Local phase transitions of Mn^+ centers in a KCl crystal

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The ESR method revealed a sequence of two local first-order phase transitions of paramagnetic Mn^+ centers in KCl. As a result of these transitions the centers exhibited abrupt changes in the local symmetry $O_h \rightarrow C_{4v}$ and $C_{4v} \rightarrow C_{3v}$ in the course of cooling. The ESR spectra indicated coexistence of both phases of the local centers near these transitions. A model of local phase transitions is developed on the basis of a contribution of a soft quasilocal mode with a frequency that decreases as a result of cooling. An effect of this kind is associated with the anharmonic interaction of a quasilocal polar vibration with an even resonance vibration. This model accounts for the experimental data of Mn^+ in KCl if an allowance is made for the Jahn-Teller pseudoeffect involving a soft quasilocal vibration.

INTRODUCTION

Radiofrequency spectroscopy methods, particularly ESR, are highly informative when applied to structural phase transitions in crystals.[1,2] It is therefore of considerable interest to study by the ESR method for characteristics of the local dynamics of impurity centers. Studies of this dynamics are important for the clarification of the fundamental problem in the physics of local centers which is the possibility of local phase transitions involving spontaneous reduction of the symmetry of local centers in low-temperture phases. In fact, there is as yet no experimental evidence in support of local phase transitions. A theoretical analysis of these transitions, first made in Ref. 3, is based on the Jahn-Teller pseudoeffect (JTPE) and it is based essentially on the condition of fast relaxation transitions between various sheets of the adiabatic potential. This condition is fairly stringent, because (within the framework of the adiabatic approximation) the transition between different sheets of the adiabatic potential occur under the action of a small perturbation which is the nonadiabatic operator. Consequently, in the case of the most favorable (for the occurrence of local phase transitions) conditions when the coupling of local centers with the lattice is strong and the adiabatic approximation criterion is satisfied, it is found that local phase transitions would be difficult to realize on the basis of the model of Ref. 3. This situation makes it necessary to carry out experimental and theoretical studies of the local dynamics of impurity centers in crystals in order to determine the feasibility of local phase transitions.

We shall report an experimental and theoretical study of local phase transitions in the specific case of paramagnetic centers in a KCl crystal.

An investigation of the ESR spectra reported in Ref. 4 led to the conclusion that the positions of ions in a KCl crystal are noncentral (off-site). The ions of Mn^+ replace the K^+ cations in the lattice and act as a neutral impurity (relative to the crystal) by analogy with, for example, noncentral Li^+ ions in alkali halide crystals. The ions of Li^+ in alkali halides are model objects for the investigation of a noncentral ions in crystals. However, since these ions have a nonparamagnetic ground state, it is not possible to use the most direct method for investigating the defect structure which is the ESR method. It has also been found that the nature of the multiwell potential for the Li^+ ions in alkali halide crystals is independent of temperature. The high information capacity of the ESR method has been demonstrated by an investigation of noncentral paramagnetic ions in alkaline earth oxides.[5] Motional temperature averaging of the ESR spectra due to the motion of the noncentral ion in a practically constant multiwell potential was reported in Ref. 5.

We shall describe the first-ever observations of the temperature dependence of the configuration of energy minima of a local center. The temperature dependences of the ESR spectra of the Mn^+ centers in a KCl crystal provided a direct evidence of local phase transitions. We developed a model of local phase transitions based on the anharmonic interaction between quasilocal and resonance vibrations associated with the investigated local centers. It was found that the JTPE involving closely spaced electron states of Mn^+ facilitates greatly local phase transitions. In our model these transitions occur because of the temperature dependence of the lower sheet of the adiabatic potential and they are not associated with fast transitions between the lower and upper sheets of this potential.

1. EXPERIMENTAL METHOD

Crystals of KCl:Mn were grown from the melt by the Kyropoulos method. Manganese was incorporated in the lattice in the form of the Mn^{2+} ions and the excess charge of these ions was compensated by the cation vacancies in the immediate environment.[6] The manganese concentration was selected so that in the process of irradiation practically all the Mn^{2+} ions were converted into Mn^+. The Mn^+ ions occupied cation sites in the regular lattice and were created by bombarding a KCl:Mn crystal with x rays at 77 K and heating it then to 300 K (Ref. 7).

