PHYSICAL REVIEW B **73**, 054429 (2006)

Defect-induced lattice magnetism: Phenomenology of magnetic-field-stimulated defect reactions in nonmagnetic solids

V. I. Belyavsky
P. N. Lebedev Physical Institute, Russian Academy of Sciences, Moscow, 119991, Russia

M. N. Levin
State University, Voronezh, 394006, Russia

N. J. Olson
Pacific Northwest National Laboratory, Richland, Washington 99352, USA

(Received 3 November 2005; revised manuscript received 12 December 2005; published 22 February 2006)

We develop the phenomenology of magnetic-field-stimulated defect reactions in nonmagnetic solids based on the concept of defect-induced lattice magnetism (DILM) associated with a rise of spontaneous orbital currents in the elastic strain field produced by a defect. We present the hierarchy of all magnetic symmetry classes corresponding to the current structures with long-range or short-range orbital antiferromagnetic order depending on the perfect crystal symmetry and the symmetry of the defect-induced strain field. This strain field can result in a confinement of orbital currents and gives rise to size-quantized orbital magnon excitations. An external magnetic field leads to the splitting of magnon levels and causes the transitions between some of the intersecting Zeeman sublevels. The excitation of orbital magnon from the discrete size-quantized level into the continuous spectrum can be considered as the principal stage of magnetic field stimulated defect reactions. One can consider the DILM phenomenology as a contribution to a new field of solid state physics which could be termed the *spin chemistry of solids*.

DOI: 10.1103/PhysRevB.73.054429 PACS number(s): 75.10.−b, 78.47.+p, 78.66.−w, 61.72.−y

I. INTRODUCTION

An external magnetic field can have a pronounced effect on molecular reactions in liquids[1,2] and on reactions of defects in solids.[3,4] Spin chemistry studies[1,2] of the kinetics of the molecular reactions are based on the assumption that the total spin should be conserved during a chemical reaction. The effect of an external magnetic field can result in a spin conversion and, therefore, promote a change in the reaction yield. It is agreed that the spin conversion may occur either due to the difference in the Zeeman energies of the unpaired electrons of a *radical pair*, i.e., the two molecular complexes with unsaturated electron spins, or due to the hyperfine interaction of the electron spins of the radical pair with a nuclear spin. In the latter case, the nuclear spin plays a role of the *third particle* providing the total spin conservation. The magnetic field can change the probability of a molecular reaction if the lifetime of the radical pair is much longer than the time of magnetic-field-induced repopulation of the spin levels, but much shorter than the time of the spin relaxation restoring the initial population of the spin levels due to an interaction of the radicals with the liquid media.[1,2]

The validity of the spin chemistry approach for an explanation of the magnetic-field effect on defect reactions in solids raises doubts[5] because of the uncertainty of the nature of radical pairs in crystals. For example, the unpaired spin of the partly occupied internal electron shell of a paramagnetic impurity, considered as one of the components of the radical pair in the explanation[6,7] of the magnetoplastic effect, does not mean that such an impurity exhibits itself as a radical, because the reactions between defects are primarily caused by the external valence electrons. The speculations[6,7] relating to a dangling bond in the core of a topological defect (e.g., a dislocation, as another component of the radical pair) ignore the highly probable reconstruction of the core. The strained covalent bond under sufficiently large deformation (actually corresponding to the break of the bond) could become a radical pair[4] but the lifetime of such a pair is apparently not long enough to produce the inverse population of the spin levels in the magnetic field.[5]

It is reasonable to conclude that the difficulty of interpretation of the magnetic-field effect on the solid state defect structure lies not only in the magnetic Zeeman energy weakness in comparison with the thermal energy but, mainly, in the likely absence of radical pairs as the objects of the effect. The fact that the numerous macroscopic manifestations of magnetic-field-induced defect reactions are observed in nonmagnetic crystals notably different in the structure and chemical composition allows one to propose that there exists a universal mechanism of such reactions associated with the nature of the electron spectrum and the quantum states of solids. Therefore it is highly probable that the magnetic field effect on defect reactions in solids admits a unified phenomenology.[8]

In molecular reactions, the transitions between the orbital states in an external magnetic field are not taken into consideration because the Zeeman energy is negligible in comparison with the distance between the ground and the first excited molecular terms. That is why one can assume, following the spin chemistry approach, that there is a conservation of the total spin $\boldsymbol{S}$, in spite of the fact that the conserved quantity is the total angular momentum $\boldsymbol{J}=\boldsymbol{L}+\boldsymbol{S}$, where $\boldsymbol{L}$ is the total orbital angular momentum.

The effect of magnetic field on the defect reactions in solids can be described within the framework of the phenomenology[8] based on the assumption that, in the extended vicinity of the defect, there are magnetoactive branches in the spectrum of elementary excitations associated with the orbital degrees of freedom. The band electron spectrum of a solid permits the transitions with the simultaneous change of the orbital angular momentum and the spin due to comparatively weak spin-orbit interaction. If the excitation of the orbital degrees of freedom is accompanied by a rise of spontaneous orbital currents, the appearance of a magnetoactive branch can be referred to the quasiparticle (*orbital magnon*) with the orbital angular momentum $L=1$ playing the role of the third particle which provides conservation of the total angular momentum. Therefore *orbital physics*[9,10] complements spin chemistry in the description of magnetic-field-induced defect reactions in solids.

In this work, we develop the concept of defect-induced lattice magnetism (DILM)[8] which is associated with the rise of spontaneous orbital currents in the elastic stress field created by the defect. A survey of the DILM phenomenology of the magnetic-field-stimulated defect reactions in crystals is contained in Sec. II. In Sec. III, we present group theory classification of orbital current structures compatible with the point symmetries of the crystal and defect-induced elastic stress field. Section IV deals with the thermodynamics of the antiferromagnetic orbital long-range and short-range ordered states. Section V addresses orbital magnons confined by the extended stress field vicinity of the defect. In Sec. VI, we estimate the rate of the defect reaction assisted by orbital magnon emission. In Sec. VII, we demonstrate the possibility that magnetic-field-induced effects can be studied using precise spectroscopy methods. Finally, possible manifestations of orbital physics on the magnetic-field-stimulated defect reactions in solids are discussed in Sec. VIII.

