaxation to the initial state [36]. The restoration of the practical properties after a single act of applying a magnetic field was observed in studies of internal friction in ionic crystals [64] and in metal alloys [93], as well as in studies of the mobility of individual dislocations in silicon crystals [70–74]. No verification of the extent to which the processes initiated by the magnetic field are reversible was done in these studies.



**Figure 8.** (a) Dependence of the microhardness  $H$  of ZnS crystals on current time  $t$ . The arrows indicate the beginning of the pulses (front edge) of a magnetic field with the amplitude  $B_0 = 7$  T and the length  $t_f = 10$  ms [108]. The horizontal dashed line indicates the value  $H_0$  of the microhardness of ZnS in the control samples not subjected to a magnetic field. (b) Curve  $\circ$  represents the number  $N$  of spins of free (i.e., not within complexes) impurity–vacancy dipoles and  $\blacksquare$  the size  $\Delta H$  of the effect of softening (variation in microhardness) of crystals caused by pulses of a magnetic field with the amplitude 6 T and length 10 ms, as functions of time  $t$  elapsed after thermal treatment of NaCl:Eu crystals; and  $\blacktriangledown$  the number  $N$  of spins of free impurity–vacancy dipoles in time  $t$  that has elapsed after thermal treatment of the crystals from 550 K, taken at 373 K. The inset shows the EPR signals of a separate spectral line corresponding to the electron spin transitions  $+3/2 \leftrightarrow +5/2$  and the projection  $I_z = +5/2$  of the spin of the  $^{153}\text{Eu}$  nucleus in the direction of the permanent field of the spectrometer, recorded at equal time intervals after thermal treatment of the crystal.

Thus, as in the physics of spin-dependent chemical reactions, a magnetic field in ionic crystals is the cause of irreversible changes, since it affects the relaxation of metastable defects. These facts, of course, do not prove the ‘spin’ origin of MPEs, but can serve as one of the ways of verifying this hypothesis.

Using thermodynamic ideas, we can immediately exclude some MPEs from the list of spin-dependent MPEs. For instance, according to Refs [81, 82], the effect that a magnetic field with the induction 25 T has on the microhardness of polymers is reversible and can be reproduced many times over, which hardly can be attributed to the effect that the magnetic field has on irreversible spin-dependent processes. This, apparently, is also true of the MPE discovered in fullerite subjected to a pulsed magnetic field [83]. The effect of a permanent magnetic field on the plasticity of fullerite [86] probably belongs to the same (‘non-spin’) MPE type, because the crystals subjected to a magnetic field prior to deformation were not excited by any other external factor prior to exposure to the magnetic field. Thus, despite the multitude of known magnetosensitive reactions in organic solids [11–22] and various MPEs, we still do not know whether spin-dependent processes have an effect on the mechanical properties of such solids.

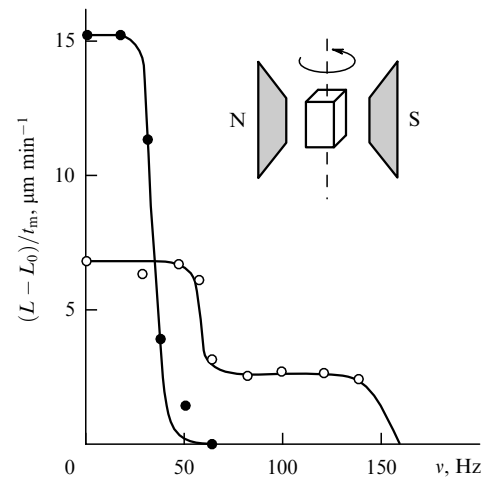


Returning to the discussion of MPEs in ionic crystals, we note that one more apparent contradiction, of thermodynamic origin, in MPEs stems from the fact that in many experiments, the time interval within which a permanent magnetic field acts on the structure of point dislocation stoppers amounts to roughly 1–2 h (see Fig. 6) or even more (see Refs [36–41, 70–74, 97–108]). This is much longer than any reasonable values of spin relaxation times at temperatures close to room temperature. Hence, it appears that in the absence of an external perturbation, no spin-correlated defect pairs sensitive to a magnetic field remain in the crystal.

The reasons for such extraordinary behavior can be understood if we turn to the results in Refs [37, 110], where an increase in the rate of the magnetically stimulated process accompanying a rise in temperature was discovered. In other words, it was found in Refs [37, 110] that in the presence of a magnetic field, thermal fluctuations increase the rate of the transient process and the effectiveness of the field. On the basis of these data, it was hypothesized in Refs [37, 111] that thermal fluctuations initiate the transitions of metastable clusters into short-lived magnetosensitive states, which are the starting point for relaxation into more favorable configurations that have a different atomic structure and are ‘transparent’ for moving dislocations, which are probes of the potential relief created by clusters. In other words, a pair of defects with spins spends most of its time in a bound state, insensitive to a magnetic field. Only for a short period is the pair excited by thermal fluctuations. Only in these rare moments (or states) may the magnetic field affect the multiplicity and atomic structure of the pair. Thus, the elementary spin-dependent state of impurity aggregation is separated by a sequence of other processes from the final response, which can be detected by changes in the plastic properties of the crystals in the magnetic field. Studies of the kinetics of magnetically stimulated variations in plasticity help, at least partially, to understand which stages of evolution of defects come before the spin-dependent stage and which come after that stage.

### 2.3.3 Kinetics of magnetically stimulated processes in crystals.

The first studies of the features of MPEs related to the effect of a magnetic field on processes of the  $D + P \leftrightarrow M_1$  type were carried out with ionic crystals rotating in a permanent magnetic field [50, 112–115]. The researchers used the fact that a magnetic field effectively acts on the mobility of dislocations when the magnetic induction vector  $\mathbf{B}_0$  is perpendicular to the line  $\mathbf{l}$  of the edge component of the dislocation and does not change the dislocation path lengths  $L$  when  $\mathbf{B}_0 \parallel \mathbf{l}$ . Hence, in a crystal rotating in a magnetic field, the conditions necessary for unpinning dislocations from stoppers emerge periodically, and the rotation period characterizes the time that the dislocations are in a favorable orientation with respect to the magnetic field. The researchers [50, 112–115] found that the dislocation path lengths in a rotating magnetic field depend on the frequency  $\nu$  of the field rotation and that there are one or several critical rotation frequencies  $\nu_{cr} \sim 1–100$  Hz above which the MPE suddenly decreases or even vanishes (Fig. 9). This can be explained only by the decrease in the time that the crystal is in the favorable orientation to a value smaller than the duration of a certain process taking place in the subsystem of the structural defects in the magnetic field,  $\tau_{dp} = 1/\nu \sim 1–100$  ms [50, 112–115]. We note that spin chemistry also exhibits a low-frequency



**Figure 9.** Dependence of the mean dislocation velocity  $(L - L_0)/t_m$  on the frequency  $\nu$  of the sample's rotation in the magnetic field for NaCl:Ca crystals (0.5 ppm) not irradiated by X-ray radiation (●) and subjected to X-ray radiation for 5 s (○) [113].  $L_0$  is the mean path that a dislocation travels under internal stresses in the absence of a magnetic field and  $t_m$  is the time the sample is kept in the rotating magnetic field.

threshold for the effect of an alternating magnetic field at the frequency 1 kHz on the polarization of nuclear spins in the decay of benzoyl peroxide [17].

Because  $\tau_{dp}$  in Refs [50, 112–115] is independent of the impurity concentration in the crystal, it characterizes the process of unpinning of a dislocation from each stopper separately, and is therefore a valuable characteristic of a single elementary act of dislocation unpinning. Usually, the spin-dependent transitions in a magnetic field are much shorter than the values of  $\tau_{dp}$  obtained in Refs [50, 112–115]. However, as shown by VI Al'shits (see Section 3.3), this contradiction can be overcome [116]. The emergence of several new values of  $\tau_{dp}$  when radiation-induced defects are injected into the crystal [112, 113], the decrease in  $\tau_{dp}$  with increasing  $B_0$  [50], and the presence of a threshold value of  $B_0$  beginning with which the magnetic field manifests itself [117] — all these factors make it possible to interpret  $\tau_{dp}$  as the time of longitudinal spin relaxation. Furthermore, according to [106], these facts are proof of the spin nature of MPEs, since they agree well with the requirement that  $\tau_{S-T} < \tau_{ex}$  (see Section 2.2).

The presence of a threshold value in the time that the magnetic field acts on the crystals has also been recorded in studying the effect of the magnetic field on dislocation stoppers, i.e., processes of the  $P + P \leftrightarrow M_2$  type [37, 118]. In NaCl:Ca crystals, this value amounts to about 1  $\mu$ s at  $T = 300$  K, which is much smaller than the S–T transition time, which amounts to approximately  $10^{-8}–10^{-9}$  s in the magnetic fields used in these processes (1–20 T). The important difference between these data and the results of measuring  $\tau_{dp}$  reported in Refs [50, 112–117] in the dislocation–stopper system is that in the magnetically stimulated transformation of the cluster structure, the critical time of action of the magnetic field is independent of  $B_0$  and decreases as the crystals are heated [37]. Because temperature usually has no effect on the duration of the S–T transition in a magnetic field, the value of  $\tau_{dp}$  given in Refs [37, 118] is not directly related to spin transitions but characterizes the thermally activated processes inside clusters. These processes serve as a necessary condition for the creation of short-lived

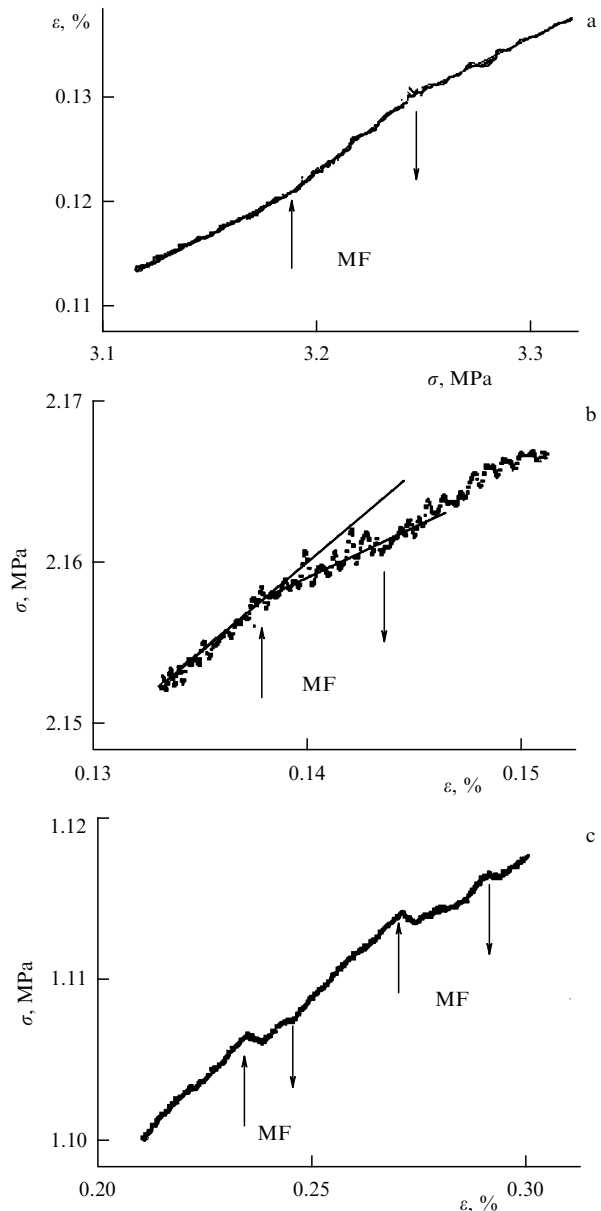
magneto-sensitive states of clusters and come before the spin-dependent stage.

The authors of Ref. [119] studied the kinetics of processes that occur in a crystal after point-defect clusters undergo transformation in a magnetic field. Dislocation mobility served as an indicator of changes in the cluster structure. It was found that a magnetic field initiates a bimolecular (recombination) process in the crystal; this process indicates that diffusing defects, which meet other recombination centers, have appeared in the crystal. The action of the magnetic field can be assumed to lead to decay of point-defect clusters, after which they participate for several days in diffusion–recombination processes. This leads us to two important conclusions: (1) the ambiguity in the direction in which the  $P + P \leftrightarrow M_2$  process runs in a magnetic field is lifted, i.e., it becomes clear that a magnetic field stimulates  $M_2 \rightarrow P + P$  processes; and (2) to explain the MPEs related to  $M_2 \rightarrow P + P$  processes, the reasons must be sought why intracluster bonds weaken in a magnetic field.

An important clue that processes of the  $M_2 \rightarrow P + P$  type participate in MPEs was provided by experiments with pulsed magnetic fields applied in the process of chemical selective etching of crystals. In contrast to conditions of continuous etching in a permanent magnetic field [50] (where the time of observing dislocation motion was equal to the time during which the magnetic field was switched on), the authors of Ref. [120] created conditions in which etching and dislocation motion continued for a much longer period than the time during which the magnetic field was applied. In NaCl:Ca crystals, the duration of velocity of the motion of dislocations initiated by the magnetic field proved to be much greater than the values of these parameters in the check samples. Thus, to explain all manifestations of magnetoplasticity in ionic crystals, it is not enough to study the processes of the  $D + P \leftrightarrow M_1$  type, which are capable of affecting the plasticity only during dislocation motion.

