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Spin effects in defect reactions

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The objective of this investigation is to evaluate the effect of weak magnetic fields on the defect structure of a wide range of nonmagnetic crystals. The available experimental data are interpreted within the framework of the phenomenological scheme of magnetic field-assisted defect reactions in solids within a concept of defect-induced lattice magnetism. We elucidate the principal difference between the defect reactions in solids and chemical reactions of radical pairs in liquids, emphasizing the role of the media in the spin-dependent effects. The defect reactions may be induced by both pulsed magnetic fields and microwaves, as well as by a constant magnetic field. A macroscopic manifestation of the quantum phenomenon is a long-time dramatic change in the defect structure and some physical and chemical properties of crystalline materials. One can use the magnetic field treatment for a control modification of the defect structure of crystals. We predict the effect of *temperature windows* inside which magnetic fields can determine the defect structure.

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I. INTRODUCTION

A sufficient amount of experimental data have been obtained that show weak magnetic fields can have an effect on the defect structure and some physical properties of various nonmagnetic crystals. Initially, a decay of impurity-defect complexes[1] and an increase of dislocation mobility[2] were discovered in the alkali-halogen crystals in magnetic fields of ∼10 kOe. The magnetic field-induced phenomena were also revealed in nonmagnetic metals,[3] metal-oxide-semiconductor structures,[4] high-oxygen silicon crystals,[5,6] semiconductor A_2B_6 (Ref. 7) and A_3B_5 (Refs. 8–10) compounds, as well as in the Sb-As solid solutions,[11] ferroelectrics,[12,13] YBaCuO ceramics,[14] and crystalline polymers.[15,16] Most of the effects were observed at room temperature.

Evaluation of the experimental data leads to a conclusion that the magnetic field-induced structural changes in nonmagnetic solids represent a decay of defect complexes accompanied by a generation of mobile point defects participating in long-time processes, forming new defect structures. In general, the structural changes considered as *defect reactions in solids* with an activation energy of ∼1 eV, resulting from the effect of magnetic fields characterized by a Zeeman energy of $\sim 10^{-6}$ eV, which is much less than the thermal energy at the temperature of the experiment. This phenomenon is puzzling and requires further study.

The effect of magnetic fields on defect reactions in solids is similar to the effect of weak magnetic fields on the kinetics of chemical reactions of radicals in liquids. It is well known from spin chemistry[17–20] that a magnetic field is able to have an effect on the probability of the reaction by acting on the spins of unpaired electrons of the radicals composing a *radical pair*. The radical reactions in liquids are sensitive to an external magnetic field when the lifetime of the radical pair is longer than the lifetime of magnetic field-induced nonequilibrium population of the energy levels relating to different spin states of the pair, but shorter than a characteristic time of spin-lattice relaxation that restores the equilibrium. However, adapting the well-developed concept of magnetosensitive chemical reactions of the spin-correlated radical pairs in liquid media to the magnetic field-induced defect reactions in crystals is difficult.

The description of the magnetoplastic effect (the magnetic field-induced increase of dislocation mobility) in the context of the model[21] of interaction of a dangling bond in the dislocation core with a paramagnetic center being an obstacle for a moving dislocation is not considered a plausible explanation of the magnetic field-induced phenomena in nonmagnetic solids, especially since there is an effect of magnetic field on the mobility of dislocations introduced into the crystal after the magnetic treatment.[22] The assumption[22] that the magnetoplastic effect is caused by magnetic field-assisted decay of defect complexes due to a change of the spin state of the short-lived radical pairs, arisen as a result of the breaking of thermally elongated stressed chemical bonds in such complexes, can be challenged. Indeed, the time of the change of the spin level population in a magnetic field ($10^{-9}-10^{-8}$ sec) significantly exceeds a lifetime fluctuation ($\sim 10^{-13}$ sec) corresponding to such bond elongations that are responsible for the Zeeman transitions. In addition, a direct experiment[23] has not detected an effect of magnetic field on the breaking of mechanically stressed chemical bonds.

In spite of the attractiveness of the concept of magnetic-spin effects in chemical reactions of radical pairs, developed in spin chemistry theory, the validity of its use for an explanation of the magnetic field-induced phenomena in crystals, observed as the changes of the defect structure and mobility of defects, is debatable. This investigation addresses the need for a more universal understanding of the effects.

II. EXPERIMENT

The special features of the magnetic field-induced changes of the defect structure of nonmagnetic crystals are