II. MAGNETIC-FIELD-INDUCED DEFECT REACTIONS IN SOLIDS

The effects under consideration are the observed changes in defect structure of nonmagnetic crystals after their treatment by an external magnetic field. There are no magnetoactive branches, similar to spin waves, in the spectrum of elementary excitations of such crystals without defects. It is natural to assume that *defects themselves are the origin of the appearance of the magnetoactive branches*, associated with spontaneous orbital currents in an extended distorted vicinity of the defect. The external magnetic field can excite the size-quantized orbital magnons confined in the vicinity of a defect.[8] Due to the total angular momentum conservation, the emission (or absorption) of the orbital magnon with a change of the orbital angular momentum $\Delta L=\pm 1$ is accompanied by a change of the total spin of the electron system $\Delta S=\pm 1$. Thus the Zeeman interaction of the spin subsystem with an external magnetic field can result in a change of the total spin.

As a simple example of the defect reaction, one can consider a decay of a defect complex (DC) into some defects treated as reaction products (RPs).[8] To describe this reaction qualitatively, we restrict ourselves to one-dimensional configuration space with the only reaction coordinate Q corresponding to the atomic displacements in the process of the transition from the DC atomic configuration into the RPs configuration. A set of adiabatic energy levels corresponds to any value of the coordinate reaction and each of these levels can be referred to definite values of the total spin S and total orbital angular momentum L, if one can neglect the spin-orbit interaction.

For the sake of simplicity, we suppose that the DC can be the origin of the confined orbital magnons whereas the RPs cannot. The two possibilities of the intersection of the ground terms corresponding to spin allowed and forbidden transitions $\mathrm{DC}\leftrightarrow\mathrm{RPs}$, respectively. The *anticrossing* of the terms due to the degeneration lifting in the intersection point of DC and RPs ground state levels occurs at the equal values of the total spin of DC and RPs electron subsystems. This leads to a rise of the ground and excited energy terms. The first of them has two local minima, which can be referred to the DC (with the lower energy) and RPs, respectively. In such a case, any reasonable magnetic field cannot affect the thermally activated transition $\mathrm{DC}\rightarrow\mathrm{RP}$ because of the large energy separation ΔE between the ground and the first excited levels in the saddle point configuration.

There is a *crossing* of the ground energy state terms of the DC and RPs with different values of the total spin. In such a case, the transitions between the DC and RPs are spin forbidden when one neglects weak spin-orbit interaction. The thermal activation of the DC gives rise to the filling of the vibrational levels including those lying above the crossing point. This can be considered as a transition of the DC into a metastable state. In the absence of the spin-orbit interaction, the transitions between the vibrational levels of the metastable DC and the RPs ground terms are spin forbidden.

The magnetoactive branch in the quasiparticle spectrum gives rise to an excitation of the DC corresponding to its transition into an intermediate metastable state DC^*. If the values of the total spin of the DC^* and RPs coincide, the transition $\mathrm{DC}^*\leftrightarrow\mathrm{RPs}$ turns out to be allowed. Indeed, one can assume that there is at least one size-quantized magnetoactive sublevel associated with each of the vibrational levels of the DC. Following this assumption, there is a possibility of the transition of the electron subsystem into such a sublevel. The transitions between the vibrational levels of the DC^* and RPs become allowed if the difference in their values of the orbital angular momentum is compensated by orbital magnon angular momentum. The magnon provides the conservation of the total angular momentum of the DC configuration. It should be noted that the thermal excitation of the magnon sublevels of each of the DC ground term vibrational levels is spin forbidden. Transitions onto the size-quantized orbital magnon sublevels can emerge in external magnetic field under the condition that its strength corresponds to the Zeeman energy exceeding the energy separation between the sublevels. The excitation $\mathrm{DC}\rightarrow\mathrm{DC}^*$ accompanied by orbital magnon emission allows the subsequent transition $\mathrm{DC}^*\rightarrow\mathrm{RP}$ which completes the defect reaction.

The phenomenology describing the effect of comparatively weak magnetic fields on the defect structure of nonmagnetic crystals is based on the assumption that there arise spontaneous orbital currents in an extended crystal lattice region distorted by a defect. This phenomenology is not able

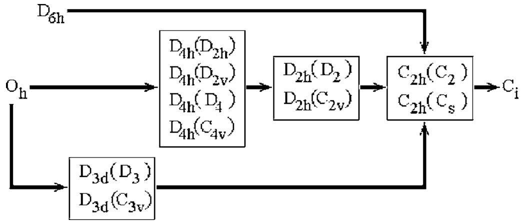

FIG. 1. The hierarchy of magnetic symmetry classes. According to the conventional notation (Ref. 12), the symbol $G(H)$ corresponds to a reduction of the crystal symmetry to the magnetic symmetry due to a rise of spontaneous currents. G has the meaning of the charge density symmetry group whereas H is the current density symmetry group (Ref. 12). Arrows show the possibilities of charge symmetry lowering due to homogeneous deforming of a nonmagnetic crystal. For example, there are three possibilities to realize the magnetic symmetry $C_{2h}(C_2)$: $D_{6h} \rightarrow C_{2h}(C_2)$, $D_{3d} \rightarrow C_{2h}(C_2)$, and $D_{2h} \rightarrow C_{2h}(C_2)$.

to estimate quantitatively the magnetic field sensitivity of the particular defect reaction in the given crystal. To address this problem, one needs an approach based on an appropriate microscopic theory taking into account inherent features of the electron states of the crystal. However, the phenomenological approach allows one to classify all orbital current structures consistent both with the crystal symmetry and the symmetry of the elastic strain field associated with the defect.

III. DEFECT-INDUCED MAGNETIC SYMMETRY BREAK

Because of the break of the translation symmetry in crystals with defects, it is sufficient to consider the symmetry of directions outgoing from some point in the core of the defect. This symmetry break is similar to that which arises in the case of uniform infinitesimal continuous deformation of the unit cell. Therefore the determination of possible magnetic symmetry manifested in a vicinity of the defect can be associated with the well-known hierarchy of crystal classes.

Deformation excludes some symmetry operators from the point symmetry group (crystal class G_0) of the perfect crystal. According to the hierarchy of groups,[11] the crystal class G of the uniformly deformed crystal is one of the subgroups of the group G_0. Such a hierarchy of the holohedral crystal classes is presented in Fig. 1 for all of the seven crystal systems. It is supposed that there is no magnetic symmetry in the case of the crystal classes of the highest symmetry (cubic O_h and hexagonal D_{6h}).