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The irradiation was carried out using a URS-55 (55 kV, 15 mA) x-ray unit. A tube with a molybdenum anticathode was used in this unit. The ESR spectra were recorded using rf spectrometers operating in 3-cm and 8-mm ranges; this was done in the temperature range 4–300 K. The orientational dependences of the spectra were determined by rotating a crystal about a [110] axis at right angles to the applied magnetic field. The average dimensions of the samples used in our experiments were $2\times1\times3$ mm (in the microwave wavelength range of 3 cm) and $1\times0.5\times2$ mm (in the microwave wavelength range of 8 mm).

The effects of an inhomogeneity of the heating of a crystal were eliminated by employing samples of different dimensions during the process of recording of the ESR spectra and by keeping each crystal at a selected temperature for some time before the measurements.

2. EXPERIMENTAL RESULTS

The Mn^+ ions represent a very convenient object for the investigation by the ESR method. In alkali halide crystals these ions have the $3d^5 4s$ electron configuration and are in the $^7S_3$ state. Since the total spin of the Mn^+ centers is $S=3$, the ESR spectrum exhibits a fine structure which can be used to determine the symmetry of the centers. The presence of an unpaired $4s$ electron increase greatly the isotropic hyperfine interaction constant compared with the corresponding constant of the Mn^{2+} ions, so that is is possible to identify reliably the Mn^+ centers.

The Mn^+ ions occupy the cation lattice sites and are formed as a result of the capture of electrons by the Mn^{2+} ions during irradiation with x rays. If such irradiation is carried out at a lower temperature when the cation vacancies compensating for the excess charge of the Mn^{2+} ions are immobile, then the Mn^+ ions have a cation vacancy in the immediate environment.[7] The ESR spectra of such centers have an anisotropic fine structure. If a crystal irradiated at 77 K is heated, the cation vacancies move away from the Mn^+ ions (the charge compensation is no longer needed) and this produces the Mn^+ ions in the regular environment. If a crystal is irradiated at 300 K, the capture of an electron by an Mn^{2+} ion is accompanied by a departure of a cation vacancy and the Mn^+ ions are formed directly in the regular environment. We shall call the latter the Mn_c^+ centers.

When temperature was varied the ESR spectra of the Mn_c^+ centers in KCl exhibited a number of reversible changes. Three different ESR spectra of these ions were observed in different temperature ranges. Above ~40 K the ESR spectrum of the Mn_c^+ centers was isotropic and practically independent of temperature until the centers were destroyed at ~350 K. Curve 1 in Fig. 1 represents such a spectrum recorded at 50 K. The centers with the isotropic spectrum will be referred to in future as the $Mn_c^+(O_h)$ phase in order to stress the symmetry of the centers in this state. The spectrum represented by curve 1 was recorded in the wavelength range of 3 cm. Since in this case the magnetic fields were comparable with the hyperfine interaction constant, an isotropic fine structure was observed because of higher-order effects. In the ESR spectrum recorded in the wavelength range of 8 mm there were ony six practically equidistant lines due to the hyperfine interaction with the manganese nuclei characterized by the spin $I=5/2$. The splitting of the fine structure was then within the limits of the line width. The ESR lines of the Mn^+ centers were considerably wider than the lines of the Mn^{2+} ions because of a strong hypersuperfine interaction of the unpaired $4s$ electrons with the magnetic nuclei of the ligands.