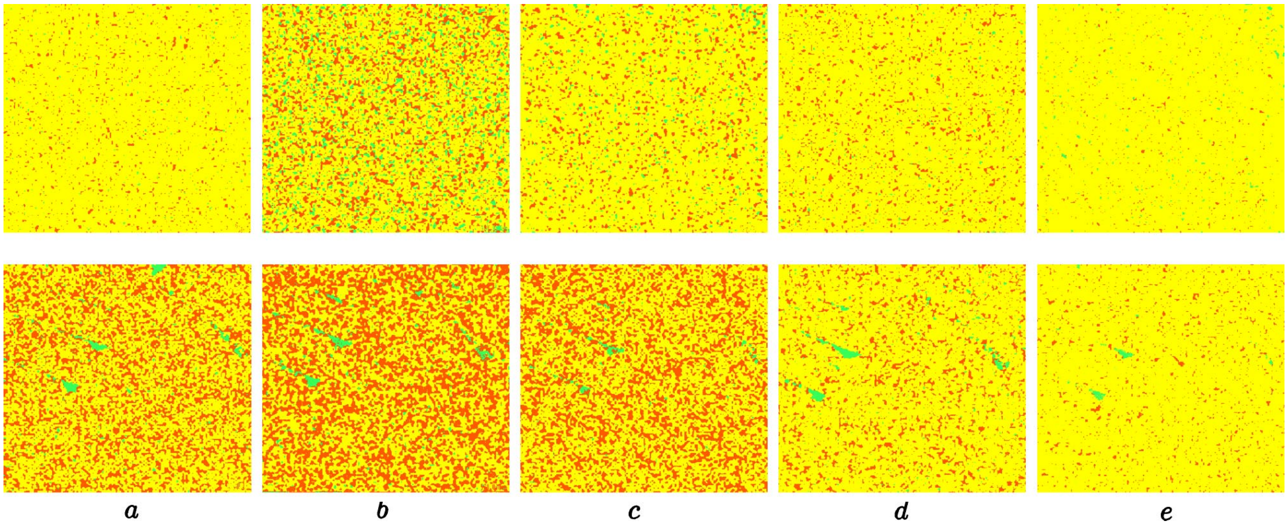

FIG. 1. (Color online) Planar distribution of elements (by EPMA data) in the surface layer ~1 μm of the InAs (top panel) and the $Sb_{0.8}As_{0.2}$ crystals (bottom panel): (a) before PMF treatment; (b) – (e) 5, 10, 20, and 100 days after the PMF treatment ($H_0=3$ kOe, $t=4\times10^{-5}$ sec, $N=1500$ pulses, $f=50$ Hz, $T=300$ K). Colors of the InAs ($Sb_{0.8}As_{0.2}$), In (Sb), and As phases are gray, black, and white (yellow, red, and green in the color online version), respectively. The size of image is 500×500 μm.

exemplified below by the effect of magnetic field-induced diffusion instability of binary phases, detected recently in the crystals of semiconductor A_3B_5 (Ref. 10) and solid solutions in the Sb-As system.[11]

The $Sb_{0.8}As_{0.2}$ and InAs crystals with a large-block structure and mechanically polished surfaces were investigated. The details of the sample preparation were described earlier.[10,11] Electron-probe microanalysis (EPMA) was used to determine the chemical component distribution in the surface layer of the samples before and after the magnetic field treatment. The measurements were performed in a *Cam-Scan S4* scanning electron microscope equipped with an energy-dispersive x-ray analysis system *Link AN10/55S*. The planar distributions or the maps of components were determined in the surface layer with a thickness ~1 μm by measuring the intensity of a characteristic x-ray radiation excited by an electron beam scanning the sample surface. The red, green, and yellow colors in the maps represent the areas occupied mainly by the nonvolatile components (antimony in the $Sb_{0.8}As_{0.2}$ samples and indium in the InAs samples), the volatile component (As) and the relevant stoichiometric compound (InAs or $Sb_{0.8}A_{0.2}$), respectively.

The pulsed magnetic fields (PMFs) generated by periodical discharging of a capacity bank through the low-inductance solenoid coil were used for the magnetic treatment of the samples. The magnetic treatment was performed inside the coil by a series of 1500 single-polarity symmetrical pulses of a triangular shape with duration of 4×10^{-4} sec, repetition rate of 50 Hz, and variable amplitude of magnetic field. Both the treatment and the after-treatment storage of the samples were carried out at room temperature. The PMF-treated samples were stored together with the control samples not exposed to the PMF.

The effect manifests itself by the long-time (up to a thousand hours at $T=300$ K) redistribution of the components in the crystals resulting from a short-time (seconds) PMF treatment. The effect is clearly demonstrated in the Fig. 1. One can see that there is one and the same evolution of the defect structure in the crystals of both types. The more dramatic appearance of the effect in the $Sb_{0.8}As_{0.2}$ samples is associated with a higher initial content of defects in these crystals in comparison with the InAs samples. The effect is characterized by the two stages with an increase of content of the nonvolatile component in the surface layer of the crystals at the first stage and the reverse process of the decrease of the content of the nonvolatile component at the second stage. The effect is also characterized by a delay in appearance (a latent stage) and results in a final increase of planar homogeneity of the crystals.

One can characterize the extent of planar inhomogeneity of the crystal by a ratio δ of the areas occupied by the nonvolatile component and by the stoichiometric compound in the planar distribution of the components, for example, by the ratio $\delta=[\mathrm{In}]/[\mathrm{InAs}]$ in the case of InAs crystal. The time dependences of the PMF-induced changes of the parameter of inhomogeneity $\delta(t)$ in the InAs crystal for different magnitudes of the magnetic field pulses are given in the Fig. 2. The time dependences of the parameter $\delta(t)$ are characterized by a latent stage (tens of hours), followed by a stage of considerable increase of the nonvolatile component content in the surface layer (up to hundreds of hours) and by a prolonged stage of restoring the component contents (up to thousands of hours). The PMF-induced effect is characterized by the magnetic field threshold (~1 kOe) and saturation (>2 kOe). It should be noted that there are no changes in the planar distribution of the components in the control samples.

The effect observed can be explained by the PMF-induced decay of the defect complexes containing excess vacancies of the volatile component V_{As} with antistructural defects; for example, with arsenic atoms in the indium sites As_{In} in the InAs lattice or in the Sb_{As} sites in the case of the Sb-As crystal. The decay of the defect complexes results in a formation of mobile point defects, including the V_{As} sites. The diffusion of the arsenic vacancies from the volume of the

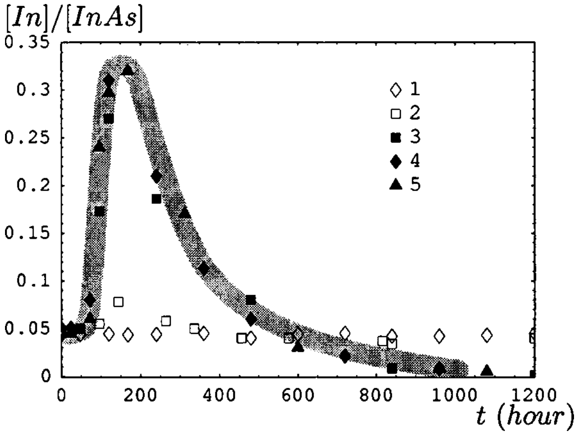

FIG. 2. Time dependence of the inhomogeneity parameter $\delta(t)$ of component distribution in the surface layer of the InAs crystal after the PMF treatment. The samples are as follows: 1 is a control sample; 2 – 5 are PMF samples treated at $H_0=1,2,3,$ and 5 kOe, respectively. Other treatment parameters are the same as defined in Fig. 1.