When a mechanical load is applied together with a magnetic field, the increase in the dislocation path length proves to be the same as when the two factors act at different times, but takes only a few seconds (see Fig. 6, experiment 4), i.e., faster than in experiments 2 and 3 by the factor  $10^3$  (see Fig. 6). This suggests that plastic deformation of crystals substantially accelerates magneto-sensitive processes in the crystals and can be explained on the basis of the data that attests to the generation of magneto-sensitive defects in the plastic deformation process [107]. The possibility of magneto-sensitive defect generation in a process in which precipitates are ‘cut’ by moving dislocations (see Fig. 7) must, apparently, be taken into account when we discuss the effect of a magnetic field on the macroscopic flow of crystals.

The effect of a magnetic field with  $B_0 < 0.75$  T on the macroplastic flow of ionic crystals at relative deformations  $\varepsilon \sim 0.1–3\%$  under conditions when the compressive stress  $\sigma$  increases linearly with time in an absolutely ‘soft’ straining machine was discovered (see Ref. [57]) by recording the changes in the slope of the curve that represented the dependence of the relative deformation  $\varepsilon$  on  $\sigma$  as the samples were exposed to a permanent magnetic field for 10–100 s (the total time of deformation was approximately  $10^3$  s). In the easy-slip stage, applying the magnetic field increased the rate of plastic flow  $d\varepsilon/dt \sim d\varepsilon/d\sigma$  twice compared to the rate before the magnetic field was switched on (Fig. 10a). In preparation of this review, special experiments were carried out to verify that subjecting ionic crystals to a magnetic field



**Figure 10.** Fragments of the following dependences: (a) the relative deformation  $\varepsilon$  as a function of the mechanical stress  $\sigma$  for NaCl:Ca crystals when the crystals are deformed in a ‘soft’ straining machine [57], (b) mechanical stress  $\sigma$  as a function of the relative deformation  $\varepsilon$  for NaCl:Eu crystals when the crystals are deformed in a ‘hard’ straining machine (Instron), and (c) mechanical stress  $\sigma$  as a function of the relative deformation  $\varepsilon$  for crystals of potassium diphthalate deformed in the Instron machine. The arrows indicate the moment when the magnetic field is switched on and off.

when they are deformed in a ‘hard’ Instron machine, where the rate of deformation  $d\varepsilon/dt$  is fixed, also leads to a decrease in the strain-hardening coefficient  $G = (d\sigma/d\varepsilon)$  of the crystals (Fig. 10b). We note that these experiments were done with crystals in which the separation of the procedures of loading and exposure to a magnetic field required an exposure of more than  $10^3$  s to the magnetic field in order to increase the dislocation path lengths twofold (see Fig. 6). The change in the slope of the deformation curve during the first second after turning on the magnetic field (see Fig. 10) makes these experiments closer to the conditions of experiment 4 in Fig. 6.

The spectrum of various dislocation obstacles in ionic crystals is extremely broad. Of course, a magnetic field can

assist dislocations in overcoming only a fraction of these obstacles. For instance, in large macroplastic deformations ( $\varepsilon > 3-5\%$ ), mutual crossing of dislocations plays a significant role in strengthening crystals. Under these conditions, the size of MPEs may decrease or disappear [57]. In ionic crystals, therefore, processes of the  $D_1 + D_2 \leftrightarrow M_3$  type are not magnetosensitive. This conclusion, arrived at in Ref. [57], has been corroborated in MPE studies involving LiF and  $\text{NaNO}_2$  crystals [58, 59].

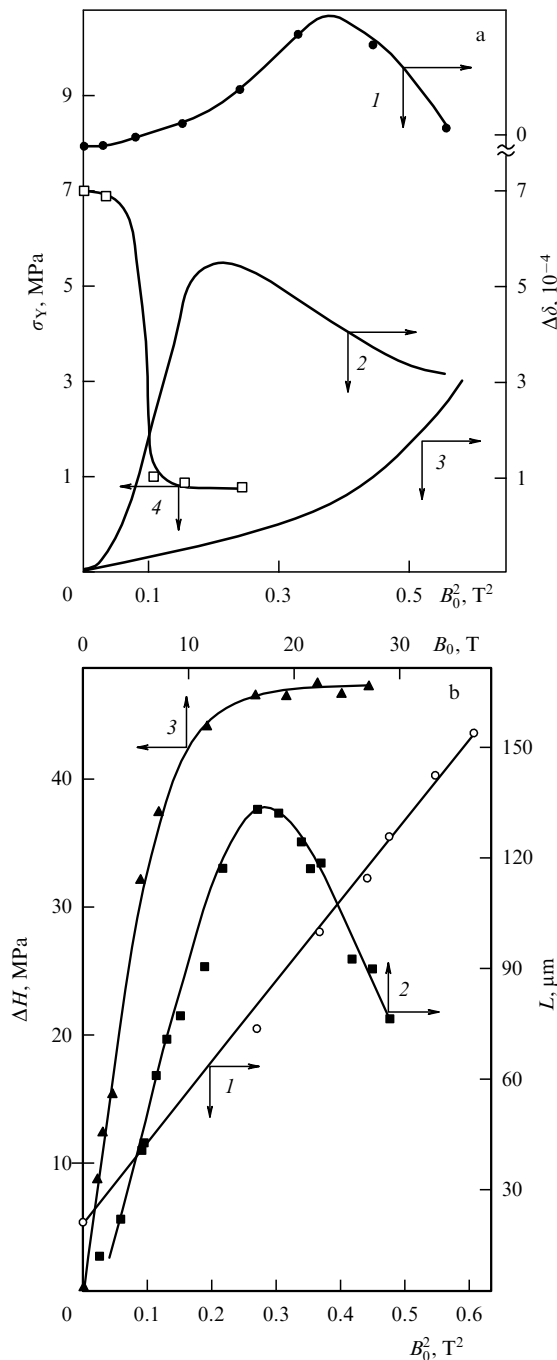
We note that the effect of a magnetic field on the rate of deformation of  $\text{NaNO}_2$  crystals subjected to multistage loading was several times stronger than in ionic crystals [59]. Because  $\text{NaNO}_2$  crystals are ferroelectric, the nature of MPEs in such crystals may differ from that in ionic crystals. In particular, the authors of Refs [121, 122] discovered that a magnetic field affects the tangent of the dielectric loss angle for ferroelectrics at  $T = 300$  K. The researchers estimated (see Ref. [121]) the Lorentz force acting on vibrating charged domain walls and found that the magnitude of this force is sufficiently large to explain the observed changes in the electrical properties of the crystals. This, of course, does not exclude the possibility of using the ideas of spin-dependent reactions, but it forces us to treat the idea that ferroelectrics are magnetoplastic with caution. The same can be said of the effect, recently discovered at the Institute of Crystallography, RAS, that a magnetic field has on the microhardness of ferroelectric crystals of potassium diphthalate [123] and the effect of a magnetic field with  $B_0 = 0.8$  T on macroplastic deformation of such crystals (Fig. 10c).

The effect of a magnetic field on the yield point  $\sigma_Y$  and the strain-hardening coefficient  $G = (d\sigma/d\varepsilon)$  of crystals has been thoroughly studied in Refs [60, 61] at different stages of deformation in a 'hard' straining machine. It has been established that in a magnetic field, the yield point  $\sigma_Y$  of samples that were subjected to thermal treatment before the magnetic field was applied decreases by a factor of three, while in crystals that had not undergone thermal treatment, this decrease amounted to only 20–25%. Similar results were reported in Ref. [98], a pulse of a magnetic field with the induction 7 T was found to affect the macroplastic flow only in quenched KCl crystals. The only difference is that the authors of Refs [60, 61] call such thermal treatment annealing, while the authors of Ref. [98] call it quenching. One criterion that determines the choice of terms here could be the comparison of the cooling rate and the rate of relaxation of high-temperature states of defects, but no data on the latter are available.

Therefore, further experiments are needed to distinguish between the ways in which a magnetic field influences  $D + P \leftrightarrow M_1$  and  $M_2 \rightarrow P + P$  processes and to establish the contribution of these processes to the kinetics of macroscopic flow of ionic crystals subjected to magnetic fields. Studies of the kinetic features of  $M_2 \rightarrow P + P$  processes have shown that thermal activation stages, which precede the spin-dependent process and prepare the emergence of an MPE, play an essential role in the MPE. After the magnetic field acts on the clusters when they are in an excited magnetosensitive state, the clusters decompose and then take a long time to recombine after the magnetic field has acted on other, unknown, defects. The procedures of plastic deformation, exposure to light and magnetic field, and cleavage of the crystals may lead to excitation of equilibrium clusters of point defects to magnetosensitive states.

**2.3.4 Dependence of crystal plasticity on magnetic field and type of impurity.** Many difficulties emerge when one attempts to determine the shape of the curves representing the dependence of the plasticity characteristics on the magnetic field induction. From spin chemistry, we know that a change in the chemical reaction yield caused by a magnetic field can be described, within any mechanism of mixing of spin states, by a polynomial containing only even powers of  $B_0$  if the number of reaction products is directly proportional to the number of elementary spin-dependent acts in the magnetic field [11–22]. This fact has stimulated attempts to theoretically describe the field dependences of the dislocation path lengths in the approximation where the dislocation path length is a linear function of the number of elementary spin-dependent acts of the dislocation unpinning from the stoppers [50, 56, 116]. The dependences of the dislocation path length  $L$  on  $B_0$  obtained through experiments in a narrow range of variations of  $B_0$  (up to 1 T) can be approximated by quadratic dependences (Fig. 11b). At first, such studies gave hope of a rapid development of theoretical ideas and of effective use of dislocation path lengths as a direct response to an elementary spin-dependent process in a magnetic field. Later, as this range has become broader, it was established that the  $L$  vs.  $B_0$  dependence is nonmonotonic [62], which discredited the 'linear' relation between  $L$  and the number of spin-dependent events (see Fig. 11b), although this nonmonotonic dependence was found in the more 'rigid'  $\text{NaCl}:\text{Ca}$  crystals. The same (linear) approximation was used to establish the theoretical dependence of the relative variation of the damping constant  $\Delta\delta(B_0)/\delta(0) = k[(1 + B_0^2/B^2)^4 - 1]$  in a magnetic field, which was expected to be true if one used the internal friction method [124] (here  $k$  and  $B$  are constant parameters independent of the magnetic field) (curve 2 in Fig. 11a). Experiments, however, did not corroborate these predictions (Fig. 11a). As reported in Refs [65–68], at  $\varepsilon \sim 1.7 \times 10^{-5}$  the  $\delta$  vs.  $B_0$  dependence is linear, while at  $\varepsilon = 1.8 \times 10^{-4}$  the dependence becomes nonmonotonic (curve 1 in Fig. 11a). The yield point, the dislocation path lengths, and the microhardness of crystals (see Fig. 11) also depend on  $B_0$  differently. These data show that the method of measuring the plastic properties affects the way in which the properties depend on the magnetic field, and the approximation of the field dependences of MPEs by different functions known from spin chemistry may not yield the necessary results. This is proof of the complex relationship that exists between the elementary process in which a magnetic field acts on structural defects and the corresponding response in plasticity.

An MPE is strongly influenced by the type of impurity in the crystals. The authors of Ref. [125] reported that they observed the softening effect of a magnetic field on ionic crystals with Ca and Ni impurities and that there were no MPEs in Pb-doped crystals. They first interpreted this fact on the basis of an analysis of the magnetic properties of the above metals in the free state, i.e., in the absence of a crystalline environment. It was assumed that the MPE was due to the paramagnetism of metallic Ca and Ni, which sets them apart from diamagnetic Pb. Later, it was discovered that the magnetic field has a strengthening effect on  $\text{NaCl}:\text{Pb}$  crystals when the magnetic field and a mechanical load are applied together [126]. Still, it is unclear how the  $\text{Ca}^{2+}$  and  $\text{Pb}^{2+}$  ions with filled electron shells and zero spins can participate in the spin-dependent interaction with paramagnetic centers at dislocations. For most of the MPEs



**Figure 11.** Different characteristics of the plasticity of NaCl:Ca crystals as functions of the magnetic induction  $B_0$ . (a) 1, 2, and 3 are changes in the damping constant,  $\Delta\delta$ , of internal friction compared to the results of experiments without a magnetic field: 1, in experiments of Ref. [68]; 2 and 3, according to the theoretical predictions made in Refs [124] and [134], respectively; and 4 is the yield point [61]. (b) 1 and 2 are lengths  $L$  of individual dislocation paths given in Refs [50] and [62], respectively, and 3 is the change in microhardness,  $\Delta H$  [62].

discovered so far, this question remains open and requires additional experimental research. It has been resolved only in situations where paramagnetic  $\text{Eu}^{2+}$  ions are intentionally injected into the crystal and the EPR spectra are detected by the changes in the crystal's plasticity [37, 38].