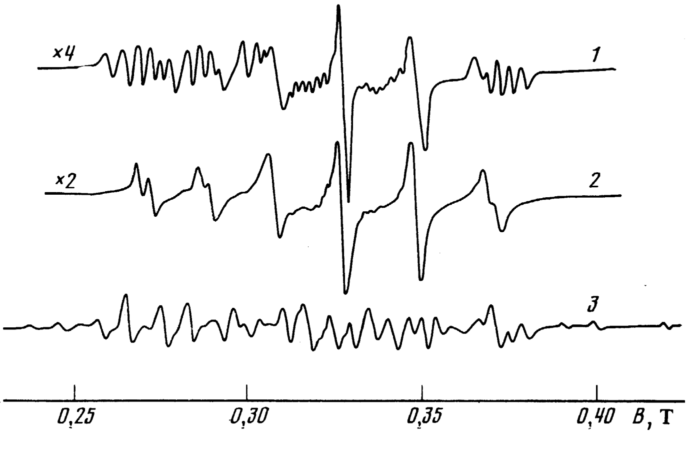

FIG. 1. Electron spin resonance spectra of the Mn_c^+ centers in KCl recorded in the $B\|\langle111\rangle$ orientation at various temperature: 1) 50 K, $Mn_c^+(O_h)$ phase; 2) 20 K, $Mn_c^+(C_4)$ phase; 3) 10 K, $Mn_c^+(C_3)$ phase. Frequency $\nu=9.1$ GHz.

In the temperature range 40–20 K the ESR signal of the $Mn_c^+(O_h)$ phase decreased to zero. The temperature dependence of the amplitude of this signal was recorded (curve 1 in Fig. 2). In the same temperature range a second ESR spectrum appeared: this spectrum was also due to the Mn_c^+ centers, but it was characterized by a weak anisotropy. The spectrum was recorded at 20 K in the $B\|\langle111\rangle$ orientation and it is shown in Fig. 2 (curve 1). The orientational dependences of the second ESR spectrum of the Mn_c^+ centers indicated that the symmetry axis of each center was oriented along the C_4 direction in a crystal. This phase of the Mn_c^+ centers will be denoted by $Mn_c^+(C_4)$. The temperature dependence of the amplitude of the signal due to the Mn_c^+ centers in the $Mn_c^+(C_4)$ phase was also determined (curve 2 in Fig. 2). Initially the amplitude of the ESR signal of these centers increased, but eventually it fell to zero. In the temperature range 14–12 K a third anisotropic ESR spectrum

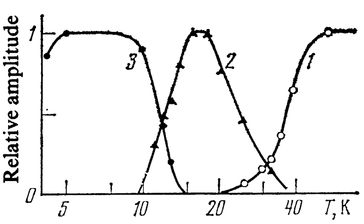

FIG. 2. Temperature dependences of the amplitude of the ESR signals of the Mn_c^+ centers in the following phases: 1) $Mn_c^+(O_h)$; 2) $Mn_c^+(C_4)$; 3) $Mn_c^+(C_3)$.

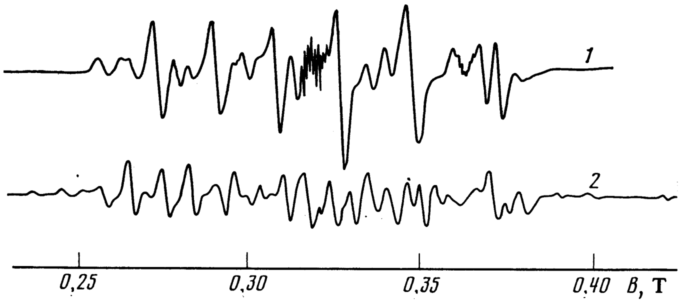

FIG. 3. Electron spin resonance spectra of Mn$_c^+$ centers in KCl recorded at 4.2 K [Mn$_c^+$ (C_3) phase] in two orientations; 1) $\mathbf{B}\|\langle 100\rangle$; 2) $\mathbf{B}\|\langle 111\rangle$; $\nu = 9.1$ GHz.

(curve 3 in Fig. 1) was observed and it was again due to the Mn$^+$ centers. Further cooling did not affect this ESR spectrum. We plotted in Fig. 3 the ESR spectra of the Mn$^+$ centers recorded in the wavelength range of 3 cm and 4.2 K employing two orientations: $\mathbf{B}\|\langle 100\rangle$ (curve 1) and $\mathbf{B}\|\langle 111\rangle$ (curve 2). An analysis of the orientational dependences indicated that the centers now had the symmetry axis C_3 so that we designated them as the Mn$^+$(C_3) phase. The anisotropy of the ESR spectra of this phase was much stronger than that of the Mn$^+$(C_4) phase. We also plotted in Fig. 2 (curve 3) the temperature dependence of the intensity of the ESR signal of the centers in the Mn$^+$(C_3) phase. The signal rose steeply in the temperature range 14–12 K and then the signal intensity remained practically constant. The fall of the amplitude in the range 5–4 K was clearly due to saturation of the ESR signal because of an increase in the spin–lattice relaxation time.