crystal toward the surface and the counterdiffusion of arsenic atoms cause a surface depletion of the volatile component that is observed as the surface is enriched with the nonvolatile component. The flow of the point defects disturbs the thickness equilibrium of the component distribution, which is restored by diffusion of the excess nonvolatile component from the surface into the volume. The higher mobility of the volatile component in comparison with the nonvolatile component explains the nonmonotonic character of the effect and the longer duration of the restoring stage. The prolonged character of the observed phenomenon, as well as the existence of the latent stage, can be explained by slow diffusion at room temperature. The diffusion character of the latent stage is shortened by performing the experiment at a higher temperature.

The long-time nonmonotonic character of magnetic field-induced changes of crystal characteristics as well as the magnetic field threshold and saturation of the effect are inherent for the most of experimentally observed PMF-induced effects resulting from a decay of defect complexes in solids. The origin of the decay of defect complexes under the influence of the comparatively weak magnetic fields remains puzzling.

III. CONCEPTION OF DEFECT-INDUCED LATTICE MAGNETISM

Any interpretation of the effect of magnetic field on defect structure of a solid requires the answers to two questions: (1) between which levels in the energy spectrum of the solid do the transitions occur under the action of the magnetic field? and (2) why do such transitions not happen in the absence of the field? The magnetic field-assisted defect reactions are observed at relatively high temperatures. That is why the characteristic magnetic energy (of the order of the distance between the levels) turns out to be much less in comparison with the characteristic thermal energy $\mu_B H \ll T$. Here, μ_B is the Bohr magneton, H is a magnetic field strength, and T is a temperature in energy units. If the transitions between the levels take place under the action of magnetic field, then in the absence of the field, these transitions must be either forbidden in principle or highly improbable.

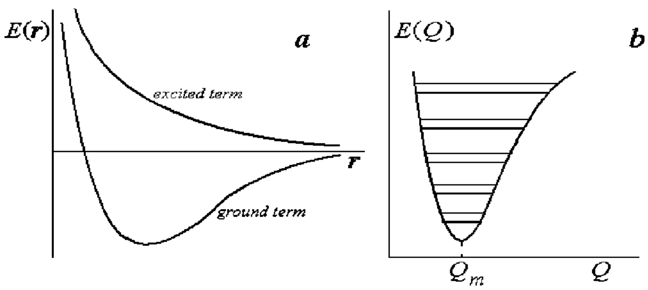

FIG. 3. Energy dependences $E(r)$ of singlet (ground state) and triplet (excited state) terms of two electrons of a radical pair as a function of distance r between the radicals (a). Vibrational (bold lines) and magnon (thin lines) structure of an adiabatic electron term $E(Q)$ of the ground state of defect in solid state, shown schematically depending only on the configuration coordinate Q (b).

In the two-electron concept of spin chemistry, the magnetic field induces a transition between the two *noncrossing* electron terms: the ground singlet level and the excited triplet level with the energies of $E_s(r)$ and $E_t(r)$, respectively, where r is a distance between the electrons in the radical pair, defined as the configuration coordinate [Fig. 3(a)]. In the absence of a magnetic field, the transition between the singlet and triplet levels is strictly forbidden by spin. The condition that $|E_s(r)-E_t(r)| \approx \mu_B H$, at which the magnetic field-induced transitions between the terms are possible, is fulfilled at large r values (of the order of several interatomic distances) in an interval δr. This interval determines the duration of the radical pair in the reaction zone. The time interval necessary for the reaction is easily achieved in the case of a liquid-phase reaction, when the distances between the radicals and their orientations with respect to each other may be arbitrary, while the molecular mobility of the radicals is lowered in the viscous liquid media.

Reactions between defects in crystals have a diffusion character, and the motion of the atoms, which were considered as composing a radical pair, mainly (excluding a very short time interval directly related to the diffusion jump) has a character of small vibrations near their equilibrium positions. That is why the concept[22] of a stressed valence bond as a radical pair leads to an extremely small duration of stay of such a pair in the reaction zone.

The description of defect reactions in crystals should take into account the characteristic features of the quantum states and the energy spectrum of elementary excitations of the solid state. Generally speaking, this cannot be reduced to the two-electron radical pair model. There must exist energy levels in the spectrum of elementary excitations and the transition between which appears to be possible in external magnetic field. As it follows from general phenomenological considerations,[24] the change, due to an external magnetic field $\delta\boldsymbol{H}$, of the free energy density at a constant temperature is equal to $\delta F=-\boldsymbol{M}\delta\boldsymbol{H}$, where $\boldsymbol{M}$ is a magnetization. Therefore, one can *assume* the magnetic field-induced transitions are associated with an existence of some magnetoactive branch in the spectrum of elementary excitations, similar to spin waves in ferromagnets and antiferromagnets.

The nontriviality of the observed magnetic field-induced phenomena lies in the fact that these phenomena occur in solids where the *ideal* crystal structure excludes any magnetic ordering. However, it is a change of the solid state defect structure that is the result of a magnetic field treatment. Therefore, one can deduce that the magnetic order arises in the distorted lattice due to the defects themselves.