The crystal symmetry can be defined as the symmetry of the average microscopic charge density, $\rho(\boldsymbol{r})$. The function $\rho(\boldsymbol{r})$ is invariant with respect to all symmetry operators of the point group G as well as with respect to the time reversal operator R: $R\rho(\boldsymbol{r}) = \rho(\boldsymbol{r})$.[12] One can define the extended point group as the direct product, $G \times K$, of the crystal point group G and the group K consisting of the two elements; the identity operator and R. Note that the extended point group of the perfect crystal, $G_0 \times K$, contains twice as many symmetry operators (the set of operators $G_0 + RG_0$) as compared to the crystal symmetry group G_0.

As the average microscopic current density, $\boldsymbol{j}(\boldsymbol{r})$, is noninvariant with respect to the time reversal operator, $R\boldsymbol{j}(\boldsymbol{r}) = -\boldsymbol{j}(\boldsymbol{r})$, the extended point group turns out to be a magnetic symmetry point group of a crystal without any magnetic structure [in such a case $\boldsymbol{j}(\boldsymbol{r}) \equiv 0$]. It should be noted that the charge density cannot become zero and can be defined in all solids whereas the nonzero current density can only be defined in a relatively few magneto-ordered crystals.[12]

There are two possibilities of the deformation-induced magnetic response in a crystal: (1) spontaneous currents do not arise, therefore the extended point symmetry group of the undeformed crystal $G_0 \times K$ transforms into the extended point symmetry group $G \times K$ being the magnetic symmetry group of the deformed crystal; and (2) in the case of a rise of spontaneous currents, the time reversal operator R altering the currents cannot itself enter the magnetic symmetry point group. Therefore half of the symmetry operators, including the time-reversal operator R, should be excluded from the extended point symmetry group of the deformed crystal to obtain its magnetic point symmetry group. The set of elements of the magnetic point symmetry group can be represented as $G(H) = H + RgH$, where H is a subgroup of index 2 of the group G (G contains twice as many symmetry operators as compared to the subgroup H) and g is a symmetry operator from G which does not enter into H.

If the order of the extended point symmetry group $G \times K$ is equal to $2n$, the order of the magnetic symmetry point group becomes equal to n. Thus a rise of spontaneous currents leads to a break of magnetic symmetry of the crystal. As the spontaneous currents exclude the symmetry operators gH, the subgroup H actually determines the symmetry of the spontaneous currents which give rise to a magnetic ordering inside the distorted region of the crystal lattice around the defect.

IV. DEFECT-INDUCED ORBITAL MAGNETIC ORDER

Magnetic order usually arises in the crystals with partially filled internal electron shells with spatially localized spins. For ferromagnets or antiferromagnets, the current density $\boldsymbol{j}(\boldsymbol{r})$ is determined by the space distribution of spin magnetic moments. In the general case, the total magnetic moment arises as a sum of the spin magnetic moment and orbital magnetic moment. That is why the magnetic order can also arise in the crystals without any localized spins. In such crystals the average current density should be associated with the orbital motion of electrons.

The excitation of orbital circular (within the unit cell) currents leads to an increase of the kinetic energy which can be (partly) compensated by the interaction of antiferromagnetically ordered currents. The concept of orbital antiferromagnetism (OAF) introduced by Halperin and Rice[13] in the theory of exciton insulators was developed later as the theory of toroidal magnetic ordered state.[14] Recently, this issue became one of the most debatable points in physics of heavy fermions[15] and layered quasi-two-dimensional compounds.[16]

The concept of OAF is an important issue in solid state physics although striking evidence of the long-range OAF order in some kind of crystals is apparently absent. This may be due to a rather weak response of such an order to external excitations.[16,17] In this sense, the long-range OAF order can be considered as a *hidden order*.[15,16] Using circularly polarized photons in the angle resolved photoemission (ARPES) technique, Kaminskii *et al.*[18] have observed the time reversal symmetry break in the pseudogap state of the cuprate compound $\mathrm{Bi_2Sr_2CaCu_2O_{8+x}}$ that can probably be referred to OAF hidden order.

The distortion of the crystal lattice can result in a redistribution of already existing spontaneous currents. For example, in spin antiferromagnets, the elastic strain leads to a nonequivalence of the AF sublattices. Due to this nonequivalence, there arises linear strain macroscopic magnetization (the piezomagnetic effect).[12]

A rise of orbital spontaneous currents under deformation of the nonmagnetic crystal can be considered as a manifestation of the piezomagnetism as well. The circular AF ordered orbital currents corresponding to such an *orbital piezomagnetism* do not result in a macroscopic magnetization. This restricts the number of magnetic crystal symmetry classes arising in distorted nonmagnetic crystals. Indeed, one has to exclude the Index 2 subgroups corresponding to ferromagnetic order from the hierarchy of the holohedral classes according to Fig. 1.

The magnetic order associated with spontaneous orbital currents breaking the magnetic symmetry of the crystal, $G\times K\Rightarrow G(H)$, is determined by the orbital currents inside the *magnetic* unit cell. The magnetic dipole moment of this unit cell is equal to zero. Therefore the orbital current distribution corresponds to a magnetic multipole and one can consider its irreducible components as the components of the OAF order parameter. In the simplest case, the order parameter, $\boldsymbol{\Lambda}=\boldsymbol{M}_1-\boldsymbol{M}_2$, can be defined in terms of the magnetizations, $\boldsymbol{M}_1$ and $\boldsymbol{M}_2$, of the two magnetic sublattices (in the absence of an external magnetic field, $\boldsymbol{M}_2=-\boldsymbol{M}_1$).

The magnetization of the magnetic sublattice arises due to comparatively weak magnetic fields of circular orbital currents; therefore one can consider the OAF order parameter to be small at any temperature. The Landau free energy functional can be represented as an expansion in powers of the components Λ_x, Λ_y, Λ_z of the vector $\boldsymbol{\Lambda}$,

$$F\{\boldsymbol{\Lambda}\} = \int d^3r(f_g + f_2 + f_4), \tag{1}$$

where the integration should be performed over the volume of the crystal. The terms f_2 and f_4 are the contributions into the free energy density of the second and fourth order, respectively. The *gradient* contribution, f_g, is the corresponding second order combination of space derivatives of the components of the order parameter. These combinations of the components and their space derivatives should be invariant under all transformations of the group $G(H)$. The thermal equilibrium components of the order parameter correspond to the absolute minimum of the Landau functional (1).