The ESR spectra recorded in the wavelength range of 3 cm were greatly complicated by the higher-order effects. These effects are very useful in studies of the orientational dependences of the ESR spectra, since the line positions are then more sensitive to changes in the orientation of a crystal in the 3-cm range than in the 8-mm range. However, it is much easier to find the parameters of the spin Hamiltonian of the Mn$_c^+$ centers in various phases of the spectra recorded in the 8-mm range where all the above-mentioned features are observed in the same temperature ranges.

The ESR spectra of the Mn$_c^+$ centers in the Mn$_c^+$(O_h) phase can be described by the following isotropic spin Hamiltonian

$$\mathscr{H}=g\beta\mathbf{HS}+A\mathbf{IS}, \tag{1}$$

where g denotes the g factor of the electron shell; A is the hyperfine interaction constant; $I = 5/2$, $S = 3$.

The ESR spectra of the Mn$_c^+$ centers in the Mn$_c^+$(C_3) and Mn$_c^+$ (C_3) phases have the spin Hamiltonian

$$\mathscr{H}=g\beta\mathbf{HS}+D[S_z^2-{}^1/_3S(S+1)]+A\mathbf{SI}, \tag{2}$$

where the z direction coincides with the symmetry axis of the centers. The parameter D represents the axial distortion of the crystal field. In an analysis of the ESR spectra we made an allowance for the fact that the centers were oriented in a crystal simultaneously along several equivalent C_4 directions in the case of the Mn$_c^+$ (C_4) phase or the C_3 directions in the Mn$_c^+$ (C_3) phase.

The parameters of the spin Hamiltonian of all the investigated ESR spectra are given in Table I. We can see that the parameter D for the Mn$_c^+$(C_3) phase is approximately an order of magnitude greater than the correponding prameter for the Mn$_c$ (C_4) phase.

Characteristic features of the low-temperature (12–14 K) and high-temperature (20–40 K) transitions between the phases are the coexistence of the two ESR spectra in the region of each of these transitions. It is clear from Fig. 2 that in the temperature range 12–14 K the Mn$_c^+$ centers are simultaneously in two phases, Mn$_c^+$(C_3) and Mn$_c^+$(C_4), whereas in the range 20–40 K, they are in the Mn$_c^+$ (C_4) and Mn$_c^+$ (O_h) phases. At temperatures 18–52 K (near the high-temperature transition) this coexistence is demonstrated uniquely by the ESR spectra in Fig. 4. Only the outer lines of the ESR spectra of the Mn$_c^+$ centers are given because these carry more information than the other lines. We can see that the ESR spectrum of the Mn$_c^+$ centers transforms from the Mn$_c^+$ (O_h) to the Mn$_c^+$ (C_4) phase and that the ESR spectra representing different phases coexist. In the same range there is some broadening of the ESR lines of the Mn$_c^+$ centers and the sum of the curves 1 and 2 in Fig. 2 is not equal to unity. (Curves 1, 2, and 3 represent the amplitude of the ESR signals obtained ignoring the line widths.) The number of the Mn$_c^+$ centers is not affected by repeated cooling and heating in the range 4–77 K. This follows from the ESR spectra of the Mn$_c^+$ centers recorded after various treatments at 77 K.

Near the low-temperature transition the broadening of the ESR lines of the Mn$_c^+$ (C_3) and Mn$_c^+$ (C_4) phases is much less than in the region of the high-temperature transition and, therefore, the sum of curves 2 and 3 in Fig. 2 is now close to unity.

TABLE I. Parameters of ESR spectra of Mn$_c^+$ centers in KCl crystals.