In such an *assumption*, the magnetoactive branch in the spectrum of elementary excitations is caused by the defect of the point symmetry group that is related to one of the magnetic classes.[24] The defect distorts the lattice, resulting in an incomplete compensation of *orbital* currents inside the distorted elementary cell. This results in the appearance of a nonuniform field of a magnetization in the extended vicinity of the defect. This region may be denoted as a "*defect-magnetized domain*" (DMD). This kind of a defect-induced piezomagnetism should not give rise to a macroscopic magnetization due to its self-averaging over all crystal equivalent defect orientations.

The established concept of orbital magnetic ordering[25–28] is the main element of this proposal. Currently, the concepts of *hidden* orbital antiferromagnetic ordering[29] and orbital antiferromagnetic fluctuations[30] are widely used to explain the unusual properties of the normal phase of cuprate superconductors, for example.

The quantum states relating to the magnetoactive elementary excitations under consideration have to be determined in an extended space-limited vicinity of the defect. A vicinity represents a peculiar type of a quantum dot in the case of a point defect, or a quantum wire in the case of a line defect. Owing to such a confinement, the spectrum corresponding to the magnetoactive branch appears to be size quantized. The size quantization levels should be associated with each vibrational level of the adiabatic electron term, which depends on atomic configuration of the defect, as is schematically shown in Fig. 3(b).

For clarification, let us consider a decay reaction of the defect complex (DC) into mobile parts with a more simple structure that we call the reaction products (RP's).

Such a reaction is carried out through diffusion displacements of atoms in the crystal lattice and may be described by trajectories in a configuration space, formed by linear combinations of coordinates of the atoms, essentially changing their positions during the reaction.

Under the qualitative analysis of kinetics of the reaction, it is common to restrict the evaluation to only one configuration coordinate Q commonly called a *coordinate of reaction*. The energy of the ground state of the electron system, related to the chosen configuration space of the DC, as a function of Q, has minima at some values Q_m and Q_m^* corresponding to the equilibrium configurations of the DC and RP's, respectively. The energy values corresponding to the points Q_m and Q_m^* determine the thermal equilibrium concentrations of the DC and RP's, respectively.

Let us *assume* (as well as in spin chemistry) the electron states of the DC and RP's correspond to the different values of the total spin of the electron system under consideration. The DC↔RP transitions may be caused either by the spin-orbit interaction or by an external magnetic field. In the absence of a magnetic field, it is a weak spin-orbit interaction that provides the *chemical equilibrium* between the DC and RP's. The external magnetic field may give rise to a shift of the chemical equilibrium, changing the concentrations of DC and RP's, which appears as an increase of mobility of some defects and as a *macroscopic* change of the crystal defect structure. *Thus, the magnetic field changes the rates of the reactions between the defects in a solid*.

IV. MAGNON-ASSISTED REACTIONS

The ground state energy of the electron system corresponding to a DC may be considered as the minimal eigenvalue of an effective Hamiltonian $\hat{H}_i(Q)$, describing the system of N electrons relating to the DC. When one can neglect the weak spin-orbital interaction, the Hamiltonian $\hat{H}_i(Q)$ does not depend on spin operators, and its eigenfunctions can be represented in the form of a product of orbital $|i;Q\rangle$ and spin $|S_i\rangle$ wave functions (here, S_i is the total spin of the electron system under consideration). The eigenfunctions of another effective Hamiltonian $\hat{H}_f(Q)$, which determines the state of the RP's, can be represented in a form similar to that of a product of the relevant orbital $|f;Q\rangle$ and spin $|S_f\rangle$ wave functions. The total wave function in the form of a product of the spin and orbital functions is antisymmetric with respect to a permutation of any pair of electrons. Therefore, at a given spin configuration (independent of the reaction coordinate)$|S_\lambda\rangle$, where $\lambda = i, f$, the orbital function must have a permutational symmetry corresponding to the given total spin. One can use the factorized wave functions in the absence of an external magnetic field since the lifetime of a DC is large enough to consider the state of the DC (as well as the state of the RP's) as being stable. In the first approximation, the states of the DC and RP's may be considered independently such that one can neglect the spin-orbital interaction that results in infrequent transitions between the DC and RP's maintaining the chemical equilibrium in the defect crystal.

Ground state orbital wave functions of the DC or RP's are the eigenfunctions of the Hamiltonians $\hat{H}_\lambda(Q)$, given by

$$\hat{H}_\lambda(Q)|\lambda;Q\rangle = E_\lambda(Q)|\lambda;Q\rangle, \tag{1}$$

depending on the reaction coordinate. The eigenvalues $E_\lambda(Q)$ of these Hamiltonians corresponding to the electronic terms for the relevant configurations of the DC and RP's also depend on Q. Taking into account the fact that the ground term of the initial configuration $E_i(Q)$ has a minimum at $Q = Q_m$, then the ground term of the final configuration $E_f(Q)$ achieves its minimal value at $Q = Q_m^* \neq Q_m$. It is possible to conclude that there is a crossing of the ground terms related to the DC and RP states at some coordinate Q_c between the coordinates Q_m and Q_m^*. This means that the two electronic terms of the ground state of either the DC or RP's may relate to one and the same value Q. In the absence of an external magnetic field, the concentration of the DC is much higher in comparison with the concentration of the RP's for the con-

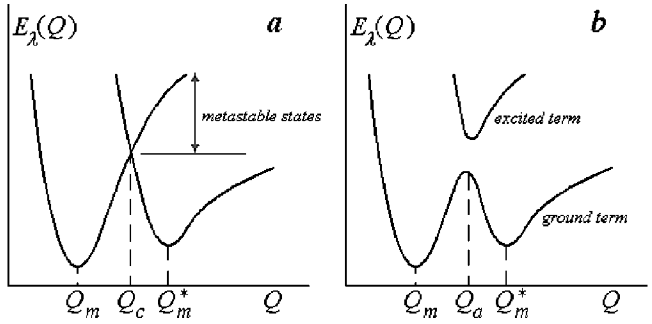

FIG. 4. Configuration diagram: (a) crossing of electron terms with spin ban on transitions between the DC and RP terms; (b) anticrossing of the terms in the case of diffusion behavior of DC↔RP transitions.

dition $E_i(Q_m) < E_f(Q_m^*)$ in thermal equilibrium.