For the sake of simplicity, we restrict ourselves to the case of the perfect crystal of the cubic symmetry O_h and suppose that a defect reduces the crystal symmetry to the tetragonal case, $O_h\rightarrow D_{4h}$. The elastic strain created by the defect varies smoothly enough in the vicinity of the defect so that one can neglect the gradient term f_g in the free energy density. In cubic crystals, there are the only invariant of the second order, $\Lambda^2=\Lambda_x^2+\Lambda_y^2+\Lambda_z^2$, and two invariants of the fourth order, $J_1=\Lambda_x^4+\Lambda_y^4+\Lambda_z^4$, $J_2=\Lambda_x^2\Lambda_y^2+\Lambda_y^2\Lambda_z^2+\Lambda_z^2\Lambda_x^2$. A variation of the free energy density due to a rise of the locally uniform OAF order can be represented in the form

$$f_2^{(0)} + f_4^{(0)} = a\Lambda^2 + b_1J_1/2 + b_2J_2/2, \tag{2}$$

where the upper index (0) indicates the perfect crystal symmetry, G_0. The coefficient a in the second-order term in the Landau free energy density (2) has to become zero on the phase transition line[19] being negative in the ordered low-temperature phase. Because of our assumption that there is no long-range magnetic order in the perfect crystal, the coefficients a, b_1, and b_2 in the expansion (2) should be positive. Therefore all of the equilibrium values of the components of the order parameter should be equal to zero.

The symmetry change, $G_0\rightarrow G$, in the distorted vicinity of the defect leads to a modification of the structure of the invariants in the Landau functional. The uniform contribution, f_2+f_4, into the free energy density should be represented as a sum of new invariants corresponding to the reduced symmetry, G. Thus the coefficients in the Landau expansion turn out to be dependent on the strain tensor, u_{ik}. For the sake of simplicity, we assume that the fourth-order terms are weakly dependent on u_{ik}. This allows one to consider these terms to be the same as in the perfect crystal. Such an approximation cannot affect the equilibrium OAF order qualitatively. On the contrary, the dependence of the second-order terms on the strain tensor may turn out to be essential, since distortion can result in the sign reversal of some of these terms. We restrict ourselves to a consideration of the linear dependence of the coefficients in the second-order terms on the strain tensor. This approximation corresponding to orbital piezomagnetism allows one to present the second-order contribution into the free energy density as

$$f_2 = a\Lambda^2 - \alpha u_{ik}\Lambda_i\Lambda_k, \tag{3}$$

where the summation over repeating indices $i,k=x,y,z$ is understood. Without loss of generality, one can assume that the phenomenological piezomagnetic constant $a>0$.

The only nonzero component of the strain tensor corresponding to tetragonal distortion of the cubic crystal along the z axis is $u_{zz}\equiv u$, therefore the uniform contribution into the free energy density takes the form

$$f_2 + f_4 = a(\Lambda_x^2 + \Lambda_y^2) + (a - \alpha u)\Lambda_z^2 + \frac{b_1}{2}J_1 + \frac{b_2}{2}J_2, \tag{4}$$

where the two second-order invariants, $\Lambda_x^2+\Lambda_y^2$ and Λ_z^2, with reference to the tetragonal symmetry are written explicitly.

As it follows from Eq. (4), the equilibrium values of transversal, with respect to the fourth-order axis, components of the order parameter are equal to zero independently of the sign and magnitude of the strain, $\langle\Lambda_x\rangle=\langle\Lambda_y\rangle=0$. In the case when $a-\alpha u>0$, the phase transition is forbidden and the equilibrium value of the longitudinal component is equal to zero as well, $\langle \Lambda_z \rangle = 0$. Thus in such a case corresponding to low strain level, the long-range OAF order turns out to be impossible.

In the opposite case, when the strain is high enough, $u > a/\alpha$, the equilibrium value of the z component becomes nonzero,

$$\langle \Lambda_z \rangle = (\alpha u - a)/b_1 . \tag{5}$$

One can see that long-range OAF order arises only under the condition that the strain u is large enough and has a definite sign. This condition may be satisfied for the crystals with a soft mode with respect to an excitation of orbital currents. It is clear that the real strain field in the extended vicinity of the defect is spatially inhomogeneous decreasing with the distance r from the defect, $u = u(r)$. Therefore the solution $r = r_l$ to the equation $\alpha u(r) = a$ can be considered as an estimating length of the region around the defect which manifests *spatially inhomogeneous* long-range OAF order.

In the case when the coefficient a is small enough, the condition that $a < \alpha u$ may be satisfied inside the region where $r < r_l$. The average value of the order parameter is equal to zero outside of the region $r < r_l$, $\langle \Lambda_z \rangle = 0$, however, its fluctuations may turn out to be significant far away from this region. In the more realistic case, when $a > \alpha u$ at any distance from the defect, the long-range order turns out to be impossible. If the coefficient $a - \alpha u$ in the Landau expansion (4) is small enough, one can expect a significant enhancement of fluctuations of the z component of the order parameter, whereas the fluctuations of the other components remain suppressed. Thus one can consider one-component OAF order parameter $\Lambda_z \equiv \Lambda$ and reduce the gradient contribution into the free energy density in the form

$$f_g = g(\nabla \Lambda)^2/2, \tag{6}$$

where g is a phenomenological parameter.

A correlation length r_c of fluctuations of the order parameter can be roughly estimated in the framework of the Ornstein-Zernicke theory,[19]

$$r_c = [g/(a - \alpha \bar{u})]^{1/2}, \tag{7}$$

where $\bar{u}$ is a characteristic elastic strain inside the extended vicinity of the defect. Due to a smallness of the value of $a - \alpha \bar{u}$, the short-range OAF order as developed fluctuations of orbital currents can manifest itself inside a rather wide region around the defect.