Center	Temperature K	Phase	Hyperfine interaction constant, 10^{-4} T	D, 10^{-4} T
Mn$_c^+$	50	Mn$_c^+$ (O_h)	201±3	–
	20	Mn$_c^+$ (C_4)	201±3	5±2
	4	Mn$_c^+$ (C_3)	201±3	45±3
Mn$_c^+$ v_c(C_4)	4,2	–	175±5	~150

All the spectra were characterized by $g = 2.00 \pm 0.005$

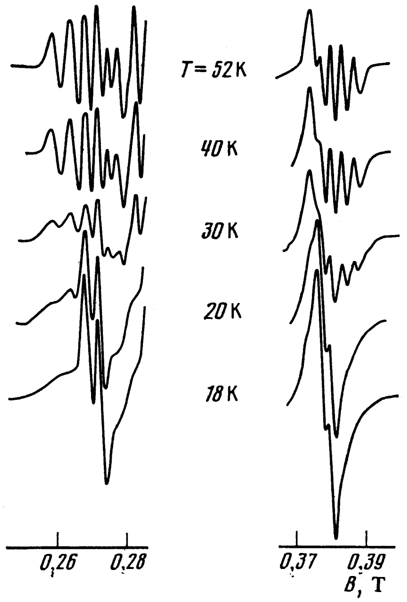

FIG. 4. Signals of the outer lines in the ESR spectra of the Mn_c^+ centers recorded at various temperatures showing the transition from the $Mn_c^+(O_h)$ to the $Mn_c^+(C_4)$ phase.

The observed temperature dependence can be explained as follows. At temperature above 40 K the Mn^+ ions are located at the centers of the cation lattice site at an energy minimum [$Mn_c^+(O_h)$ phase]. Cooling results in a local phase transition which displaces the energy minimum (and, consequently, the Mn^+ ion) in the direction C_4 and the symmetry of the center becomes C_{4v} [$Mn_c^+(C_4)$ phase]. Further cooling in the range 14–12 K gives rise to a second local phase transition as a result of which the Mn^+ ion is displaced in the C_3 direction and the symmetry of the centers becomes C_{3v} [$Mn_c^+(C_3)$ phase]. The shift in the C_3 direction is considerably greater than the shift of C_4. It should be pointed out that a practically abrupt change in the constant D as a result of variation of temperature is direct evidence that the observed local phase transitions are of the first order.

The temperature ranges in which the ESR spectra of two phases coexist are characterized by an approximate equality of the energy minima corresponding to the two phases: in the case of the high-temperature transition the minimum is at the center of a site or displaced along the C_4 direction (six positions); in the case of the low-temperature transition the minimum is displaced along the C_4 and C_3 directions, respectively (eight positions).

As pointed out already, the Mn^+ ions with a cation vacancy in the immediate environment ($Mn_c^+ v_c$ centers) may be created in KCl. Table I shows, by way of comparison, the parameters of the ESR spectra of such centers with a cation vacancy located at the nearest (relative to the Mn_c^+ ion) position along the C_4 axis. The ESR spectrum of such centers is described by the spin Hamiltonian of Eq. (2). We can see that the parameter D governed by the influence of the cation vacancy is considerably greater than D for the Mn_c^+ centers in the $Mn_c^+(C_4)$ and $Mn_c^+(C_3)$ phases. It is important to note that the ESR spectra of the $Mn_c^+ v_c$ centers are not affected by variation of temperature in the range 4–100 K. (At higher temperatures the change in the ESR spectra due to the displacement of the cation vacancy away from the Mn^+ ion are irreversible.)

Moreover, the ESR spectra of the Mn^{2+} ions located at cation sites of a KCl crystal in a regular environment are also unaffected by temperature. Such ions were created when the Mn_c^+ centers were bleached optically at low temperatures.

We shall now consider a model which accounts for the change to the noncentral position of the ions as a result of cooling, which corresponds to local phase transitions, and we shall compare this model with the experimental results obtained for the Mn^+ ions in KCl.

3. MODEL OF A SOFT QUASILOCAL MODE

We shall consider local centers characterized by low-frequency polar quasilocal vibrations of freqency ω_q and resonance nonpolar vibrations of natural width Γ_R.

Our model of a soft quasilocal mode postulates a fourth-order anharmonic interaction between a dynamic variable Q_q of a quasilocal mode and a dynamic variable Q_R of a resonance vibration associated with the same lattice defect. Consequently, the potential energy of quasilocal vibrations can be represented in the form

$$\mathcal{H}_1=\chi Q_K^2 Q_R^2+{}^1/_2 m\omega_q^2 Q_q^2, \tag{3}$$

where χ is the anharmonic interaction parameter. The second term in Eq. (3) represents the elastic energy of vibrations with a mass coefficient m of the quasilocal vibration.