Depending on the spin configuration corresponding to the DC and RP's, the following options are possible:

(1) The crossing of the terms takes place if the spin wave functions of the DC and RP's are orthogonal to each other ($\langle S_f | S_i \rangle = 0$) and any transition between the electron terms of the DC and RP's turns out to be spin forbidden. When $Q \neq Q_c$, the state (either the DC or RP's) corresponding to the term with the higher energy is metastable. If the transition between the DC and RP's is not spin forbidden, due to a finite overlap of the orbital wave functions $\langle Q; f | i; Q \rangle \neq 0$, then the transition from the metastable state into the ground state would certainly be possible. The reverse transition would also be possible. In this sense, both branches of the configuration diagram, schematically presented in Fig. 4(a), exist independently of one another.

(2) If $\langle S_f | S_i \rangle \neq 0$, then the transitions between the ground terms of the DC and RP's are allowed and the degeneracy at the point of crossing should be eliminated. This results in an *anticrossing* of the terms; that is, in the appearance of the Q-dependent ground and the first excited terms of the electron system. Neglecting the transitions between these terms, one may consider that the electron system follows the atomic displacements adiabatically. This leads to diffusion transitions DC↔RP's with activation energies determined by the difference of the ground term energies corresponding to the points Q_a and Q_m or Q_m^*, as shown in Fig. 4(b).

Considering the influence of an external magnetic field on the rate of the defect reactions in solids, one has to assume the orthogonality of the spin configurations of the DC and RP's. This is because in the opposite case, the effect of the external magnetic field on the diffusion transitions may be ignored.

The reaction coordinate Q has the meaning of a translational mode in the configuration space. Thus, the energy $E_\lambda(Q)$ may be defined as the potential energy of the oscillating atoms in the configuration of the DC ($\lambda = i$) or RP's ($\lambda = f$). The quantization of atomic vibrations leads to a vibrational structure of the electron terms. At a finite temperature, the population of the vibrational quantum states, characterized by the corresponding quantum numbers n, is determined by a partition function $w_n(T)$. The spin wave function $|S_\lambda\rangle$, relating to the ground electron term, does not depend on the vibrational degrees of freedom. Accounting for the condition that $\langle S_f | S_i \rangle = 0$, the transitions between any of the vibrational states of the DC and RP's ($i \leftrightarrow f$) should be strictly forbidden.

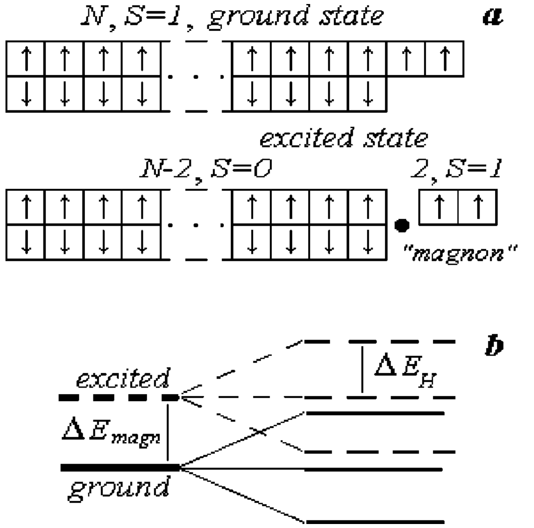

FIG. 5. Structure of spin wave functions (a) and Zeeman splitting (b) of the ground and the first excited levels of the i-configuration.

Such transitions become possible if there exist excited states $|S_i^*\rangle$ in the spin subsystem of the i-configuration for which the transition $i \to f$ is not forbidden. In such a case, the probability of the transition from *an excited DC state of the i-configuration* (DC*) into any vibrational state of the f-configuration can be estimated as

$$P_{fi}(T) = |\langle S_f | S_i^* \rangle|^2 \sum_{n,n'} w_n(T) |\langle f; n' | n, *; i \rangle|^2. \qquad (2)$$

Here, $|n, *; i\rangle$ is an orbital wave function of the excited state associated with nth vibrational level. The permutational symmetry of this function corresponds to the total spin S^*. Equation (2) corresponds to the "instantaneous" change $\hat{H}_i \to \hat{H}_f$ of the Hamiltonian[31] due to the DC*→RP transition. Thus, the overlap integrals of the eigenfunctions, relating to the different operators, are certainly nonzero: $\langle f; n' | n, *; i \rangle \neq 0$.

The spin wave function of the N electron system may be represented as a two-row Young tableau.[24] The total spin of the system is then determined by the difference of the row lengths. For simplicity, let us assume that the ground state of the i-configuration is characterized by the spin wave function with the total spin $S=1$, as is shown in Fig. 5. One of the simplest excited states with the same total spin $S=1$ can be represented as a "product" of the Young tableaus for $N-2$ electrons (the spin function of the excited state of the i-configuration with the total spin $S^*=0$) and a one-row Young tableau corresponding to the other two electrons composing a "magnon"-type quasiparticle with the total spin $S=1$ in the system of N electrons, as is shown in Fig. 5. The minimal excitation energy ΔE_m of such a magnon is nonzero and has a meaning of a binding energy of a magnon split off from the system including N electrons.

The factorized spin function should be associated with a factorized orbital function, in which a multiplier, related to the $N-2$ electrons with the total spin $S^{*}=0$, describes the excited state of the defect complex DC*. It is natural for an open system, such as the electron system under consideration, to preset not a number of particles, but a chemical potential. There is then no need to consider the number of electrons as being conserved.