V. CONFINED ORBITAL MAGNONS

The Landau free energy functional corresponding to the Ornstein-Zernicke approximation[19] can be written as

$$F\{\Lambda\} = \int d^3 r [g(\nabla \Lambda)^2 + (a - \alpha u(\boldsymbol{r}))\Lambda^2], \tag{8}$$

where the integral is taken over the volume of the crystal. The order parameter $\Lambda = \Lambda(\boldsymbol{r})$ can be determined by the minimization of the functional (8) under the condition that

$$\int d^3 r \Lambda^2 = \text{const.} \tag{9}$$

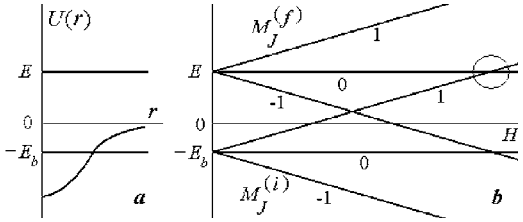

FIG. 2. The effective potential well and orbital magnon spectrum (a). Zeeman splitting of DC levels in the state with total angular momentum $J=1$ (b).

The value of the normalization constant restricting the magnitude of fluctuations of the order parameter is actually determined by the fourth-order terms in the functional (1) which are neglected in the Ornstein-Zernicke theory.

Minimization of Eq. (8) leads to the equation

$$-g\nabla^2 \Lambda + (a - \alpha u(\boldsymbol{r}))\Lambda = \varepsilon \Lambda , \tag{10}$$

where ε is a Lagrange multiplier which should be determined from the condition in Eq. (9). One can see that this equation is formally similar to the one-particle Schrödinger equation. Indeed, one can consider $U(\boldsymbol{r}) \equiv -\alpha u(\boldsymbol{r})$ and $E \equiv \varepsilon - a$ as the potential and total energy of a particle with the effective mass $m = \hbar^2/2g$, respectively.

For the sake of simplicity, we restrict ourselves to the case corresponding to fluctuations of the order parameter in the vicinity of a point defect. In such a case, under the condition that $u(\boldsymbol{r}) > 0$, $U(\boldsymbol{r})$ can be considered approximately as a spherically symmetrical effective attractive potential. The strain created by the point defect with a characteristic core size r_0 decreases with r as $u(r) \approx (r_0/r)^3$ when $r \gg r_0$ and has a finite value $u(0) \approx 1$ when $r \to 0$. Thus the effective potential has the form of a potential well as it is shown schematically in Fig. 2.

A solution to Eq. (10) can be presented in the form

$$\Lambda_{nlm} = R_{nl}(r) Y_{lm}(\vartheta, \varphi), \tag{11}$$

where $Y_{lm}(\vartheta, \varphi)$ is the spherical harmonics depending on the spherical angles ϑ and φ, the function $R_{nl}(r)$ determines the radial dependence of the order parameter, and $\{n, l, m\}$ is a set of the quantum numbers typical of the spherical symmetry.

The parameter E has a meaning of an eigenvalue of Eq. (10). The set of the eigenvalues $E = E_{nl}$ belongs to the discrete spectrum if $-U_0 < E < 0$, whereas there is a continuous spectrum when $E > 0$ (see Fig. 2).

The short-range order magnitude is determined by occupation numbers n_{nlm} of the levels E_{nl}. A change in the occupation number, $\Delta n_{nlm} = \pm 1$, can be considered as absorption or emission of an orbital magnon confined by the effective potential well $U(r)$.

An excitation of the orbital magnon results in a transition of the system into a new orbital state. Such a transition is accompanied by a change $\Delta L = 1$ of the orbital angular momentum. Because of the conservation of the total angular momentum, this simultaneously corresponds to the transition of the system into a new spin state with a change of the total spin $\Delta S=1$. Thus the orbital magnon as an elementary excitation with orbital angular momentum $L=1$ and spin $S=1$ can arise in one of the three states which differ from each other by the value of the total angular momentum J: $J=0,1,2$.

The external magnetic field lifts the degeneracy of magnon levels with $J\neq 0$ both in the discrete and continuous spectrum resulting in the Zeeman splitting of the levels with different projections along the quantization axis. The Zeeman splitting of the levels of confined magnons is presented schematically in Fig. 2. In the case of two levels close to each other, the corresponding Zeeman sublevels with different projections of the total angular momentum can be intersected at a moderate magnetic field strength (Fig. 2). In such a case, the external magnetic field raises one occupied Zeeman sublevel of the discrete level $E=-E_b$ into the continuous spectrum. This occupied sublevel can intersect the unoccupied Zeeman sublevel of the continuous spectrum at $E>0$. It should be noted that the external magnetic field causes not only the crossing of the Zeeman sublevels but can also lead to transitions between these sublevels, allowed by the selection rules.

VI. MAGNON MECHANISM OF DEFECT REACTIONS

To calculate the probability of the transition between the intersecting Zeeman sublevels arising under an external magnetic field one can take advantage of the perturbation theory for the transitions in continuous spectrum.[20] The perturbation operator has the form

$$\hat{V}=\mu_B(\hat{\boldsymbol{L}}+2\hat{\boldsymbol{S}})\boldsymbol{H}, \tag{12}$$

where μ_B and $\boldsymbol{H}$ are the Bohr magneton and magnetic field strength, respectively. The energies of the initial, $|i\rangle$, and final, $|f\rangle$, states are the Zeeman sublevels,

$$E_i=-E_b+\mu_B g_i M_J^{(i)}H, \quad E_f=E+\mu_B g_f M_J^{(f)}H, \tag{13}$$

where g_i (g_f) is the effective Lande factor and $M_J^{(i)}$ ($M_J^{(f)}$) is a projection of the total angular momentum onto the magnetic-field direction for the initial (final) state, respectively.

If one ignores the spin-orbit interaction, the wave functions of the initial and final states, $|M_i\sigma_i\rangle$ and $|M_f\sigma_f\rangle$, with definite values of the projections of the spin, σ_i, σ_f, and orbital angular momentum, M_i, M_f, can be presented as products of the orbital and spin functions. In addition, the final state is characterized by the energy belonging to the continuous spectrum.

The initial and final states with definite values of the projections, $M_J^{(i)}$ and $M_J^{(f)}$, of the conserving total angular momentum J can be presented as linear combinations of the wave functions with definite projections of the spin and orbital angular momentum,

$$|JM_J^{(s)}\rangle=\sum_{M_s\sigma_s}|M_s\sigma_s\rangle\langle M_s\sigma_s|JM_J^{(s)}\rangle, \tag{14}$$

where $s=i,f$, $\langle M_s\sigma_s|JM_J^{(s)}\rangle$ are the Klebsh-Gordan coefficients. The functions $|M_s\sigma_s\rangle$, aside from the angle variables, depend on a radial variable.