The following conclusions can be drawn by comparing the phenomenological features of MPEs with the modern ideas about spin-dependent processes:

(1) a magnetic field is capable, at least in principle, of affecting the kinetics of several (at least two) types of spin-dependent processes in pairs formed by (a) point-defect clusters or (b) a point defect and a dislocation;

(2) in some cases, the effect of a magnetic field amounts to changing the kinetics of relaxation of the excited subsystem of structural defects, which agrees well with the main principles according to which a magnetic field acts on spin-dependent reactions, but is not proof that the spins of short-lived defect pairs participate in MPEs;

(3) studies of the atomic structure of defects subjected to a magnetic field in crystals are made more difficult because the relationship between the measured characteristics and the elementary acts of defect interaction in a magnetic field is ambiguous. This produces barriers for direct comparison of the various plasticity characteristics as functions of, e.g., the duration and induction of the magnetic field and the predictions of spin chemistry, which can be used only if the relation between the measured quantity and the number of spin-dependent events in the magnetic field is linear. The fact that the ideas of spin chemistry are not substantial enough to be transferred to solid state physics stems from the need to allow for the anisotropy of the  $g$  factor, the dipole–dipole interactions between defects, and other factors that come to the fore in crystalline solids but are insignificant in liquid-phase systems studied in spin chemistry.

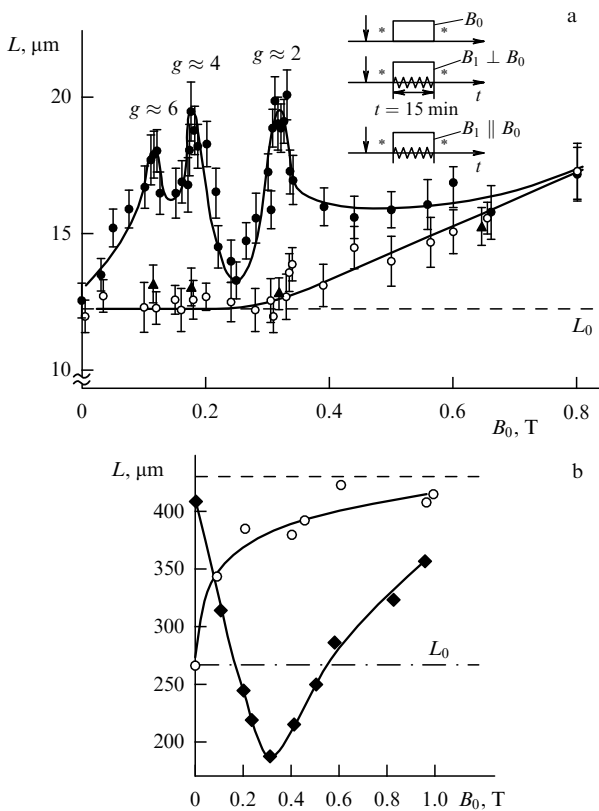
### 3. Magnetoplastic effects in microwave fields

To obtain rigorous proof of the effect of spins of defects on plasticity, we must create conditions of selective action on the spin states in particle pairs. Such a possibility is provided by a microwave magnetic field, which is capable of changing the multiplicity of short-lived pairs if it is applied at right angles to the permanent magnetic field and cannot affect the orientation of spins if it is parallel to the induction vector of the magnetic field.

#### 3.1 Plasticity of crystals as an indicator of EPR of structural defects

It was first theoretically shown in Ref. [127] that a microwave field applied together with a permanent magnetic field is capable of initiating not only  $S-T_0$  spin transitions but also  $T_0-T^\pm$  transitions and can provide an additional contribution to the dislocation path lengths. The first experimental proof of resonant changes in the plastic properties of crystals placed in mutually perpendicular permanent and microwave fields under EPR conditions was given in Ref. [36]. NaCl samples with Cu or Eu impurity aggregation initiated by pre-quenching were placed in an antinode of the magnetic-field standing wave  $H_{102}$  in a cavity matched with a  $\sim 0.3$ -W klystron (frequency  $\nu = 9.5$  GHz). The cavity was positioned between the poles of an electromagnet. After fresh edge dislocations had been injected and the first etching stage completed (this exposed the initial positions of the dislocations), the crystals were placed inside the cavity, where they were exposed to the crossed magnetic fields for 15 min. Then, in the second etching stage, the new positions of the dislocations were exposed. Thus, each point on the  $L$  vs.  $B_0$  curve was recorded at a certain value of  $B_0$  using two or three samples and measuring 500 to 1000 path lengths of individual dislocations.

The procedure of double etching in the absence of magnetic fields was found to result in displacements of



**Figure 12.** (a) Dependence of the mean length  $L$  of the edge dislocation path in NaCl:Ca ( $\sim 10^{-3}\%$ ) crystals on the induction  $B_0$  of a permanent magnetic field applied for 15 min:  $\circ$ , in the absence of a microwave field;  $\bullet$ , when a microwave field is applied together with the permanent magnetic field in the  $\mathbf{B}_1 \perp \mathbf{B}_0$  configuration, where  $\mathbf{B}_1$  is the induction of the microwave magnetic field; and  $\blacktriangle$ , when a microwave field is applied together with the permanent magnetic field in the  $\mathbf{B}_1 \parallel \mathbf{B}_0$  configuration. The length  $L_0$  of the dislocation path caused by etching in the absence of external magnetic fields is indicated by the horizontal dashed line. The inset shows a sequence of procedures in each type of experiment: an arrow indicates injection of dislocations, an asterisk indicates etching, and a rectangle indicates exposure of crystals to the permanent magnetic field. (b) Dependence of the mean length  $L$  of the edge dislocation path in silicon single crystals on the induction of a permanent magnetic field applied for 30 min:  $\circ$ , in the absence of a microwave field;  $\blacklozenge$ , when a microwave field ( $\nu = 9.5$  GHz) is applied together with the permanent magnetic field and is perpendicular to the latter. The dashed line indicates the maximum dislocation path length in crystals exposed to the permanent magnetic field, and the dotted-dashed line indicates the length  $L_0$  of the dislocation path caused by loading the crystals mechanically without exposing them to a magnetic field before loading [130].

dislocations (the same in all experiments) that were caused by internal stresses, with the average distance of such displacements being  $L_0 = 12 \pm 1 \mu\text{m}$ . The exposure of the crystals subjected to a permanent magnetic field and a microwave field (in the  $\mathbf{B}_1 \perp \mathbf{B}_0$  configuration, where  $\mathbf{B}_1$  is the induction vector of the microwave magnetic field) was found to lead to an increase in  $L$  near three distinct values of  $B_0$  (Fig. 12a). These values correspond to the values of the permanent field  $B_0 = h\nu/\mu_B g$  at which resonant transitions occur, at the frequency  $\nu = 9.5$  GHz of the microwave field used in the experiment, between the electron spin levels split by the permanent magnetic field.

Experiments in which the dislocation path lengths were studied for different orientations of  $\mathbf{B}_1$  in relation to  $\mathbf{B}_0$  are needed to verify that the reason for the appearance of peaks in the  $L$  vs.  $B_0$  dependence is EPR, rather than another type of

resonance or dielectric absorption of microwaves. It was found that when the permanent and microwave fields were applied in the  $\mathbf{B}_0 \parallel \mathbf{B}_1$  configuration, all peaks disappeared and  $L(B_0)$  became the same as in the absence of the microwave field, i.e., a common MPE with a threshold at  $B_0 > 0.35$  T was observed (see Fig. 12a). This suggests that the effect of the microwave field on plasticity cannot be explained by heating and proves that EPR in structural defects brings about a magnetic-resonance change in dislocation mobility.

The shape of the EPR spectrum detected by changes in plasticity (Fig. 12a) coincides with that of the classical EPR spectrum for  $\text{Fe}^{2+}$  ions in ionic crystals ( $S_e = 2$ ). Although the numbers of ions and clusters of iron were much smaller than the number of atoms of the main Ca impurity (by a factor of about 10), the change in the structure of Fe-containing clusters in a magnetic field had an effect on the dislocation path lengths. The reason is that Ca is in a dispersed state in the crystal, while the size of  $\text{Ca}^{2+}$  ions is approximately the same as that of  $\text{Na}^{2+}$  ions, which are replaced by  $\text{Ca}^{2+}$  ions in the crystal lattice and capture the cation vacancy to ensure electroneutrality. The impurity–vacancy dipole  $\text{Ca}^{2+}$  creates smaller distortions of the lattice and is therefore more ‘transparent’ for a moving dislocation compared to  $\text{Fe}^{2+}$  ions, which substantially differ in size from  $\text{Na}^+$ . Thus, not only the concentration of dislocation stoppers but also their ‘strength’ determine their contribution to plasticity and the MPE. Conclusive evidence that the type of paramagnetic impurity affects the EPR spectrum detected by changes in plasticity was provided by the discovery of resonant softening of NaCl:Eu crystals [37, 38]. Because europium was contained in NaCl only as  $\text{Eu}^{2+}$  ions ( $S_e = 7/2$ ), the EPR spectrum detected by changes in microhardness contained  $2S_e$  lines split by the crystalline field and coincided with the classical EPR spectrum to within hyperfine splitting ( $\sim 10$  Oe), which was indistinguishable because of the level of stability ( $\sim 100$  Oe) of the permanent magnetic field used in Refs [37, 38].

In the series of experiments discussed here, the EPR spectrum was recorded by the indirect detection method. Such an approach was used earlier for optical detection of magnetic resonance (ODMR) and in spin-chemistry experiments, where EPR is recorded through changes in the reaction yield detected magnetic resonance (RYDMR). The first applications of this approach in physics made it possible to prove without a doubt that an MPE in ionic crystals is caused by spin-dependent reactions involving structural defects. Later, the plasticity of crystals subjected to permanent and microwave magnetic fields was studied by three standard methods of recording magnetic resonance: (1) by measuring the path lengths of individual edge dislocations, (2) by measuring the microhardness  $H$  of the crystals, and (3) by measuring the rate of macroplastic flow of the crystals in a ‘soft’ straining machine. In all these cases, it was found that the EPR spectra detected by changes in plasticity were identical and that *the position and the number of the resonance bands were independent of the selected plasticity characteristic* [37]. The possibility of discovering magnetic-resonance softening was first confirmed by the group headed by V I Al’shits, who interpreted the increase in dislocation mobility in a high-frequency magnetic field as the result of excitation of EPR in the Earth’s magnetic field [128]. A special attempt was made (see Ref. [129]) to prove that EPR detected by changes in plasticity can be observed in a microwave field whose

frequency is decreased by two orders of magnitude with the induction of the permanent magnetic field decreased accordingly. Moreover, it was shown in Ref. [38] that it is impossible to explain the observed softening of crystals in EPR conditions by the local heating of paramagnetic defects.

The first indications that the combination of permanent and microwave magnetic fields has a resonant effect on dislocation path lengths in silicon was obtained at the Institute of Solid State Physics, RAS, and Ul'yanovsk State University [130] (Fig. 12b). The position of the dip in the dependence of the dislocation path length on the induction of the permanent magnetic field at the frequency of the microwave field used in the experiment was found to correspond to a magnetic moment close to the Bohr magneton. Although the power of the microwave field used in the experiments was about 15 W, the researchers observed a decrease, rather than an increase, in the dislocation path lengths, which made it possible to immediately exclude the possibility of the crystals being heated by the microwave field (Fig. 13). Studies of the dependence of the dislocation path lengths on the size of the magnetic and electric components in the microwave showed that the effect of strengthening reaches its maximum at an antinode of the magnetic field and its minimum at an antinode of the electric field. Thus, silicon exhibits magnetic-resonance strengthening, despite the effect of softening caused by the permanent magnetic field and the microwave field acting separately. The effect of the combined permanent and microwave fields on the dislocation path lengths can be observed only when the two fields are crossed. This suggests that the discovered dip in the dislocation path lengths is caused by excitation of EPR (rather than

some other type of resonance). Within the approximation of the  $\Delta g$  mechanism of mixing spin states, the results of these experiments imply that nonequilibrium magnetosensitive pairs of defects are created by thermal fluctuations in the triplet state, and not in the singlet state (as in ionic crystals).

Here is a brief list of the main results obtained through measurements of the plastic properties in EPR conditions:

(1) it has been found that in the process of impurity aggregation in NaCl:Ca, NaCl:Eu, and KBr:In crystals, short-lived intermediate pairs of defects emerge whose evolution is affected by the presence of a magnetic field. These defect pairs are created in the singlet state as a result of thermal fluctuations exciting metastable clusters of point defects. The detection of magnetic resonance by the changes in the dislocation path lengths has been successfully used in studies of the magnetoplastic effect in silicon;

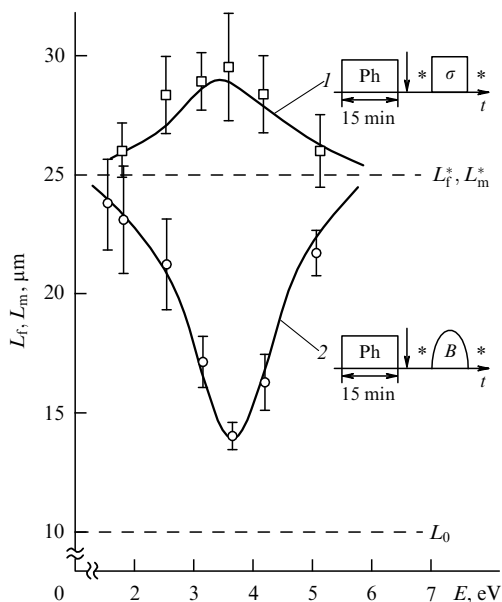
(2) EPR spectra have been recorded for clusters of point defects and for pairs formed by a dislocation and a point defect;

(3) the type of atoms that comprise magnetosensitive clusters of point defects has been determined by comparing the EPR spectra detected by plasticity changes with the standard EPR spectra of various impurity ions;

(4) estimates of the lifetime of intermediate complexes of paramagnetic defects have shown that this time amounts to approximately 10 ns [39]. Before that work, the process of plastic flow was not studied with so high a time resolution, and practically nothing was known of the existence of short intermediate defects affecting the plasticity of crystals.