The application of the external magnetic field $\boldsymbol{H}$ leads to a contribution into the Hamiltonian $\hat{H}_i$, which depends on the total spin operator $\hat{\boldsymbol{S}}$. Linear by $\boldsymbol{H}$ approximation, this contribution can be written in the form[31]

$$\hat{V} = -\frac{e\hbar}{2mc}(\hat{\boldsymbol{L}} + 2\hat{\boldsymbol{S}})\boldsymbol{H}. \tag{3}$$

Here, $\hat{\boldsymbol{L}}$ is the operator of the total angular momentum of the system of N electrons. An external magnetic field thus results in a linear by $\boldsymbol{H}$ Zeeman splitting of the ground state triplet term. One can present the corresponding energy splitting in the form of $\Delta E_H=\mu_B g^{*} H$, where g^{*} is the effective Lande factor. It should be noted that there is a splitting of each of the vibrational terms of the i-configuration.

The coincidence of the Zeeman components of the ground and excited levels of the i-configuration takes place at the magnetic field strength H_0, determined by the condition $\Delta E_H=\Delta E_m$, so that the transitions between these levels are possible at $H \approx H_0$. Such transitions, accompanied by either emission or absorption of a magnon, lead to a change of the spin configuration $(S_i=1 \rightarrow S_i^{*}=0)$ and to the corresponding change of the orbital wave function, in Eq. (2), denoted as $|n,*;i\rangle$.

It is clear that the magnetic field strength H_0 is determined by a specific feature of the electron-electron interaction as well as by quantization of "magnon" excitations. These excitations may exist inside the DMD. Let us suppose that L is a characteristic linear scale of the DMD. A separation between any two neighboring size-quantized levels can then be estimated as $\Delta E_m \sim \hbar^2/2mL^2$. In the case of a sufficiently small L, the contribution of the size quantization into the ΔE_m turns out to be predominant. In such a case, one can estimate a quantization scale L. For example, considering a point DC, one should take into account the fact that the elastic stress due to the DC decreases with the distance r from the DC as r^{-3}, so that the scale L can be estimated as $L \sim n_d^{-1/3}$, where n_d is the DC volume concentration. Hence, $\Delta E_m \sim \hbar^2 n_d^{2/3}/2m$, and the estimation of the magnetic field strength H_0 can be written in the form

$$H_0 \sim \frac{\hbar c}{g^{*} e} n_d^{2/3}. \tag{4}$$

For a typical value of the DC concentration $n_d \sim 10^{15}$ cm^{-3}, Eq. (4) gives $H_0 \sim 1-10$ kOe, which is in good agreement with the experimental data available.

The decay of the metastable state of the DC (DC*) is not forbidden by spin and results in a transformation of the DC into RP's. If the RP's do not have a lattice distortion resulting in a magnetoactive branch in the elementary excitation spectrum, the reverse transition RP's →DC turns out to be spin forbidden. In such a case, a transition from the metastable RP state into the stable DC state may occur only with weak spin-orbit interaction. This transition may be considered as a microscopic mechanism of the after-treatment long-time relaxation, which is controlled by the diffusion of RP's.

As pointed out previously, the probability of the transition $f \rightarrow i$, determined by Eq. (2), corresponds to an "instantaneous" change of the Hamiltonian. That is why the transition from a given initial state turns out to be possible into any one of the final states $|n';f\rangle$. Keeping in mind that the change of the Hamiltonian $\hat{H}_i \rightarrow \hat{H}_f$ takes place during a finite time interval Δt, corresponding to a characteristic time of emission or absorption of a magnon, one can conclude that the transitions from a vibrational level n are allowed only into the levels n' inside an energy interval $\Delta E \sim \hbar/\Delta t$ in close proximity to the energy corresponding to the n level. Let us assume that spin levels of the metastable DC* are populated due to the well-known Δg mechanism with a characteristic time $\sim 10^{-9}-10^{-8}$ sec. The nonequilibrium population of the metastable DC* level survives when the spin-lattice relaxation is slower process $(\sim 10^{-7}$sec).[18] The transformation DC* → RP's is controlled by transitions in the electron subsystem and corresponds to a shorter characteristic time $\Delta t \ll 10^{-9}$ sec.Thus, the energy interval ΔE considerably exceeds a separation between neighboring vibrational levels of the RP term.

V. DISCUSSION

A comparison of our scenario of spin-dependent defect reactions in nonmagnetic solids with the conception of spin effects in chemical reactions of radical pairs in liquids elucidates the principal difference in the role of the media.

In spin chemistry, a liquid medium is considered as a nonmagnetic uniform unstructured viscous continuum inhibiting the molecular kinetics of radicals and keeping the radical pairs in the reaction zone (the "cage" effect).[17,20] Since the magnetic field-induced change of the spin state of the radical pair is impossible in an isolated system of two radicals (excluding a special case of the S–T_0 transitions), one needs a "third particle" to conserve the total angular momentum of the radical pair. It is believed that such a third particle may be a nucleus of one of the radicals participating in the spin-dependent reaction by the hyperfine interaction.[17,19]

The ideal crystal under consideration has a symmetry that does not permit any magnetic ordering. It is in the defect crystals where the lattice magnetism appears. The lattice distortion in the extended vicinity of the defect may result in a nonuniform magnetization corresponding to a magnetoactive branch in the spectrum of elementary excitations. The appearance of a magnon-type excitation, localized in the DMD, may be associated with noncompensated orbital currents manifesting themselves as fluctuations of the magneto-ordered state. It is the magnetization of the distorted lattice that plays a role of the third particle providing the conservation of the total angular momentum in the transition between the ground and excited states of the DC. The external magnetic field leads to the Zeeman splitting both of the ground and excited levels of the DC, thus providing a possibility of transitions between the crossed Zeeman levels. Thus, there is no need to involve the nuclear magnetism[32] for the explanation of the experimentally observed threshold in the magnetoplastic effect.