The rate of the transition from any Zeeman initial state into any final state can be written as

$$w=\frac{2\pi}{\hbar}\sum_{i,f}n_J|V_{fi}|^2 N(E'), \tag{15}$$

where $V_{fi}=\langle JM_J^{(f)}|\hat{V}|JM_J^{(i)}\rangle$ and the summation over i,f is performed over the total angular momentum and its projections both in the initial and final states, n_J is an average occupation number of the initial state corresponding to the total angular momentum J, and $N(E)\sim\sqrt{E}$ is magnon density of states in the continuous spectrum. The argument of the density of states is determined from the condition that the energies of the initial and final states in the magnetic field should be equal to each other.

For the sake of simplicity, we assume that there is equiprobable occupation of the initial states with different J, that is we assume that $n_J=1/3$. The assumption that $E'\geqslant 0$ results in the fact that $M_J^{(i)}>M_J^{(f)}$. Therefore the selection rules corresponding to the perturbation operator (12) provide two kinds of transitions: $M_f=M_i-1$, $\sigma_f=\sigma_i$ and $M_f=M_i$, $\sigma_f=\sigma_i-1$. The selection rules also permit the transitions without a change of the projections of the spin and orbital angular momentum, $M_f=M_i$, $\sigma_f=\sigma_i$. However, under the necessary condition that $E'\geqslant 0$, these transitions turn out to be possible only at $g_i>g_f$, that is in the considerably strong magnetic fields. We do not consider such transitions and restrict ourselves to the simplest case when $g_i=g_f\equiv g$. Then, the energy $E'=\mu_B H-E$ does not depend on the quantum numbers of the initial and final states. One can see that the transitions between Zeeman sublevels turn out to be possible if the magnetic field strength exceeds the threshold value, $H_0=E_b/\mu_B g$.

The matrix element can be written in the form $V_{fi}=\mu_B H_+ C_J A$, where $H_+=H_x+iH_y$. The dimensionless quantities C_J are determined by the Klebsh-Gordan coefficients in the linear combinations (14): $C_1^2=10/9$, $C_2^2=55/54$. The factor A is the overlap integral between the radial wave functions $R_b(r)$ and $R_k(r)$ belonging to the discrete spectrum and continuous spectrum, respectively. Here, $k^2=2m^*(\mu_B gH-E_b)/\hbar^2$, where m^* has a meaning of orbital magnon effective mass.

The simplest choice of the radial wave functions,

$$R_b(r)=\frac{2\kappa^{5/2}}{\sqrt{3}}re^{-\kappa r}, \quad R_k(r)=\frac{4\pi i}{\sqrt{V}}j_1(kr), \tag{16}$$

where V is a normalization volume, $\kappa^2=2m^*E_b/\hbar^2$ determines the spatial localization scale, κ^{-1}, of the confined orbital magnon, results in the estimation of the transition rate averaged over magnetic-field orientations,

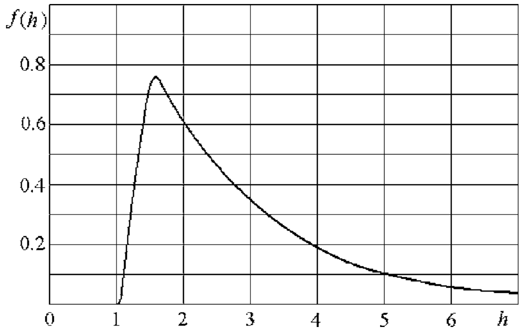

FIG. 3. Normalized DC decay rate as a function of the reduced magnetic-field strength $h=H/H_0$.

$$w = \frac{2^{11}\cdot 5\cdot 23\pi E_b}{3^6 g^2 \hbar}\frac{(h-1)^{3/2}}{h^4}. \qquad (17)$$

Here $h=H/H_0$ is a reduced magnetic-field strength.

The DC decay rate as a function of the reduced magnetic-field strength, $w(h)$, is shown in Fig. 3. The function $w(h)$ exhibits a threshold at $h=1$ and a maximum at $h=8/5$. An estimation of the DC decay rate at $h=8/5$, $w_m=w(8/5)$ results in $w_m \sim 10^{12}-10^{14}$ s^{-1}, if one supposes that m^* is of the order of free electron mass. Note that this estimation is of the order of a rate of thermal phonon excitation. However, as it is mentioned above, the phonon mechanism of magnetic-field-stimulated defect reactions is forbidden by the angular momentum selection rules.

VII. EXPERIMENT

The effects of a magnetic field on nonmagnetic materials have been previously investigated primarily by evaluating macroscopic properties, such as plasticity of crystals,[3,4] chemical activity of their surfaces,[21] electric conductivity,[22] homogeneity of solid solutions and compounds,[8] etc. Such investigations on a wide range of materials of different nature lead to the suggestion that the origin of these effects is a launch of defects reactions by the magnetic field. To confirm or refute such a suggestion one needs direct investigations of the magnetic-field effect on electron spectra of defects in crystals. However, there have been few relevant spectroscopic studies performed up to now.

Here we present two examples of the effect of magnetic field on the spectrum of a defect subsystem of a crystal. In particular, we show the possibility of investigating the effect of magnetic field on defects in the well-studied AgCl crystals using the precise photoluminescence (PL) technique. Also, we use deep level transient spectroscopy (DLTS) to study this effect in GaAs crystals.

The first effect is the long-term increase of the PL intensity of the Bridgeman-grown AgCl crystals after the short-term pulsed magnetic-field (PMF) treatment. The samples were treated by symmetrical triangular magnetic-field pulses with an amplitude of 4 kOe, a duration of 4×10^{-5} s, and a frequency of $f=50$ Hz. The time of treatment was 30 s. The PL spectra were measured under nitrogen laser ($\lambda=337$ nm) excitation at 77 K. The effect is shown in Fig. 4.