### 3.2 Effect of optical, X-ray, and gamma-ray radiation on spin-dependent processes in plastic deformation

The first experimental evidence that the electronic processes contribute to the MPE in ionic crystals was obtained long before EPR detected by changes in plasticity was discovered. In Ref. [131], it was found that the MPE in ionic crystals caused by the effect that a magnetic field has on processes of the  $M_2 \rightarrow P + P$  type is sensitive to the irradiation of the crystals by UV light with a photon energy much smaller than the band gap. The irradiation of crystals before they have been exposed to the magnetic field leads to a decrease in the dislocation path lengths in the magnetic field (see Fig. 13). It is important that this light-stimulated magnetoplastic effect manifested itself in all the clusters under investigation (KCl, KBr, NaCl, and LiF) only within a certain part of the spectrum, which depended on the crystal lattice parameter in accordance with the Molvo–Ivey rule [132], i.e., as the lattice parameter becomes smaller, so does the value of the light wavelength at which the maximum of optical quenching in the MPE is observed. The fact that this rule is obeyed suggests that the structure of excited centers is the same in different crystals and that these centers belong to the intrinsic defect type, rather than to the impurity defect type. Because impurity centers play the leading role in the MPE, as shown above, the action of light amounts to initiating the transfer of electrons from the intrinsic centers to those that participate in the MPE. This viewpoint was later corroborated by the fact that a crystal that has lost the sensitivity of its plastic properties to a magnetic field can be sensitized by IR light [133] in NaCl crystals and by light that ionizes F-centers (F-light) in gamma-ray irradiated KCl crystals [104]. Thus, by controlling the distribution of electrons on the different levels in the band gap of the crystal by using light of certain wavelengths in the optical range, it is possible to decrease or



**Figure 13.** Dependence of the mean lengths  $L_m$  and  $L_f$  of the dislocation paths caused by mechanical loading  $\sigma$  ( $\square$ ) and by a magnetic field with the induction 6 T ( $\circ$ ) in NaCl crystals on the energy  $E$  of the photons to which the crystals were exposed before loading them mechanically or applying the magnetic field. The upper dashed line marks the values  $L_m^*$  and  $L_f^*$  of the lengths of the dislocation paths caused by loading or by a pulse of magnetic field in crystal that had not been exposed to light, while the lower dashed line indicates the value  $L_0$  of the background path caused by double etching [131]. The insets show a sequence of procedures in different types of experiments (Ph, photoexposure;  $B$ , exposure to a magnetic field;  $\sigma$ , mechanical loading;  $\downarrow$ , injection of dislocations; and  $*$ , etching).

increase the size of the MPE in ionic crystals. Hence, to explain the MPE, we must take the special features of the electronic structure of the centers into account. Although the described experiments do not prove the decisive role of the spins of the electrons localized at the structural defects, they are indications of the electron nature of the MPE.

Section 2.3.3 in this review described the results of experiments with a rotating magnetic field, experiments in which the MPE was found to disappear when the rotation frequency reached one of its critical values sensitive to the presence of radiation-induced defects in the crystals [112, 113]. It was noted in Ref. [112] that all the critical frequencies of rotation of crystals in a magnetic field, frequencies that had been created by X-ray irradiation of the crystals, can be removed by simply illuminating the system with light from an incandescent lamp. This phenomenon is possibly related to the ‘burning-off’ of the F-centers. The data agree well with the idea that electrons localized at structural defects participate in the MPE.

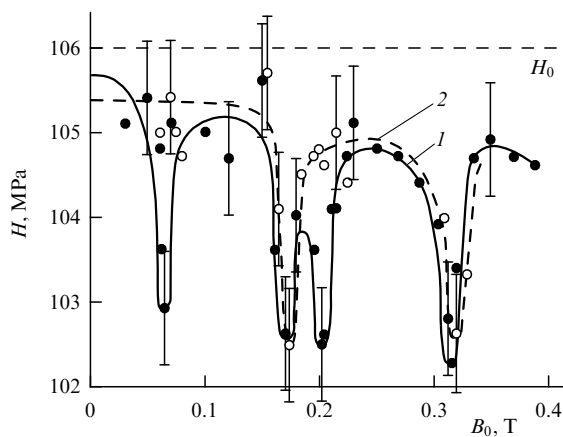
We conducted experiments in which we studied the effect of F-light on the EPR spectra detected by changes in plasticity in gamma-ray irradiated KBr crystals. In crystals that are kept in darkness, the EPR spectrum detected by changes in the microhardness  $H$  consists of four bands (Fig. 14). After the crystals are illuminated by F-light for 10 s (i.e., without ‘burning-off’ the majority of F-centers), only two bands are left in the spectrum (see Fig. 14). This suggests that there are two types of magnetosensitive clusters of point defects in the crystal, and each type contributes to the EPR spectrum. Illumination with F-light leads to a loss in sensitivity of one type of center in a magnetic field. F-centers are known to be the smallest of the known electron centers in ionic crystals. Hence, F-light may be the cause of a transition of electrons to the conduction band, followed by trapping of the electrons by magnetosensitive defects. One of the reasons for the loss of sensitivity of some of the clusters to a magnetic field may be their relaxation to a more stable state initiated by the magnetic field of an electron captured by a magnetosensitive center. In other words, the observed effect of the light-stimulated transformation of the EPR spectrum resembles the phenomenon known in spin chemistry as ‘spin catalysis’, i.e., initiation of a spin-dependent reaction not by an external

magnetic field but by the intrinsic magnetic field of the system of particles [13].

### 3.3 Physical ideas about the effect of defect spins on crystal plasticity

As noted earlier, at the beginning of the 1990s, V I Al’shits [50] and M I Molotskiĭ [56] suggested, independently from each other, to use the theory of spin-dependent chemical reactions in order to describe the interaction that exists between a dislocation and a point paramagnetic center. The theoretical models that they proposed used the  $\Delta g$  mechanism of mixing of spin states of the defects at the instant that  $U_S - U_T \sim \mu_B \Delta g S_e B_0$  as the paramagnetic center at the dislocation moves closer to the paramagnetic point defect in the bulk of the crystal [50, 56]. In the absence of a magnetic field, these defects may form a stable quasimolecule in a triplet ( $T_0$ ) or singlet ( $S$ ) state. The binding energy in such a pair is higher in the  $T_0$  state than in the  $S$  state. Hence, the control of the population of these states by a magnetic field at the stage where the dislocation and stopper move closer to each other may change the population of the levels, the probability of bond formation, and the mean ‘strength’ of the obstacles. The averaging of the probability of pair transition over the Gaussian distribution of the times that the pairs spend in the region where the spectral terms move closer to each other predicts a relative change in the dislocation velocity,  $\Delta v/v = (B/B_0)^2$  [56]. This agrees with the experimental dependence of the dislocation path lengths on the size of the magnetic field in NaCl:Ca [50] (curve 2 in Fig. 11). Since that time, this scheme has undergone modifications. The density matrix approach and the Liouville equations [134–137] replaced the steady-state wave function used in Ref. [56] to describe the time evolution of the nonequilibrium spin system. The dependence of the internal friction on the induction of the magnetic field was found for the MPE in Cu, with the results being in perfect agreement with those of the experiments described in Ref. [134] and also in qualitative agreement with those of the experiment in which the magnetic field effect on the internal friction in NaCl:Ca crystals was studied [65–68] (Fig. 11a). In Ref. [135], it was found that the hyperfine interaction can contribute substantially to the internal friction in a magnetic field. The presence of spin correlations in D–P pairs was postulated in these works without any indication of the possible reasons why such pairs emerge.

Al’shits [116] studied the spin-dependent stage in the interaction of a dislocation and a stopper by using the ‘relaxation’ mechanism for the mixing of  $S$  and  $T$  states. The advantage of this model is that it allows for the difference in the rates at which the intermediate pairs leave the  $S$  and  $T^\pm$  states. This provides an explanation of the buildup of pairs that are predominantly singlet and of the existence of spin correlations. But to explain the low values of the critical rotation frequencies of crystals in a magnetic field,  $\sim 10^2 \text{ s}^{-1}$ , at which ‘steps’ are observed in the dependence of the dislocation path lengths on the rotation frequencies (see Fig. 9), the authors of Ref. [116] proposed using the ‘slower’ relaxation mechanism of the mixing of states instead of the  $\Delta g$  mechanism. This mechanism is based on studying the longitudinal spin relaxation corresponding to  $S \leftrightarrow T^\pm$  transitions. Applying these ideas to MPEs has allowed achieving good agreement between the theoretical dependence of dislocation path lengths on the magnetic field ( $L(B_0) \sim [(B_0/B)^2 + 1]^{-1}$ ) and the results of experiments involving LiF crystals [116].



**Figure 14.** Dependence of microhardness of gamma-ray irradiated KBr crystals on the induction  $B_0$  of a static magnetic field that was used to produce paramagnetic resonance in point defect complexes in combination with a crossed microwave field with the frequency 9.5 GHz: 1, in the absence of illumination; 2, after 10 s of exposure of the crystals to F-light [104].

We believe that an inarguable advantage of the above models is the possibility to study the short plasticity stages, whose duration is smaller than the spin–lattice relaxation time, thus resolving the thermodynamic contradictions in the interpretation of MPEs. However, certain difficult points remain unresolved in the above MPE schemes:

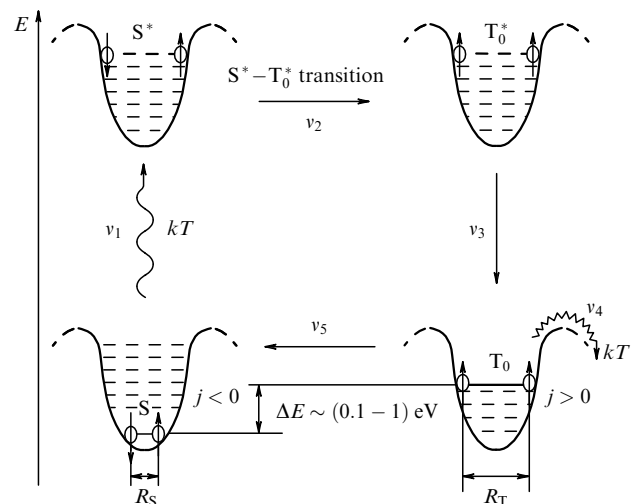
(1) The absence of an EPR signal in the standard spectrometer with a sensitivity of approximately  $10^{12}$  spins per oersted and the low magnetic susceptibility of ionic crystals, whose characteristic feature is a high dislocation density ( $\sim 10^9 \text{ cm}^{-2}$ ) suggest that the linear concentration of unpaired electron centers in the dislocation core does not exceed  $10^{-2} - 10^{-3}$  per lattice parameter in NaCl:Ca, NaCl:Ni, and NaCl:Pb. This implies that the probability of such spin carriers meeting paramagnetic defects in the bulk of the crystal is low. When this probability is multiplied by the probability of a dislocation unpinning itself from a stopper because of the magnetic field [116], we obtain an increase in the dislocation path length of about 1%, which is much smaller than the observed effect,  $\Delta L/L \sim 100\%$ . To resolve this contradiction, it was suggested in Ref. [124, 136] that the spins are transferred along the dislocation core together with kinks, topological distortions of the edge of the extra plane associated with the edge dislocation core. However, the extremely low Peierls relief in ionic crystals (lower than  $kT$  at temperatures at which most experiments were held) makes the existence of kinks improbable, to say nothing of their contribution to plasticity.

(2) The MPE mechanism has been developed only to explain the magnetic field effect on moving dislocations. At the same time, the results of the experiments in Refs [49–52] suggest that a magnetic field stimulates the unpinning from stoppers of even those dislocations that were immobile prior to the action of the magnetic field. For such dislocations, there is no stage at which they move closer to the paramagnetic stoppers, which are the only entities that can be sensitive to a magnetic field within the mechanisms proposed in Refs [50, 56, 116, 133–136]. Apparently important are here the thermal-fluctuation vibrations of the fixed segment of a dislocation, which can lead to a situation where the dislocation center at a dislocation moves towards or away from a paramagnetic point defect even when the dislocations are immobile on the whole. But under this assumption, the reason for the athermal nature of MPEs remains unclear [50].

(3) No physical reasons for the emergence of spin correlations in D–P pairs have been established.

(4) Finally, the models leave no place for a correct interpretation of the magnetically stimulated variations in plasticity in many situations where a magnetic field is applied to the crystals prior to plastic deformation. In other words, they do not allow for all possible spin-dependent processes affecting plasticity (such as paramagnetic defect aggregation, to name just one).