A macroscopic manifestation of spin-dependent reactions both in liquids and solids is a change of the reaction yield due to a chemical equilibrium shift initiated by an external magnetic field. In the framework of the scenario of magnetic field-induced defect reactions in nonmagnetic crystals, a rise of mobile RP's resulting from a decay of the DC's corresponds to a nonequilibrium state of the defect subsystem. Thus, there arises a trend of some kind of a homogenization of the defect structure due to diffusion flows, resulting in an establishment of an equilibrium space distribution of RP's. However, such a new equilibrium state turns out to be metastable because of the thermodynamic tendency towards a restoring of the initial concentration of the DC's. The restoration of DC's after a magnetic field treatment caused by the spin-orbit interaction leads to a lowering of the free energy of the crystal. In the framework of our consideration, it is the spin-orbital interaction that controls this last stage of crystal structure evolution after the magnetic field treatment.

The transitions into the metastable state are controlled by a diffusion time that can be estimated as $\tau_h \sim D^{-1} n_d^{-2/3}$, where D is a diffusion constant of the RP's, and $L \sim n_d^{-1/3}$ is an average distance between the DC's. These parameters also control the establishment of chemical equilibrium. The corresponding characteristic time t_r differs from the t_h only by a "capture coefficient" $K > 1$ connected with the probability of the transition $f \to i$ due to the spin-orbit interaction during an "inelastic collision" of two RP's, $\tau_r = K\tau_h$.

Using the values of $t_h \approx 200$ h, $t_r \sim 1000$ h (see Fig. 2), and a reasonable initial concentration of DC's $n_d \sim 10^{15}\ \mathrm{cm}^{-3}$, one can estimate the diffusion coefficient of the RP's as $D \sim 10^{-17}\ \mathrm{cm}^2/\mathrm{sec}$. Such an estimation is in good agreement with the data[33] related to considerably higher temperatures. The possible reasons for an enhancement of the low-temperature diffusion after the PMF treatment were discussed earlier.[5]

The diffusion character of the defect structure evolution after magnetic field treatment allows one to conclude that a temperature increase should result in a suppression of the effects of PMF treatment, since the characteristic times τ_h and τ_r decrease exponentially with an increase of the storage temperature of the treated samples. An increase of PMF treatment temperature should also lead to an attenuation of this effect manifestation due to either a decrease of defect-induced order parameter or temperature suppression of magnetization fluctuations in the DMD.

Following the above developed hypothesized scheme, one can predict one more temperature effect that may be called "a temperature window" of defect reaction rate enhancement. Taking into account the temperature dependence of the partition function $w_n(T)$ and also the fact that the overlap integral $\langle f; n' | n, *; i \rangle$ in Eq. (2) has a maximum when the vibrational levels n and n' are situated in a vicinity of the crossing point of the electron terms corresponding to the DC and RP's, one can come to a conclusion that the probability $P_{fi}(T)$ of the DC → RP transition must have a maximal value at a certain temperature T_0. Therefore, this transition should be clearly pronounced near T_0, exhibiting "a temperature window" for the effect.

The defect reactions occur when the magnetic field strength is equal to H_0, [Eq. (4)]. Therefore, one can easily detect such reactions "scanning" a crystal by magnetic pulses with linear fronts under the condition that the pulse magnitude should be higher than H_0. Thus, PMF-induced effects must be characterized by a threshold strength H_0 exhibiting a saturation in the fields over H_0. The number of pulses must be sufficient in order to provide the time necessary for the transition $\mathrm{DC} \to \mathrm{DC}^*$. In this connection, it should be noted that the spin-dependent reactions have been also observed both in the case of constant magnetic field treatment,[13] with the strength corresponding to H_0, and in the case of microwave treatment.[34,35]

In conclusion, there may be a wide range of applications for the PMF-induced effects in material science for controlled modification of defect structure and properties of a number of solid-state materials.

Note added in proof. We have recently learned of a paper[36] in which the effect of magnetic field exposition on dislocation mobility in high-oxygen silicon crystals is observed. The effect is supposed to be due to spin-dependent transitions in silicon-oxygen complexes in the dislocation core and, thus, is strongly dependent on the defect structure. The magnetic effects were not observed in the low-oxygen silicon crystals.[5,36] Therefore, in order to obtain the reproducibility of the magnetic field effects, one should carefully control the defect structure of the solids under investigation.

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[1] G. L. Distler, V. M. Kanevsky, V. V. Moskvin, S. N. Postnikov, L. A. Rjabinin, V. P. Sidorov, and G. D. Shnyrev, Dokl. Akad. Nauk **268**, 591 (1983) [Sov. Phys. Dokl. **28**, 43 (1983)].

[2] V. I. Alshits, E. V. Darinskaya, and T. M. Perekalina, Fiz. Tverd. Tela (Leningrad) **29**, 467 (1987) [Sov. Phys. Solid State **29**, 265 (1987)].

[3] V. I. Alshits, E. V. Darinskaya, O. L. Kazakova, E. Yu. Mikhina, and E. A. Petrzhik, J. Alloys Compd. **211/212**, 548 (1994), and references therein.

[4] M. N. Levin and V. M. Maslovsky, Solid State Commun. **90**, 813 (1994).

[5] M. N. Levin and B. A. Zon, Zh. Eksp. Teor. Fiz. **111**, 1373 (1997) [JETP **84**, 760 (1997)], and references therein.

[6] M. N. Levin and B. A. Zon, Phys. Lett. A **260**, 386 (1999).

[7] V. P. Vlasov, F. A. Zaitov, V. M. Kanevsky, A. A. Purtzhvanidze, and G. M. Shaljapin, Fiz. Tverd. Tela (Leningrad) **34**, 3264 (1992) [Sov. Phys. Solid State **34**, 1747 (1992)].