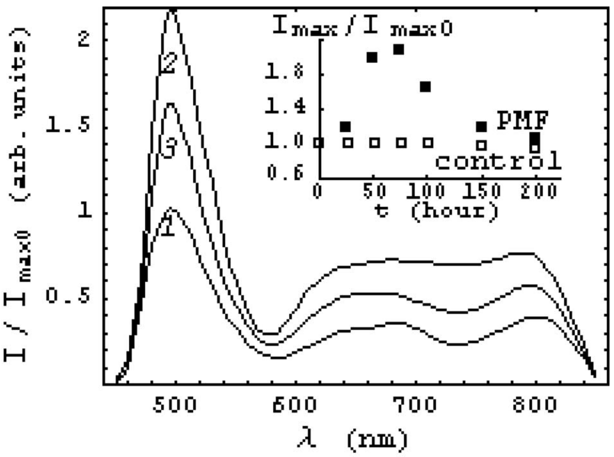

FIG. 4. PL spectra of AgCl crystal: 1-before, and 2, 3-three and four days after the PMF treatment. Inset: the time dependence of short-wave (490 nm) band maximum of PL intensity.

It is assumed[23] that the PL intensity short-wave band with the maximum at 490 nm is associated with the presence of cation vacancies Ag_V^+ in the volume of the AgCl crystals, while the wide band in the range of 600–800 nm is due to Ag-containing DC at the surface of the crystals. Thus the PMF-induced increase of the PL intensity indicates the corresponding increase of the concentrations of the Ag_V^+ vacancies in the volume and of the Ag-containing DC at the surface of the crystal.

This first effect can be qualitatively explained similar to the previously reported[8] effect of the PMF on InAs crystals. It is reasonable to assume a deficiency of the volatile component (Cl) in the AgCl crystals resulting in the existence of initial DC with chlorine vacancies (Cl_v) in the crystal volume. The PMF treatment may cause a decay of the Cl_v-containing DC with a formation of mobile chlorine vacancies. The motion of these vacancies towards the surface results in a generation of antistructural point defects (Ag in the Cl sites) and Ag_V^+ in the volume of the crystal. The motion of the chlorine vacancies is accompanied by the opposite motion of Cl atoms from the surface into the volume. The depletion of the surface with Cl disturbs a stoichiometry of the surface layer making it enriched with the metal element. Thus the PMF treatment of the AgCl crystal results in a generation of the Ag_V^+ vacancies in the volume of the crystal and of the Ag-containing DC inside the surface layer. These defects are responsible for the PL short-wave band and the wide long-wave band, respectively. It is highly probable that the decrease of the PL intensity in the final stage of the PMF-induced relaxation occurs due to the partial decay of the Ag-containing surface DC and annihilation of the Ag_V^+ vacancies in the volume caused by a diffusion of Ag atoms from the metal-enriched surface layer into the crystal volume.

The second effect is the PMF-induced irreversible change of the energy distribution of the surface electron states in the GaAs crystals. This effect is clearly demonstrated by the DLTS spectra in Fig. 5. We studied the Al-GaAs Schottky barriers with thermally deposited Al electrodes on the chemi-

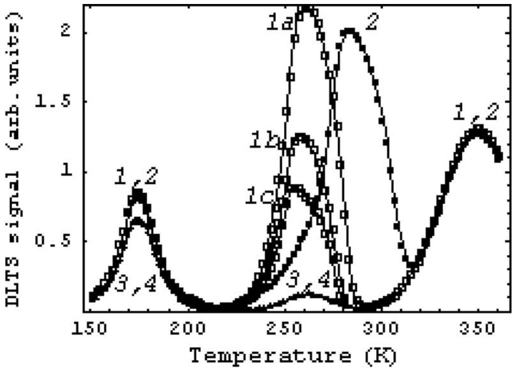

FIG. 5. DLTS spectra of the GaAs crystals with initial (1, 2) and selenium passivated (3, 4) surfaces: 1, 3-before, and 2, 4-a day after the PMF treatment. The curves 1a, 1b, 1c correspond to $V_{rev}=-0.2,-1,-2$ V.

cally polished surface of *n*-type Czochralski-grown GaAs (100) substrate and In-Ga paint ohmic contact at the backside of the wafer. The PMF treatment was the same as in the former case. The DLTS spectra were measured with constant delay times ratio $t_1/t_2=10$ ms/210 ms, the charging time $t_0=10$ ms, and the charging voltage $V_d=2$ V. The discharge voltage V_{rev} was varied. The initial DLTS spectrum of the GaAs crystal has three bands with the energies $E_c-0.38\pm0.02$ eV, $E_c-0.57\pm0.02$ eV, and $E_c-0.85\pm0.02$ eV, where E_c is the energy of the conduction band bottom. The decrease of the central peak with increasing of V_{rev} indicates the surface localization of the relevant electron traps. Such traps are considered[24,25]as the surface electron traps responsible for the pinning of the Fermi level at the GaAs surface. The PMF treatment of the Al-GaAs structure results in an irreversible temperature shift of the central DLTS peak. This temperature shift corresponds to a new energy distribution of the surface electron states density with the maximum at $E_c-0.65\pm0.02$ eV. The passivation of the GaAs surface in selenium vapor results in an elimination of the surface states which is demonstrated by a drastic decrease of the central DLTS peak. The residual central peak, the low-temperature peak, and the high-temperature peak in the DLTS spectra may be ascribed to the well- known[24,26] electron levels EL6, EL3, and EL2, respectively. We did not observe any effect of the PMF treatment on these levels. The Se-reconstructed surface of the GaAs crystal was insensitive to the PMF. We are unable to give a microscopic explanation of the PMF effect on the energy distribution of the surface electron states in the initial GaAs crystal because the structure of these states has been studied insufficiently. Nevertheless, the results we present here agree with the DILM phenomenology[8] which admits an enhancement of magnetic-field sensitivity of distorted surface layers. It should be noted that the one-dimensional potential well $U(\boldsymbol{r})$ created by the surface necessarily leads to at least one discrete magnon level.[20]

The results of the DLTS and PL spectroscopic studies directly demonstrate the ability of weak magnetic fields to induce defect reactions in nonmagnetic crystals due to magnetic field-induced change in the electron spectrum of the defect crystal. The origins of these effects are qualitatively explained by the above-developed DILM phenomenology, while a quantitative comparison of the experiment and theory (e.g., dependences of the effects on the magnetic-field strength) needs further investigation.