An attempt to solve the last problem above was made in Refs [37, 111]; a model of the magnetic field effect on the structure of nonequilibrium point-defect clusters emerging during aggregation of paramagnetic impurity–vacancy dipoles was suggested there. According to [37, 111], the sequence of events in magnetosensitive defect clusters in a magnetic field can be represented by a diagram (see Fig. 15). Thermal fluctuations excite a cluster consisting of two impurity–vacancy dipoles with spins by stretching the covalent bond, which has a length  $R_S$  in the singlet S state. In the absence of a magnetic field, the cluster returns from the



**Figure 15.** Schematic of a sequence processes running in point defect complexes in a magnetic field on the scale of the energies  $U$  of the complexes. S is a long-lived metastable singlet state of a complex,  $S^*$  is an intermediate singlet state of a complex excited by thermal fluctuations,  $T_0^*$  is an intermediate triplet state, a transition into which is allowed only in the presence of a magnetic field, and  $T_0$  is a stable triplet state of a new configuration of the complex with a lower binding energy.

excited  $S^*$  state to the initial S state because of the electric forces with which the crystal lattice acts on it. The pair of dipoles in the cluster are incapable of changing the multiplicity in the absence of an external or internal (e.g., spin–orbit) magnetic field, since such a change is forbidden by the conservation law of the total spin. In spin chemistry, this law requires that the total spin of the initial spin carriers and that of the final reaction product be the same. In the semiclassical approximation, this exclusion principle can be explained by the conservation law of the total angular momentum of the spin system.

When a magnetic field is present, the  $\Delta g$  mechanism of mixing lifts this restriction and the cluster with its new multiplicity goes over to the triplet  $T_0^*$  state. We assume that the  $S^*$  and  $T_0^*$  states are fairly short-lived, i.e., the spin correlation that is present at the first moment after the stretching of the chemical bond between the dipoles is conserved during the lifetime of these states. After the magnetically stimulated transition of the complex to the stable antibonding state  $T_0$  (characterized by a new increased distance  $R_T$  between the ions) has been completed, the binding energy of the dipoles with the complex is lower than in the S state. This is the cause of further transformation of the atomic structure of the complex into a more energetically favorable configuration. According to studies of the kinetics of processes that run in the crystals after exposure to a magnetic field (see Section 2.3.3), the most probable result of a spin-dependent process in a magnetic field is the decomposition of the cluster into parts, which then recombine with other defects. This model may be correct in relation to the experiments with silicon crystals [74], because the action of the magnetic field and the motion of dislocations in these experiments were separated in time, as in the experiments described in Refs [19, 97–108].

One of the drawbacks of this model is that it can be used to describe spin dynamics only in clusters that consist of spin-1/2 particles. But even if we consider only the EPR spectra detected by changes in the plasticity of the NaCl:Eu and



NaCl:Ca crystals [36–41], we see that the spins of the particles in the cluster are larger in real experiments. The effect of higher-spin particles in spin-dependent processes has not been studied thoroughly enough even in spin chemistry, and this hinders the analytical description of the spin dynamics [11–22].

In addition, the number of paramagnetic particles in complexes is greater than two, because the stage of nucleation of magnetosensitive effects is detected in experiments much later than dimers begin to form (Fig. 8b). The study of MPEs will therefore require studying three-particle and even more complicated processes instead of using the well-developed theory of pair spin-dependent interactions of particles. At present, no theoretical approaches to solving such problems exist.

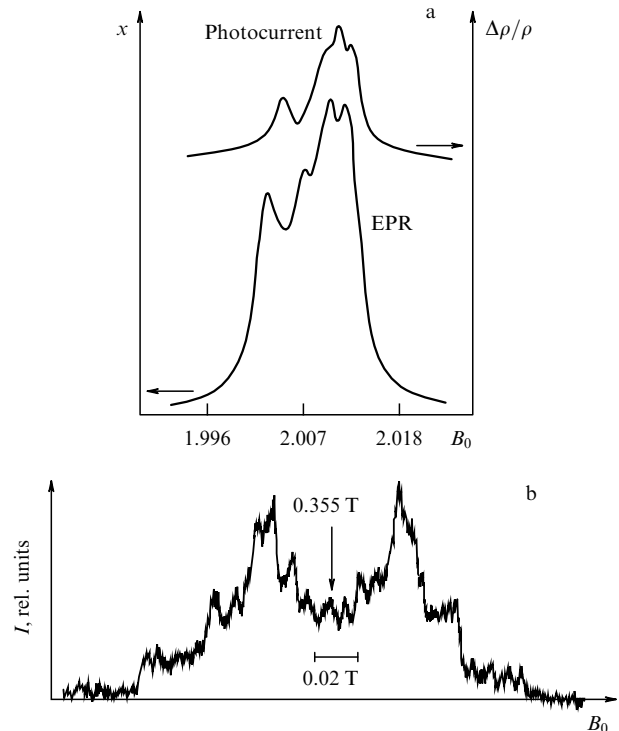
Finally, the possibility of accelerating the relaxation of point defects in a magnetic field by hundreds and even thousands of times is a nontrivial effect for the magnetic-spin phenomena in chemistry and in the physics of charge transfer. Probably, this is due to the substantial increase in the number of contacts of paramagnetic particles in the crystal lattice compared to liquid-phase systems and semiconductors containing highly mobile conduction electrons, which are usually studied.

#### 4. Magnetic field effect in the optical and electrical properties of crystals with defects

As we have seen, the characteristics of plasticity serve as a very distant and indirect response to events taking place in the subsystem of structural defects in a magnetic field. We can get closer to understanding the elementary plasticity processes if we discover what effect a magnetic field has not only on plasticity but also on other properties that would enable us to directly calculate the number of defects participating in the MPE. Such quantities usually include the number of photons emitted in luminescence and the amount of electric charge passing through the crystal (to name just two). The discovery of the magnetoelectric and magneto-optical effects that accompany an MPE would allow comparing the results with the predictions of the various models of spin-dependent processes in structural defects.

##### 4.1 Detecting EPR in nonequilibrium defects by changes in the optical and electrical properties of crystals

A decrease in the photoconductivity of silicon crystals when EPR is saturated on dislocation dangling bonds (DDB) has been discovered at 1.4 K [4] and at room temperature [5]. When the conditions of EPR for electron spins of DDB were met, the resistivity of the sample increased and the shape of the EPR spectrum detected by changes in the photocurrent coincided with that of the classical EPR signal from dislocations (Fig. 16a). Indirect detection of the EPR signal from DDB was thus implemented in Ref. [4]; this is direct experimental proof that paramagnetic centers on dislocations participate in spin-dependent processes in solids. Estimates of the relative variation of the resistivity  $\Delta\rho/\rho$  under the assumption that the polarizations of the conduction electron spins and DDB spins are in equilibrium in a magnetic field yielded values of  $\Delta\rho/\rho$  that were several times smaller than those observed in the experiment in Ref. [6]. Thus, the magnetic fields used in the experiment satisfied the condition  $U_M/kT \ll 1$ . To explain the observed value of the magnetic effect, two alternative courses of the processes were proposed



**Figure 16.** (a) EPR spectrum and the dependence of the relative variation of the specific resistance of a silicon crystal with dislocations placed in a microwave field and excited by IR light [4] on the induction  $B_0$  of a permanent magnetic field. (b) Dependence of the photocurrent in polycrystals anthracene-dimethylpyromellitimide on the induction of a permanent magnetic field combined with a microwave field at  $T = 293$  K [141].

in Refs [7, 8]: it was assumed that charge carriers from the conduction band are first captured into a shallow intermediate state, from which they can either be activated back to the conduction band or recombine. Because the rates of capture from the singlet and triplet states of a pair consisting of DDB and a conduction electron are different, pairs in a certain spin state accumulate on the intermediate level (i.e., *spin correlation* appears). The high mobility of the spin carriers along the dislocation core guarantees that *the lifetime of the intermediate states is short compared to the spin-lattice relaxation time*, i.e., the temperature of the spin subsystem is lower than the mean temperature of the crystal. Hence, the equilibrium values of spin polarizations could be used as  $P_e$  and  $P_{DDB}$ . Rigorous theoretical estimates of the magnitude of the magnetic field effect on the conductivity and an analysis of the dependence of this effect on various factors were carried out in Ref. [8], while the general theoretical approaches to studying the spin-dependent reactions involving structural defects in semiconductors were developed in Ref. [9]. Thus, the model of spin-dependent recombination of charge carriers on dislocations in silicon has all the necessary elements required by studies on spin-dependent processes in chemical reactions that are sensitive to ‘weak’ magnetic fields (see Section 2.2). The results obtained in this area of research have been generalized in Ref. [7], but because the experiments were not accompanied by studies on the effect of spin-dependent recombination of charge carriers on plasticity, this information does not make the interpretation of MPEs in silicon crystals any easier.

During the same period, the physics of spin-dependent process was developed for other solids [138–141]. The first

published works were those written by E L Frankevich and coworkers [138, 141], who reported on the effect of a magnetic field on the photo- and dark conduction of organic semiconductors at temperatures close to room temperature. First, it was found that the photocurrent increased in anthracene and tetracene crystals by 1–5% in a magnetic field with  $B_0 \sim 0.1$  T at  $T = 293$  K [138] (under conditions of thermodynamic equilibrium, the size of the effects of photocurrent changes could be expected to be  $\sim 0.01\%$ ). The effect of the spin-dependent stages in the evolution of electron–hole pairs on the photocurrent was discovered when crossed permanent magnetic and microwave fields were applied simultaneously to the crystals with EPR conditions met [141]. Indirectly detectable EPR spectra were recorded, and the signal in such registration was not the absorption of the microwave by paramagnetic particles but the change in the photocurrent or fluorescence (Fig. 16b). In contrast to experiments with spin-dependent recombination of charge carriers on dislocations in silicon, the concentration of charge carriers (and spin) in organic semiconductors was too low for registering classical EPR, because the spin-dependent process amounted to the tunneling of electrons from one defect to another. Thus, the magnetic resonance spectra detected by changes in the photocurrent presented the only possibility of identifying and separating the spin-dependent stages in the recombination of charge carriers in Ref. [141].

#### 4.2 Changes in the optical and electrical properties of real crystals in permanent and pulsed magnetic fields

In addition to the physically clear and fully substantiated phenomena described in the previous section, there are a large number of experiments that attest to the effect of permanent and pulsed magnetic fields on the electrical and other properties of crystals. At present, there is no proof that the spins of defects played a role in the experiments that are described below. The literature contains reports on the effect of magnetic fields with an induction of approximately 1 T at room temperature on the following properties of semiconductors and structures based on semiconductors: the charge stability of metal–insulator–semiconductor (MIS) structures [142], the relaxation time of transient capacitance [143], high-frequency capacitance–voltage characteristics [144], surface topography [145], the Auger electron spectra of the surface [146], IR transmission spectra [145], the crystallization of near-surface amorphous silicon layers [145], deep level transient spectroscopy (DLTS) spectra [145], and X-ray diffractometry spectra [145].

Generalizing the experiments we have mentioned, we now list the main phenomenological features of changes in the macroproperties of semiconductors in a magnetic field that are repeated in the different experiments. These effects have the following features: (1) they become much stronger when an alternating or pulsed magnetic field is used instead of a permanent one, (2) they become stronger as the temperature grows or manifest themselves only within a certain temperature range, (3) they can be observed long after the exposure of the sample to the magnetic field has ended, (4) they require long exposure times of the crystals to the magnetic field (several dozen seconds or even longer) for detection of changes in the electrical properties, (5) they are sensitive to the type of impurity in the crystal, and (6) they are characterized by a complex relationship between the changes in the near-surface and bulk properties of the materials in a magnetic field. Thus, there are a fairly large number of

features suggesting that the changes in the properties of the structural defects in a magnetic field lead not only to MPEs but also to changes in many other properties of the crystals. Understanding the nature of the MPEs requires experiments in which the magnetic field effect on plasticity is recorded with the variations of at least some of the spectroscopic characteristics of the crystals.

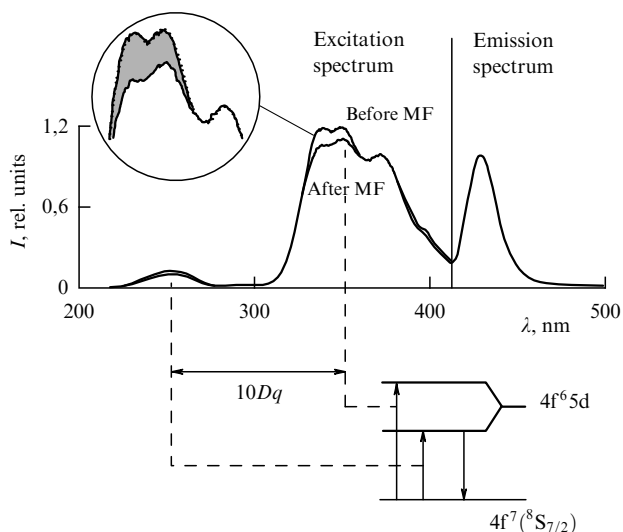
#### 4.3 Using rf and optical spectroscopy in MPE studies

The short list of works in which the simultaneous effect of a magnetic field on plasticity and on electro-optical properties of crystals is studied includes two works devoted to the magnetic field effect on the microhardness and the photo- and electroluminescence of ZnS single crystals [108, 147]. However, there are two factors that hinder further studies of MPEs in ZnS: (1) the unknown nature of the luminescent magnetosensitive centers and (2) poor reproducibility of the MPE, which can be explained by differences in the thermal preparation regime in other series of crystals. Here are the experiments where these obstacles were overcome.