[8] V. N. Davydov, E. A. Loskutova, and E. P. Nayden, Fiz. Tekh. Poluprovodn. (S.-Peterburg) **23**, 1596 (1989) [Sov. Phys. Semicond. **23**, 989 (1989)].

[9] E. A. Petrzhik, E. V. Darinskaya, S. A. Erofeeva, and M. R. Raukhman, Fiz. Tverd. Tela (Leningrad) **45**, 254 (2003) [Phys. Solid State **45**, 266 (2003)].

[10] M. N . Levin, G. V. Semenova, and T. P. Sushkova, Dokl. Akad. Nauk **388**, 608 (2003) [Dokl. Phys. **48**, 62, (2003)].

[11] M. N. Levin, G. V. Semenova, T. P. Sushkova, V. V. Postnikov, and B. L. Agapov, Fiz. Tverd. Tela (Leningrad) **45**, 609, (2003) [Phys. Solid State **45**, 639 (2003)].

[12] M. N. Levin, V. V. Postnikov, M. Yu. Palagin, and A. M. Kostsov, Fiz. Tverd. Tela (Leningrad) **45**, 513 (2003) [Phys. Solid State **45**, 542 (2003)].

[13] M. N. Levin, V. V. Postnikov, and M. Yu. Palagin, Ferroelectrics **285**, 173 (2003); Fiz. Tverd. Tela (Leningrad) **45**, 1680 (2003) [Phys. Solid State **45**, 1763 (2003)].

[14] M. N. Levin, V. V. Postnikov, and M. A. Dronov, Pis'ma Zh. Tekh. Fiz. **29**, 7 (2003) [Tech. Phys. Lett. **29**, 444 (2003)].

[15] Yu. I. Golovin and R. B. Morgunov, Fiz. Tverd. Tela (Leningrad) **43**, 827 (2001) [Phys. Solid State **43**859 (2001)].

[16] M. N. Levin, V. V. Postnikov, and N. N. Matveev, Zh. Fiz. Khim. **77**, 758 (2003) [Russ. J. Phys. Chem. **77**, 675 (2003)], and references therein.

[17] K. M. Salikhov, Yu. N. Molin, R. Z. Sagdeev, and A. L. Buchachenko, *Spin Polarization and Magnetic Effects in Radical Reactions* (Elsevier, Amsterdam, 1984).

[18] Ya. B. Zel'dovich, A. L. Buchachenko, and E. L. Frankevich, Usp. Fiz. Nauk **155**, 3 (1988) [Sov. Phys. Usp. **31**, 385 (1988)].

[19] U. E. Steiner and T. Ulrich, Chem. Rev. (Washington, D.C.) **89**, 51 (1989).

[20] K. A. McLauchlan and U. E. Steiner, Mol. Phys. **73**, 241 (1991).

[21] M. I. Molotskii, Fiz. Tverd. Tela (Leningrad) **33**, 3112 (1991) [Phys. Solid State **33**, 1760 (1991)]; M. I. Molotskii and V. Fleurov, Phys. Rev. Lett. **78**, 2779 (1997).

[22] Yu. I. Golovin and R. B. Morgunov, in *Advances in Mechanochemistry: Chemistry Reviews* (Harwood Academic, Amsterdam, 1998), Vol. 23, Pt. 2, pp. 23–58; Zh. Eksp. Teor. Fiz. **115**, 605 (1999) [JETP **88**, 332 (1999)].

[23] V. A. Zakrevskii, V. A. Pakhotin, and A. V. Shul'diner, Fiz. Tverd. Tela (Leningrad) **44**, 1990 (2002) [Phys. Solid State **44**, 2083 (2002)].

[24] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Nauka, Moscow, 1982; Pergamon, Oxford, 1984).

[25] B. I. Halperin and T. M. Rice, Solid State Phys. **21**, 115 (1968).

[26] B. A. Volkov, A. A. Gorbatsevich, Yu. V. Kopaev, and V. V. Tugushev, Zh. Eksp. Teor. Fiz. **81**, 729 (1981) Sov. Phys. JETP **54**, 391 (1981)].

[27] I. Affleck and J. B. Marston, Phys. Rev. B **37**, 3774 (1988).

[28] H. J. Schulz, Phys. Rev. B **39**, 2940 (1989).

[29] S. Chakravarty, R. B. Laughlin, D. K. Morr, and C. Nayak. Phys. Rev. B **63**, 094503 (2001).

[30] X.-G. Wen and P. A. Lee, Phys. Rev. Lett. **76**, 503 (1996); P. A. Lee,N Nagaosa, T K Ng, and X.-G. Wen, Phys. Rev. B **57**, 6003 (1998).

[31] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Non-Relativistic Theory* (4th ed., Nauka, Moscow; 3rd ed., Pergamon, Oxford, 1977).

[32] M. Molotskii and V. Fleurov, Phys. Rev. B **56**, 10809 (1997).

[33] D. J. Fisher, *Diffusion in GaAs and Other III-V Semiconductors: 10 Years of Research* (Trans. Tech., 1998).

[34] V. K. Novik, G. I. Ovchinnikova, Yu. A. Pirogov, and A. N. Soloshenko, Izv. Ross. Akad. Nauk, Ser. Fiz. **64**, 2452 (2000).

[35] M. I. Molotskii, Mater. Sci. Eng., A **287**, 248 (2000); Yu. I. Golovin, R. B. Morgunov, and A. A. Dmitrievsky, *ibid.* **288**, 261 (2000).

[36] M. V. Badylevich, Yu. L. Iunin, V. V. Kveder, V. I. Orlov, and Yu. A. Osipyan, Zh. Eksp. Teor. Fiz. **124**, 664 (2003) [JETP **97**, 610 (2003)].