VIII. CONCLUSION

The phenomenology of magnetic-field effect on defect reactions in solids developed on the DILM concept allows one to explain qualitatively all of the currently available experimental data in the framework of the mechanism of orbital magnon excitations. In particular, such an approach gives a possibility to associate the magnetic field effect on a defect reaction with the symmetries of the perfect crystal and the strain field of the defect. The magnon mechanism allows one to obtain reaction rate dependence on the magnetic field.

One can consider the DILM phenomenology as an expansion of the well-known spin chemistry concept of magneto-sensitive molecular reactions of radicals in liquids into the field of defect reactions in solids. Both in liquids and in solids, the effect of an external magnetic field appears as a result of lifting of a spin ban on the reaction. However, contrary to the spin-dependent reactions in liquids, the lifting of the spin ban in solid-state defect reactions can occur because of the participation of the orbital degrees of freedom. In the solid state, transitions between different orbital states are possible due to band structure of the electron spectrum.

Orbital currents with short-range antiferromagnetic order arising due to defect-created strain field result in a rise of the magnetic structure of the crystal. Corresponding local magnetization (dynamic short-range hidden order) is linear in the strain and can be considered as a manifestation of the orbital piezomagnetism. Magnetization fluctuations can be associated with the emission and absorption of orbital antiferromagnetic magnons being the elementary excitations, which correspond to a defect-induced magnetoactive branch of the crystal energy spectrum. The orbital magnon plays a role of a third particle providing a balance between the total spin and the total orbital angular momentum under the condition that the total angular momentum has to be conserved.

The DILM phenomenology can be a basis for a new field, which we name the *spin chemistry of solids*. Despite the absence of direct evidence of hidden orbital antiferromagnetic (long-range) order in crystals, we believe that the concept of such a short-range order is a fruitful approach for understanding spin effects in solids. The field of the spin chemistry of solids is not restricted by a simple reaction as the decay of quasi-zero-dimensional (point) defect complexes, but can include the reactions of more complicated defects such as dislocations and surfaces. One can expect that a wide class of spin-forbidden structural transitions in solids should be initiated by both constant and pulsed external magnetic field.

ACKNOWLEDGMENTS

We acknowledge helpful discussions with Yu. V. Ivankov. This study was supported by JSC "AIIC EFKO."

[1] U. E. Steiner and T. Ulrich, Chem. Rev. (Washington, D.C.) **89**, 51 (1989).
[2] A. L. Buchachenko, Pure Appl. Chem. **72**, 2243 (2000).
[3] V. I. Al'shitz, E. V. Darinskaya, M. V. Koldaeva, and E. A. Petrzhik, Kristallografiya **48**, 768 (2003) [Crystallogr. Rep. **48**, 826 (2003)].
[4] Yu. I. Golovin, Fiz. Tverd. Tela (Leningrad) **46**, 769 (2004) [Phys. Solid State **46**, 789 (2004)].
[5] V. A. Zakrevskii, V. A. Pakhotin, and A. V. Shul'diner, Fiz. Tverd. Tela (Leningrad) **44**, 1990 (2002) [Phys. Solid State **44**, 2083 (2002)].
[6] V. I. Al'shitz, E. V. Darinskaya, and E. A. Petrzhik, Fiz. Tverd. Tela (Leningrad) **33**, 3001 (1991) [Sov. Phys. Solid State **33**, 1694 (1991).]
[7] M. I. Molotskii, Fiz. Tverd. Tela (Leningrad) **33**, 3112 (1991) [Sov. Phys. Solid State **33**, 1760 (1991)].
[8] V. I. Belyavsky and M. N. Levin, Phys. Rev. B **70**, 104101 (2004).
[9] Y. Tokura and N. Nagaosa, Science **288**, 462 (2000).
[10] A. Kiss and P. Fazekas, Phys. Rev. B **68**, 174425 (2003).
[11] G. L. Bir and G. E. Pikus, *Symmetry and Strain-Induced Effects in Semiconductors* (Wiley, New York, 1974).
[12] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Nauka, Moscow, 1982).
[13] B. I. Halperin and T. M. Rice, Solid State Phys. **21**, 115 (1968).
[14] 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)].
[15] N. Harrison, K. H. Kim, M. Jaime, and J. A. Mydosh, Physica B **346-347**, 92 (2004).
[16] S. Chakravarty, R. B. Laughlin, D. K. Morr, and C. Nayak, Phys. Rev. B **63**, 094503 (2001).
[17] P. A. Lee, N. Nagaosa, and X.-G. Wen, Rev. Mod. Phys. **78**, 17 (2006).
[18] A. Kaminski, S. Rosenkranz, H. M. Fretwell, J. C. Campuzano, Z. Z. Li, H. Raffy, W. G. Cullen, H. You, C. G. Olson, C. M. Varma, and H. Höchst, Nature (London) **416**, 610 (2002).
[19] L. D. Landau and E. M. Lifshitz, *Course of Theoretical Physics, Vol. 5: Statistical Physics*, 4th ed. (Nauka, Moscow, 1995) Part 1.
[20] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Non-Relativistic Theory*, 5th ed. (Nauka, Moscow, 2001).
[21] M. N. Levin, A. V. Tatarintzev, O. A. Kostsova, and A. M. Kostsov, Zh. Tekh. Fiz. **73**, 85 (2003) [Tech. Phys. **48**, 1304 (2003)].
[22] M. N. Levin, V. I. Belyavsky, V. V. Postnikov, E. A. Dolgopolova, and M. A. Dronov, Ferroelectrics **307**, 161 (2004).
[23] A. N. Latyshev, O. V. Ovchinnikov, and M. S. Smirnov, Zh. Prikl. Spektrosk. **71**, 223 (2004) [J. Appl. Spectrosc. **71**, 223 (2004)].
[24] G. J. Hughes, L. Roberts, M. O. Henry, K. McGuigan, G. M. O'Connor, F. G. Anderson, G. P. Morgan, and T. Glynn, Mater. Sci. Eng., B **9**, 37 (1991).
[25] B. L. Agapov, I. N. Arsent'ev, N. N. Bezryadin, G. I. Kotov, and M. P. Sumetz, Fiz. Tekh. Poluprovodn. (S.-Peterburg) **33**, 712 (1999) [Semiconductors **33**, 658 (1999)].
[26] A. V. Markov, A. Y. Polyakov, N. B. Smirnov, Y. N. Bolsheva, A. V. Govorkov, and B. N. Sharonov, Solid-State Electron. **46**, 269 (2002).