We studied (see Refs [100, 102, 107]) the MPE in NaCl:Eu crystals, which we chose because europium is not only a remarkable spectroscopic tag for studying structural defects by the EPR and photoluminescence methods but also a direct participant in elementary spin-dependent processes. The EPR and photoluminescent spectra are extremely sensitive to the aggregation of impurity–vacancy dipoles into complexes. All this enabled us to identify the objects affected by a magnetic field as complexes consisting of a small number of impurity–vacancy dipoles and appearing at the intermediate stage of aggregation of dipoles into large precipitates. Furthermore, it was found that the magnetoplastic effect in such crystals appears at the stage when the decrease in the intensity of the EPR spectrum, which characterizes the number of free impurity–vacancy dipoles, temporarily stops (Fig. 8b). In other words, the MPE begins to manifest itself when some of the newly formed clusters disintegrate again into dipoles due to thermal fluctuations, because they find themselves in a metastable state. This conclusion verifies the hypothesis that a magnetic field initiates the decomposition of clusters and agrees well with the earlier results for NaCl:Ca crystals in which a bimolecular process is observed after exposure of the crystals to the magnetic field (see Section 2.3.3), as well as with the proposed model of the magnetic field effect on the state of clusters of paramagnetic ions (see Section 3.3).

Magnetosensitive clusters of europium, formed as a result of aggregation of individual dipoles, contribute to the luminescence of crystals. The luminescence spectrum of hardened NaCl:Eu crystals, in which a sufficiently large number of magnetosensitive clusters are accumulated in the process of aggregation, undergoes a transformation in which there is a decrease in the intensity of luminescence within the region of excitation by light with the wavelength 350 nm, and an increase in intensity when the exciting light has the wavelength 250 nm (Fig. 17). Because these bands of the luminescence excitation spectrum correspond to the splitting of levels by the crystalline field [148], we can assume that the observed changes in the spectra characterize the transformation of the atomic structure of complexes and the surroundings of  $\text{Eu}^{2+}$  ions.

As noted earlier, not only the process of aggregation of impurity–vacancy dipoles into clusters but also the plastic deformation of the crystals may lead to the appearance of clusters with a small number of atoms in the crystals, clusters



**Figure 17.** Photoluminescence excitation spectra and emission spectra recorded 50 h after quenching of NaCl:Eu crystals from 700 K. Also shown is the variation in the excitation spectrum of the crystal caused by a magnetic field ( $B_0 = 20$  T, pulse length 10 ms). The respective optical transitions and electron energy levels of the  $\text{Eu}^{2+}$  ion split by the crystalline field  $10Dq$  [100] are shown in the lower half of the figure.

sensitive to a magnetic field. In Ref. [107], we reported that the flat  $\text{EuCl}_2$  precipitates in the (111) and (301) planes are destroyed as a result of plastic deformation and then transform into nonequilibrium impurity–vacancy dipole complexes with a small number of atoms, and among these complexes there are clusters sensitive to a magnetic field. Such a field accelerates the process of their transformation into  $\text{EuCl}_2$  precipitates. The generation of magnetosensitive defects in NaCl:Eu by a process in which precipitates are ‘cut’ by moving dislocations occurs chiefly at the easy slip stage. At the strengthening stage ( $\epsilon > 3\text{--}5\%$ ), dislocation obstacles undergo a rapid transformation, and magnetosensitive defects stop being generated. This agrees with the earlier data, according to which the MPE in ionic and molecular crystals reaches its maximum size at the easy slip stage and disappears at the strengthening stage [57–59].

The formation of atomic ideas about the transformation of clusters initiated by hardening, plastic deformation, and applying a magnetic field became possible thanks to the use of detailed information about Eu clusters, information obtained long before the discovery of MPEs by the X-ray diffraction, EPR, and luminescence methods [148–152]. Further development of these spectroscopic methods of MPE studies will allow us, at least for one model system, to establish the entire sequence of events, initiated by a magnetic field, at the spin, electron, atomic, and macroscopic levels of investigation.

## 5. Final remarks

In Russia, there are about ten independent scientific groups whose interests are focused on the discovery and study of the effect that a magnetic field has on plasticity and other physical properties of solids. These groups are headed by V I Al’shits (Institute of Crystallography, RAS, Moscow), V V Kveder (Institute of Solid State Physics, RAS, Chernogolovka, Moscow Region), B I Smirnov (A F Ioffe Physicotechnical Institute, RAS, St. Petersburg), Yu I Golovin (G R Derzhavin Tambov State University, Tambov), B A Zon (Voronezh

State University, Voronezh), A M Orlov (Ul’yanovsk State University, Ul’yanovsk), and N A Tyapunina (M V Lomonosov Moscow State University, Moscow, and Kostroma State University, Kostroma). Abroad, the theory of the magnetoplastic effect is being actively developed by M I Molotskii and V I Fleurov (Israel). Other foreign groups include the one headed by O I Datsko (Donetsk State University, Donetsk, Ukraine). Experimental work in this area of research is done by the group headed by Y Tanimoto (Institute for Molecular Science, Japan) and the group headed by V A Makara (T G Shevchenko Kiev State University, Ukraine). What results can the research done by all these groups lead to?

## Possible applications of magnetoplastic effects

Apparently, MPEs can be used for the following practical purposes: (1) to control the plastic properties of materials in the process of molding, forging, and other technological procedures. For instance, a change in the plastic properties of polymers at least by several percentage points may lead to considerable economy of energy; (2) to initiate the relaxation of internal mechanical stresses in materials where thermally stimulated relaxation is impossible or ineffective; (3) to create new methods of studying elementary processes of plastic deformation at the electron–spin level of research; and (4) to control spin-dependent phase transitions. We now briefly discuss some of the actual results illustrating these possibilities.

The results reported in Refs [69–79], where the discovery of MPEs in silicon crystals and other semiconductors was described and the details of this effect were given, may help in solving one of the problems of electronics related to the ‘ageing’ of crystals in the course of relaxation of metastable defects and internal stresses. The displacement of dislocations in a magnetic field will make it possible, without resorting to heating, to lower the level of nonequilibrium and to diminish uncontrollable variations in the properties of the devices during their operational life.

Complex research involving many aspects of the MPE problem has been carried out. It can generally be characterized as a set of measures by which one can control dislocation mobility by applying a magnetic field in solids where defects act as triggers of a certain process. For instance, it is known that in single crystals of heavy metal azides, which serve as explosives, the chain reaction begins near dislocation cores when the crystal is subjected to electrical or mechanical stress. Hence, initiating the relaxation of clusters of such defects in a magnetic field is equivalent to controlling the probability of an explosion. The authors of Ref. [153] reported on displacements of dislocations caused by a magnetic field with the induction 0.35 T in  $\text{AgN}_3$  single crystals. It was established that the exposure of crystals to the magnetic field led to a delay in the explosion in the event that the crystal was subsequently kept in the initiating electric field.

Another example is provided by medicinal drugs, whose effectiveness often depends on the presence of defects in the polycrystals of the powder. Of course, heating such substances, which in most cases are low-melting-point organic substances, is undesirable and certainly cannot be used as a method for controlling concentrators of stresses and their relaxation. The displacement of dislocations in single-crystal paracetamol caused by a permanent magnetic field with  $B_0 < 1$  T in the absence of mechanical loading was discovered in Ref. [154]. This raises hopes for new ways of

controlling the properties of medicinal drugs. Thus, ‘magnetic’ initiating of the detachment and movement of dislocations in crystal is a new and promising method for controlling many processes that follow critical paths of development near local structural distortions.

NaCl:Eu crystals are also of practical importance. These crystals are characterized by a high quantum yield of  $\text{Eu}^{2+}$  luminescence centers, a convenient range of excitation and emission of luminescent radiation, and a fairly low cost. Lately, there have been active investigations into the possibility of using these crystals as highly effective converters of UV radiation into visible light [155], as scintillators and dosimeters for radiation monitoring [156], and, in particular, as devices for monitoring the state of the Earth’s ozone layer. The main obstacle in using these crystals in practical devices is the instability of their optical properties related to the aggregation of the Eu impurity into precipitates. Initiating artificial ‘ageing’ by applying a magnetic field and switching the relaxation channels such that complexes of a given type can form will allow using these crystals as simple and cheap detectors of the state of the ozone layer and various sensors of UV radiation.

Another important point is that the MPE and the effect of a magnetic field on the photoluminescence of NaCl:Eu crystals are detected at the early stages of impurity aggregation [101–103]. These stages have been neglected in research, although they play a very important role in understanding such processes in materials used in electronics (e.g., in silicon). Moreover, these stages are probably controlled by universal physical principles, which may become general principles for different materials. The study of spin-dependent processes in small impurity complexes in a model situation will allow extracting information about small nuclei of the aggregation process and thus understanding the dynamics of nucleation of large precipitates.

The first theoretical works on the effect of spin-dependent phenomena on the plasticity of alloys in phase transitions have also appeared [158]. It was shown in Ref. [158] that the effect of internal fluctuating magnetic fields in a phase transition near the Curie point on the spin-dependent process of the unpinning of dislocations from stoppers can explain the anomalous jumps in microhardness of magnetic alloys in phase transitions [159, 160].

Finally, bearing in mind that the study of magnetosensitive reactions in spin chemistry has led to the discovery of new phenomena such as magnetically stimulated isotope separation in chemical reactions [14], spin catalysis [13], and chemically induced radio emission [15], we can expect that similar divisions will be developed in the physics of plasticity. In this case, the use of moving dislocations for transportation of the impurity atoms of certain isotopes and the recording of the radio emission generated in the elementary acts of unpinning of dislocations from stoppers will open grand new possibilities for using the information gathered in spin chemistry to control the plasticity of crystals.

It must also be noted that the existing experimental data on MPEs provide a new approach to some effects that were discovered earlier but still have to find a reasonable explanation. For instance, there were reports concerning the effect of a permanent magnetic field with an induction smaller than 1 T on the formation of cracks and on the strength of LiF crystals [161–163]. According to [161–163], a magnetic field changes the radius of the orbits of electrons emitted from one bank of a crack to another. However, according to the rigorous

theoretical study in Ref. [164], the induction of the magnetic field needed to control the electron paths and to create noticeable effects of variation on the strength of crystals amounts to  $\sim 10^2\text{--}10^3$  T, which is much higher than the induction of the magnetic field used in Refs [161–163]. This is a direct indication that other mechanisms of the effect of a magnetic field on the development of cracks must be considered, e.g., the allowance of the spin-dependent increase in the mobility of dislocations.

In conclusion, we note that the possibility of employing the modern achievements of spin design (the synthesis of crystals with a given distribution of spin density) can be used to purposefully create new materials whose plastic properties will be sensitive to magnetic fields. The first attempts in exposing the structural defects [165] and discovering MPEs in such high-spin crystals are promising.

## Conclusions

1. It has been established in experiments that the magnetic moments of objects that react to a magnetic field in ionic and covalent crystals and determine the emergence of an MPE are equal to the Bohr magneton (or are close to this value). This irrevocably suggests that the MPE is of spin origin and that one should take into account the multiplicity of the pairs (and greater numbers) of defects in the formation of plastic properties of crystals even in the absence of a magnetic field. Research has shown that in ionic crystals, spin-correlated pairs can be formed by either (1) a paramagnetic point defect and a dislocation or (2) several paramagnetic impurity ions in the metastable clusters of point defects.

2. The use of magnetic-resonance methods allows using MPEs as a powerful instrument in studies of structural defects, which are responsible for the mechanical properties of solids. It becomes possible to detect EPR in structural defects under conditions in which the concentration of such defects is so low that detecting the resonance by the absorption of electromagnetic waves becomes impossible. The new method has found its place in the study of materials such as silicon, which is very important for practical reasons; the method allows extracting unique information about short-lived spin states of structural defects and their role in the formation of the plasticity of crystals of different types.

3. The necessary experimental conditions for MPE studies by optical spectroscopy methods have been created. The use of  $\text{Eu}^{2+}$  ions as spectroscopic probes has made it possible to establish that impurity–vacancy dipole clusters with a small number of atoms are magnetosensitive. Such clusters can form as a result of aggregation and in a process in which dislocations cut through large precipitates.

4. It has been found that to detect MPEs in conditions where  $U_M/kT \ll 1$ , nonequilibrium defects must be generated by an external factor, such as light, an alternating electric field, plastic deformation, or quenching of the crystals. Concerning MPEs caused by variation in the structure of nonequilibrium clusters of paramagnetic ions, we now know that thermal fluctuations generate short-term transitions of clusters into magnetosensitive states. The role of a magnetic field is to initiate spin transitions inside the cluster at the moments when the cluster is in a thermally excited state and then to transform the cluster into a configuration more favorable energetically.

5. Establishing the contribution of spin-dependent processes to the plasticity of ionic crystals has stimulated the development of a new section of material science known as

spin micromechanics, which appeared at the junction of the physics of the electron–spin properties of defects, spin chemistry, and the physics of plasticity.

The author is grateful to Yu A Osip'yan, A L Buchachenko, V V Kveder, and V L Berdinskii for their unflinching interest in this work and for fruitful discussions, to VI Al'shits, N A Tyapunina, A A Urusovskaya (deceased), and S Z Shmurak for fruitful contacts and overall support, and to Yu I Golovin for our collaboration that has lasted for many years and has stimulated the interest in the phenomena discussed in this review.

This work was made possible by grants from the Presidential Program of State Support of Leading Scientific Schools (Project No. 00-15-96703) and Research of Young Doctors of Science (Project No. 332.2003.2).

## References

- Mott N F *Rev. Mod. Phys.* **50** 203 (1978) [Translated into Russian: *Usp. Fiz. Nauk* **127** 41 (1979)]
- Ziese M, Thornton M J (Eds) *Spin Electronics* (Lecture Notes in Physics, 569) (New York: Springer, 2001)
- Meier F, Zakharchenya B P (Eds) *Optical Orientation* (Modern Problems in Condensed Matter Sci., Vol. 8) (Amsterdam: North-Holland, 1984) [Translated into Russian (Leningrad: Nauka, 1989)]
- Kveder V V, Osip'yan Yu A *Izv. Akad. Nauk SSSR Ser. Fiz.* **51** 626 (1987)
- Wosinski T, Figielski T *Phys. Status Solidi B* **71** K73 (1975)
- Kveder V V, Osip'yan Yu A *Zh. Eksp. Teor. Fiz.* **80** 1206 (1981) [*Sov. Phys. JETP* **53** 618 (1981)]
- Osip'yan Yu A et al. *Elektronnye Svoïstva Dislokatsii v Poluprovodnikakh* (Electronic Properties of Dislocations in Semiconductors) (Ed. Yu A Osip'yan) (Moscow: Editorial URSS, 2000)
- Berdinskii V L *Zh. Eksp. Teor. Fiz.* **91** 2120 (1986) [*Sov. Phys. JETP* **64** 1260 (1986)]
- Bagraev N T, Gusarov A I, Mashkov V A *Zh. Eksp. Teor. Fiz.* **92** 968 (1987) [*Sov. Phys. JETP* **65** 548 (1987)]
- Grazhulis V A, Kveder V V, Osip'yan Yu A *Pis'ma Zh. Eksp. Teor. Fiz.* **21** 708 (1975) [*JETP Lett.* **21** 335 (1975)]
- Buchachenko A L *Usp. Khim.* **62** 1139 (1993) [*Russ. Chem. Rev.* **62** 1073 (1993)]
- Buchachenko A L, Sagdeev R Z, Salikhov K M *Magnitnye i Spinovye Effekty v Khimicheskikh Reaktsiyakh* (Magnetic and Spin Effects in Chemical Reactions) (Novosibirsk: Nauka, 1978)
- Buchachenko A L, Berdinsky V L *Chem. Phys. Lett.* **298** 279 (1998)
- Buchachenko A L, Khudyakov I V *Usp. Khim.* **60** 1105 (1991) [*Sov. Chem. Rev.* **60** 555 (1991)]
- Buchachenko A L, Berdinskii V L *Usp. Khim.* **52** 3 (1983)
- Zel'dovich B Ya, Buchachenko A L, Frankevich E L *Usp. Fiz. Nauk* **155** 3 (1988) [*Sov. Phys. Usp.* **31** 385 (1988)]
- Buchachenko A L *Khimicheskaya Polyarizatsiya Elektronov i Yader* (Chemical Polarization of Electrons and Nuclei) (Moscow: Nauka, 1974)
- Salikhov K M et al. *Spin Polarization and Magnetic Effects in Radical Reactions* (Studies in Physical and Theoretical Chemistry, Vol. 22, Ed. Yu N Molin) (Amsterdam: Elsevier, 1984)
- Buchachenko A L *Usp. Khim.* **68** 99 (1999) [*Russ. Chem. Rev.* **68** 85 (1999)]
- Buchachenko A L, Frankevich E L *Chemical Generation and Reception of Radio- and Microwaves* (New York: VCH, 1994)
- Buchachenko A L *Usp. Khim.* **64** 863 (1995) [*Russ. Chem. Rev.* **64** 809 (1995)]
- Buchachenko A L *Lektsii po Spinovoi Khimii* (Lectures in Spin Chemistry) (Moscow: Khimicheskii Fakul'tet MGU, 2001)
- Osip'yan Yu A, Savchenko I B *Pis'ma Zh. Eksp. Teor. Fiz.* **7** (4) 130 (1968) [*JETP Lett.* **7** 100 (1968)]
- Osip'yan Yu A *Vestn. Akad. Nauk SSSR* **42** (4) 32 (1972)
- Osip'yan Yu A, Shikhsaidov M Sh *Fiz. Tverd. Tela* **15** 3711 (1973)
- Lebedev V P, Krylovskii V S *Fiz. Tverd. Tela* **27** 1285 (1985) [*Sov. Phys. Solid State* **27** 777 (1985)]
- Gostishchev V I et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **30** 102 (1979) [*JETP Lett.* **30** 92 (1979)]
- Natsik V D, Potemina L G *Zh. Eksp. Teor. Fiz.* **67** 240 (1974) [*Sov. Phys. JETP* **40** 121 (1975)]
- Kravchenko V Ya *Zh. Eksp. Teor. Fiz.* **51** 1676 (1966) [*Sov. Phys. JETP* **24** 1135 (1967)]
- Kaganov M I, Kravchenko V Ya, Natsik V D *Usp. Fiz. Nauk* **111** 655 (1973) [*Sov. Phys. Usp.* **16** 878 (1974)]
- Osipyan Yu A, Bobrov V S *Cryst. Res. Technol.* **19** 827 (1984)
- Lebedev V P, Krylovskii V S *Fiz. Tverd. Tela* **32** 544 (1990) [*Sov. Phys. Solid State* **32** 315 (1990)]
- Kravchenko V Ya *Fiz. Tverd. Tela* **9** 1050 (1967)
- Bobrov V S, Lebedkin M A *Pis'ma Zh. Eksp. Teor. Fiz.* **38** 334 (1983) [*JETP Lett.* **38** 400 (1983)]
- Spitsyn V I, Troitskii O A *Elektroplasticheskaya Deformatsiya Metallov* (Electroplastic Deformation of Metals) (Moscow: Nauka, 1985); see also Gromov V E et al. *Elektrostimulirovannaya Plastichnost' Metallov i Spilavov* (Electrically Stimulated Plasticity of Metals and Alloys) (Moscow: Nedra, 1996)
- Golovin Yu I, Morgunov R B *Zh. Eksp. Teor. Fiz.* **115** 605 (1999) [*JETP* **88** 332 (1999)]
- Golovin Yu I et al. *Zh. Eksp. Teor. Fiz.* **117** 1080 (2000) [*JETP* **90** 939 (2000)]
- Golovin Yu I, Morgunov R, Baskakov A *Mol. Phys.* **100** 1291 (2002)
- Golovin Yu I et al. *Fiz. Tverd. Tela* **41** 1778 (1999) [*Phys. Solid State* **41** 1631 (1999)]
- Golovin Yu I, Morgunov R B, Dmitrievskii A A *Mat. Sci. Eng.* **288** 261 (2000)
- Golovin Yu I et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **68** 400 (1998) [*JETP Lett.* **68** 426 (1998)]
- Jaccard C et al. *Phys. Status Solidi B* **50** 187 (1972)
- Cavenett B C *Adv. Phys.* **30** 475 (1981)
- Baranov P G, Romanov N G *Izv. Akad. Nauk SSSR Ser. Fiz.* **50** 224 (1986)
- Schnegg P A, Jaccard C, Aegerter M *Phys. Status Solidi B* **63** 587 (1974)
- Liidya G G, Nagel U Kh *Izv. Akad. Nauk SSSR Ser. Fiz.* **52** 418 (1988)
- Korovkin E V *Pis'ma Zh. Eksp. Teor. Fiz.* **35** 481 (1982) [*JETP Lett.* **35** 595 (1982)]
- Al'shits V I et al. *Fiz. Tverd. Tela* **29** 467 (1987) [*Sov. Phys. Solid State* **29** 265 (1987)]
- Al'shits V I et al. *Izv. Akad. Nauk SSSR Ser. Fiz.* **57** (11) 2 (1993) [*Bull. Acad. Nauk USSR Ser. Phys.* **57** 1865 (1993)]
- Al'shits V I, Darinskaya E V, Petrzhik E A *Fiz. Tverd. Tela* **33** 3001 (1991) [*Sov. Phys. Solid State* **33** 1694 (1991)]
- Alshits V I et al. *J. Alloys Comp.* **211/212** 548 (1994)
- Zagoruiko N V *Kristallografiya* **10** 81 (1965)
- Smirnov A E, Urusovskaya A A *Fiz. Tverd. Tela* **29** 852 (1987) [*Sov. Phys. Solid State* **29** 485 (1987)]
- Zuev L B *Fizika Elektroplastichnosti Shchelochno-galoidnykh Kristallov* (Physics of Electrically Stimulated Plasticity of Alkali-halide Crystals) (Novosibirsk: Nauka, 1990)
- Al'shits V I, Darinskaya E V, Petrzhuk E A *Izv. Vyssh. Uchebn. Zaved. Chernaya Metallurg.* (10) 85 (1990)
- Molotskii M I *Fiz. Tverd. Tela* **33** 3112 (1991) [*Sov. Phys. Solid State* **33** 1760 (1991)]
- Golovin Yu I, Morgunov R B *Pis'ma Zh. Eksp. Teor. Fiz.* **61** 583 (1995) [*JETP Lett.* **61** 596 (1995)]
- Golovin Yu I, Morgunov R B *Dokl. Ross. Akad. Nauk* **354** 632 (1997) [*Dokl. Phys. Chem.* **354** 178 (1997)]
- Smirnov B I, Peschanskaya N N, Nikolaev V I *Fiz. Tverd. Tela* **43** 2154 (2001) [*Phys. Solid State* **43** 2250 (2001)]
- Urusovskaya A A et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **65** 470 (1997) [*JETP Lett.* **65** 497 (1997)]
- Al'shits V I et al. *Zh. Eksp. Teor. Fiz.* **115** 951 (1999) [*JETP* **88** 523 (1999)]
- Golovin Yu I et al. *Phys. Status Solidi A* **160** R3 (1997)
- Golovin Yu I, Morgunov R B, Ivanov V E *Fiz. Tverd. Tela* **39** 630 (1997) [*Phys. Solid State* **39** 550 (1997)]
- Golovin Yu I, Morgunov R B, Tyutyunnik A V *Izv. Ross. Akad. Nauk Ser. Fiz.* **59** (10) 3 (1995) [*Bull. Russ. Acad. Sci. Ser. Phys.* **59** 1639 (1995)]

65. Tyapunina N A, Krasnikov V L, Belozerova E P *Fiz. Tverd. Tela* **41** 1035 (1999) [*Phys. Solid State* **41** 942 (1999)]
66. Tyapunina N A, Belozerova E P, Krasnikov V L *Materialovedenie* (12) 21 (1999)
67. Belozerova E P, Svetashov A A, Krasnikov V L *Izv. Ross. Akad. Nauk Ser. Fiz.* **61** 291 (1997) [*Bull. Russ. Acad. Sci. Ser. Phys.* **61** 227 (1997)]
68. Tyapunina N A et al. *Fiz. Tverd. Tela* **45** 95 (2003) [*Phys. Solid State* **45** 98 (2003)]
69. Soloshenko I I, Zolotarev A F, in *Mekhanizmy Vnutrennego Treniya v Poluprovodnikakh i Metallicheskih Materialakh: Vsesoyuz. Soveshch., Sukhumi, 1970* (Mechanisms of Internal Friction in Semiconductors and Metallic Materials: All-Union Symp., Sukhumi, 1970) (Ed. F N Tavazde) (Moscow: Nauka, 1972) p. 35
70. Orlov A M, Skvortsov A A, Gonchar L I *Fiz. Tverd. Tela* **43** 1207 (2001) [*Phys. Solid State* **43** 1252 (2001)]
71. Skvortsov A A et al. *Fiz. Tverd. Tela* **42** 1814 (2000) [*Phys. Solid State* **42** 1861 (2000)]
72. Orlov A M, Skvortsov A A, Solov'ev A A *Zh. Eksp. Teor. Fiz.* **123** 590 (2003) [*JETP* **96** 523 (2003)]
73. Skvortsov A A, Orlov A M, Gonchar L I *Zh. Eksp. Teor. Fiz.* **120** 134 (2001) [*JETP* **93** 117 (2001)]
74. Badylevich M V et al. *Zh. Eksp. Teor. Fiz.* **124** 664 (2003) [*JETP* **97** 601 (2003)]
75. Makara V A et al. *Fiz. Tverd. Tela* **43** 462 (2001) [*Phys. Solid State* **43** 480 (2001)]
76. Samsonenko M D et al. *Zh. Strukt. Khim.* **20** 1116 (1979)
77. Zhmykhov G V et al. *Fiz. Khim. Stekla* **15** 52 (1989)
78. Darinskaya E V et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **70** 298 (1999) [*JETP Lett.* **70** 309 (1999)]
79. Darinskaya E V, Petrzhik E A, Erofeeva S A *J. Phys.: Condens. Matter* **14** 12883 (2002)
80. Peschanskaya N N, Yakushev P N *Fiz. Tverd. Tela* **39** 1690 (1997) [*Phys. Solid State* **39** 1509 (1997)]
81. Morgunov R B et al. *Vysokomolekulyarnye Soedineniya B* **44** 129 (2002) [*Polymer Sci. B* **44** 16 (2002)]
82. Golovin Yu I, Morgunov R B *Fiz. Tverd. Tela* **43** 827 (2001) [*Phys. Solid State* **43** 859 (2001)]
83. Osip'yan Yu A et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **69** 110 (1999) [*JETP Lett.* **69** 123 (1999)]
84. Osip'yan Yu A et al. *Fiz. Tverd. Tela* **43** 1333 (2001) [*Phys. Solid State* **43** 1389 (2001)]
85. Lebedev V T et al. *Fiz. Tverd. Tela* **44** 616 (2002) [*Phys. Solid State* **44** 641 (2002)]
86. Smirnov B I et al. *Fiz. Tverd. Tela* **44** 1915 (2002) [*Phys. Solid State* **44** 2009 (2002)]
87. Molotskii M, Fleurov V *Phys. Rev. B* **52** 15829 (1995)
88. Okazaki K, Kagawa M, Conrad H *Scripta Metall.* **13** 473 (1979)
89. Jemielniak R, Krolikowski J *J. Phys. Colloq. (Paris)* **46** 160 (1985)
90. Abraimov V V *Fiz. Nizk. Temp.* **6** 1335 (1980) [*Sov. J. Low Temp. Phys.* **6** 651 (1980)]
91. Al'shits V I et al. *Kristallografiya* **35** 1014 (1990) [*Sov. Phys. Crystallogr.* **35** 597 (1990)]
92. Al'shits V I, Darinskaya E V, Petrzhik E A *Fiz. Tverd. Tela* **34** 155 (1992) [*Sov. Phys. Solid State* **34** 81 (1992)]
93. Datsko O I, Alekseenko V I *Fiz. Tverd. Tela* **39** 1234 (1997) [*Phys. Solid State* **39** 1094 (1997)]
94. Datsko O I, Alekseenko V I, Shakhova A D *Fiz. Tverd. Tela* **38** 1799 (1996) [*Phys. Solid State* **38** 992 (1996)]
95. Zakharchenya B P et al. *Usp. Fiz. Nauk* **136** 459 (1982) [*Sov. Phys. Usp.* **25** 143 (1982)]
96. Golovin Yu I, Morgunov R B *Izv. Ross. Akad. Nauk Ser. Fiz.* **61** 850 (1997) [*Bull. Russ. Acad. Sci. Ser. Phys.* **61** 667 (1997)]
97. Golovin Yu I, Morgunov R B *Pis'ma Zh. Eksp. Teor. Fiz.* **58** 189 (1993) [*JETP Lett.* **58** 191 (1993)]
98. Golovin Yu I, Morgunov R B, Ivanov V E *Izv. Vyssh. Ucheb. Zaved. Fiz.* **41** (4) 117 (1998)
99. Golovin Yu I et al. *Fiz. Tverd. Tela* **40** 2065 (1998) [*Phys. Solid State* **40** 1870 (1998)]
100. Morgunov R B et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **76** 366 (2002) [*JETP Lett.* **76** 307 (2002)]
101. Morgunov R B, Baskakov A A *Fiz. Tverd. Tela* **43** 1632 (2001) [*Phys. Solid State* **43** 1700 (2001)]
102. Morgunov R B, Baskakov A A *Fiz. Tverd. Tela* **45** 91 (2003) [*Phys. Solid State* **45** 94 (2003)]
103. Morgunov R B et al. *Fiz. Tverd. Tela* **45** 257 (2003) [*Phys. Solid State* **45** 270 (2003)]
104. Golovin Yu I, Morgunov R B, Lopatin D V *Izv. Vyssh. Ucheb. Zaved. Fiz.* **42** (4) 66 (1999)
105. Golovin Yu I et al. *Fiz. Tverd. Tela* **40** 2184 (1998) [*Phys. Solid State* **40** 1981 (1998)]
106. Lopatin D V, Thesis for Candidate of Physics and Mathematical Sciences (Tambov: Tambov State Univ., 1999)
107. Morgunov R B et al. *Zh. Eksp. Teor. Fiz.* **124** 840 (2003) [*JETP* **97** 754 (2003)]
108. Golovin Yu I et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **69** 114 (1999) [*JETP Lett.* **69** 127 (1999)]
109. Golovin Yu I et al. *Fiz. Tverd. Tela* **38** 3047 (1996) [*Phys. Solid State* **38** 1666 (1996)]
110. Golovin Yu I, Morgunov R B *Fiz. Tverd. Tela* **37** 1239 (1995) [*Phys. Solid State* **37** 674 (1995)]
111. Golovin Yu I, Morgunov R B *Izv. Ross. Akad. Nauk Ser. Fiz.* **64** 1683 (2000) [*Bull. Russ. Acad. Sci. Ser. Phys.* **64** 1342 (2000)]
112. Al'shits V I, Darinskaya E V, Kazakova O L *Pis'ma Zh. Eksp. Teor. Fiz.* **62** 352 (1995) [*JETP Lett.* **62** 375 (1995)]
113. Al'shits V I, Darinskaya E V, Kazakova O L *Zh. Eksp. Teor. Fiz.* **111** 615 (1997) [*JETP* **84** 338 (1997)]
114. Al'shits V I et al. *Fiz. Tverd. Tela* **38** 2426 (1996) [*Phys. Solid State* **38** 1333 (1996)]
115. Al'shits V I et al. *Kristallografiya* **48** 838 (2003) [*Crystallogr. Rep.* **48** 768 (2003)]
116. Al'shits V I, Darinskaya E V *Pis'ma Zh. Eksp. Teor. Fiz.* **70** 749 (1999) [*JETP Lett.* **70** 761 (1999)]
117. Al'shits V I, Darinskaya E V, Kazakova O L *Fiz. Tverd. Tela* **40** 81 (1998) [*Phys. Solid State* **40** 70 (1998)]
118. Golovin Yu I et al. *Kristallografiya* **43** 1115 (1998) [*Crystallogr. Rep.* **43** 1056 (1998)]
119. Golovin Yu I et al. *Fiz. Tverd. Tela* **39** 634 (1997) [*Phys. Solid State* **39** 554 (1997)]
120. Golovin Yu I, Morgunov R B, Zhulikov S E *Kristallografiya* **43** 689 (1998) [*Crystallogr. Rep.* **43** 640 (1998)]
121. Gridnev S A, Drozhdin K S, Shmykov V V *Kristallografiya* **42** 1135 (1997) [*Crystallogr. Rep.* **42** 1058 (1997)]
122. Gridnev S A, Drozhdin K S, Smykov V V *Phys. Status Solidi B* **214** R7 (1999)
123. Koldaeva M V, in *1-ya Ross. Konf. Molodykh Uchenykh po Fizicheskomu Materialovedeniyu* (The 1st National Conf. of Young Scientists in Physical Materials Science), October 2001, Kaluga: Abstracts of Reports (Kaluga: Manuskript, 2001) p. 39
124. Molotskii M I *Fiz. Tverd. Tela* **35** 11 (1993) [*Phys. Solid State* **35** 5 (1993)]
125. Al'shits V I, Darinskaya E V, Koldaeva M V *Fiz. Tverd. Tela* **43** 1635 (2001) [*Phys. Solid State* **43** 1703 (2001)]
126. Darinskaya E V, Koldaeva M V *Pis'ma Zh. Eksp. Teor. Fiz.* **70** 226 (1999) [*JETP Lett.* **70** 228 (1999)]
127. Molotskii M, Fleurov V *Philos. Mag. Lett.* **73** 11 (1996)
128. Al'shits V I et al. *Fiz. Tverd. Tela* **41** 2004 (1999) [*Phys. Solid State* **41** 1839 (1999)]
129. Golovin Yu I, Morgunov R B *Dokl. Ross. Akad. Nauk* **361** 352 (1998) [*Dokl. Phys. Chem.* **361** 227 (1998)]
130. Osip'yan Yu A et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **79** 158 (2004)
131. Golovin Yu I et al. *Fiz. Tverd. Tela* **39** 1389 (1997) [*Phys. Solid State* **39** 1232 (1997)]
132. Golovin Yu I, Morgunov R B, Shmurak S Z *Dokl. Ross. Akad. Nauk* **360** 753 (1998) [*Phys. Dokl.* **43** 340 (1998)]
133. Golovin Yu I et al. *Izv. Ross. Akad. Nauk Ser. Fiz.* **62** 1296 (1998) [*Bull. Russ. Acad. Sci. Ser. Phys.* **62** 1053 (1998)]
134. Molotskii M I, Kris R E, Fleurov V *Phys. Rev. B* **51** 12531 (1995)
135. Molotskii M, Fleurov V *Phys. Rev. B* **56** 10809 (1997)
136. Molotskii M, Fleurov V *Phys. Rev. Lett.* **78** 2779 (1997)
137. Molotskii M I *Mat. Sci. Eng. A* **287** 248 (2000)
138. Frankevich E L, Balabanov E I *Pis'ma Zh. Eksp. Teor. Fiz.* **1** 33 (1965)
139. Frankevich E L, Pristupa A I, Kobryanskii V M *Pis'ma Zh. Eksp. Teor. Fiz.* **40** 13 (1984) [*JETP Lett.* **40** 733 (1984)]
140. Lesin V I et al. *Phys. Status Solidi B* **84** 513 (1977)

141. Frankevich E L, Lesin V I, Pristupa A I *Zh. Eksp. Teor. Fiz.* **75** 415 (1978) [*Sov. Phys. JETP* **48** 208 (1978)]
142. Levin M N, Lichmanov Yu O, Maslovskii V M *Pis'ma Zh. Tekh. Fiz.* **20** (2) 27 (1994) [*Tech. Phys. Lett.* **20** 145 (1994)]
143. Maslovskii V M et al. *Fiz. Tekh. Poluprovodn.* **28** 772 (1994) [*Semiconductors* **28** 453 (1994)]
144. Tsmots V M et al. *Solid State Commun.* **63** 1 (1987)
145. Levin M N, Zon B A *Zh. Eksp. Teor. Fiz.* **111** 1373 (1997) [*JETP* **84** 760 (1997)]
146. Vlasov V P, Kanevskii V M, Purtskhvanidze A A *Fiz. Tverd. Tela* **33** 2194 (1991) [*Sov. Phys. Solid State* **33** 1236 (1991)]
147. Golovin Yu I et al. *Fiz. Tverd. Tela* **41** 1944 (1999) [*Phys. Solid State* **41** 1783 (1999)]
148. Rubio J O *J. Phys. Chem. Solids* **52** 101 (1991); Jacobs P W M *J. Phys. Chem. Solids* **52** 35 (1991)
149. Cordero-Borboa A E et al. *J. Phys. C: Solid State Phys.* **19** 7113 (1986)
150. Muñoz J A et al. *J. Luminescence* **72–74** 233 (1997)
151. López F J et al. *Phys. Rev. B* **22** 6428 (1980)
152. Muñoz-Santiuste J E, Garcí-Solé J *Phys. Rev. B* **38** 10874 (1988)
153. Krashenin V I et al. *Khim. Fiz.* **14** 126 (1995)
154. Boldyrev V V, Krashenin V I, in *Materialy Mezhhregional'noi Nauchno-Prakticheskoi Konf. s Mezhdunarodnym Uchastiem "Novye Khimicheskie Sistemy i Protessy v Meditsine"* (Proc. Interregional Scientific and Practical Conf. with Foreign Participants on New Chemical Systems and Processes in Medicine), Novosibirsk, December 21–22, 2001 (Novosibirsk: SibUPK, 2002) p. 199
155. Qi J et al. *J. Luminescence* **87–89** 1102 (2000)
156. Akimoto R, Kobayashi M, Suzuki T *J. Phys. Soc. Jpn.* **63** 4616 (1994)
157. Cordoba-Jabonero C et al. *J. Alloys Comp.* **323–324** 847 (2001)
158. Molotskii M, Fleurov V *Phys. Rev. B* **63** 184421 (2001)
159. Nabutovskaya O A *Fiz. Tverd. Tela* **11** 1434 (1969)
160. Zackay V F, Hazlett T H *Acta Metal.* **1** 624 (1953)
161. Gershenson N I et al. *Fiz. Tverd. Tela* **28** 708 (1986) [*Sov. Phys. Solid State* **28** 394 (1986)]
162. Gershenson N I et al. *Fiz. Tverd. Tela* **30** 2209 (1988) [*Sov. Phys. Solid State* **30** 1273 (1988)]
163. Biadzhi P F et al. *Fiz. Tverd. Tela* **32** 2328 (1990) [*Sov. Phys. Solid State* **32** 1352 (1990)]
164. Molotskii M I, in *Electronic Excitation During the Plastic Deformation and Fracture of Crystals* (Soviet Scientific Reviews, Sec. B, Vol. 13, Pt. 3, Ed. M E Vol'pin) (London: Harwood, 1989) p. 1
165. Osip'yan Yu A et al. *Fiz. Tverd. Tela* **45** 1396 (2003) [*Phys. Solid State* **45** 1465 (2003)]