The rate of establishment of equilibrium values of the dynamic variable Q_R is of the order of the reciprocal of the width of the resonance vibration $1/\Gamma_R$. If the relationship $\Gamma_R \gg \omega_q$ is obeyed, for example, if $\Gamma_R \approx 2\pi\times 10^{12}$ sec^{-1} and $\omega_q \approx 2\pi\times 10^{11}$ sec^{-1}, then we can consider quasilocal vibrations assuming equilibrium values of Q_R^2:

$$\langle Q_R^2\rangle=\frac{1}{2\omega_R}\,\mathrm{cth}\left\{\frac{\omega_R}{2kT}\right\}, \tag{4}$$

where ω_R is the resonance vibration frequency (here and later we are assuming that $\hbar=1$).

If we make the substitution $Q_R^2 \to \langle Q_R^2\rangle$ in Eq. (3) when the condition $\Gamma_R \gg \omega_q$ is satisfied, we obtain the following temperature-dependent energy of elastic quasilocal vibrations:

$$\mathcal{H}_1 \approx \frac{1}{2}\left[m\omega_q^2+\frac{\chi}{\omega_R}\,\mathrm{cth}\left\{\frac{\omega_R}{2kT}\right\}\right]Q_q^2. \tag{5}$$

The expression in the brackets plays the role of the effective elastic constant of a quasilocal vibration and it describes the temperature dependence of the square of the effective fequency of such a vibration in the situation under discussion.

It is particuarly interesting to consider the case when $\chi > 0$ and cooling lowers the effective frequency of the quasilocal mode $\tilde{\omega}_q(T)$:

$$\tilde{\omega}_q(T)=\left[\omega_q{}^2+\frac{\chi}{m\omega_R}\operatorname{cth}\left\{\frac{\omega_R}{2kT}\right\}\right]^{1/2}. \tag{6}$$

This situation corresponds to a soft quasilocal mode. If $\omega_q^2>0$, then the "softening" of the quasilocal mode is incomplete and the minimum value of the frequency of this mode is

$$\tilde{\omega}_q(T=0)=\left[\omega_q^2+\frac{\chi}{m\omega_R}\right]^{1/2}.$$

If without an allowance for the investigated anharmonic interaction we find that the unrenormalized frequency obeys $\omega_q^2<0$, then cooling can result in a transition to $\tilde{\omega}_q^2(T)>0$. At a temperature T_C^l, defined by

$$\frac{m\omega_R|\omega_q^2|}{\chi}=\operatorname{cth}\left\{\frac{\omega_R}{2kT_C{}^l}\right\}, \tag{7}$$

the soft quasilocal mode condenses and this corresponds to a second-order local phase transition.

This mechanism of local phase transitions is fundamentally different from the mechanism of the same transitions resulting from fast relaxation at a rate of $1/\tau$ between different sheets of the adiabatic potential under the conditions of the JTPE (Ref. 3). Such transitions occur only under the action of the nonadiabatic operator. Consequently, $1/\tau$ is in the case sufficiently small and the inequality $1/\tau\gg\omega_q$ needed for the occurrence of local phase transitions is more stringent than the inequality $\Gamma_R\gg\omega_q$ needed for the appearance of a soft quasilocal mode and local phase transitions in our case. This mechanism of the appearance of a soft quasilocal mode is analogous to the mechanism of the formation of a soft lattice mode in ferroelectrics considered in the quasiharmonic approximation,[2] where instead of the interaction between the lattice modes a study is made of the interaction of quasilocal and resonance vibrations of a local center.

If the investigated local center is an electron center with closely spaced or degenerate energy states which are mixed by the electron–vibrational interaction involving the quasilocal vibration under discussion, then the criterion for the JTPE and the magnitude of the equilibrium distortion both depend on temperature because of the contribution $\tilde{\omega}_q(T)$. In the present case, because of a reduction in the frequency of a soft quasilocal mode in accordance with Eq. (6), cooling relaxes significantly the criterion for the JTPE and, therefore, the criterion for the existence of local phase transitions. In fact, if the electron states participating in the electron–vibrational interaction are separated by an energy gap 2Δ, the criterion for the JTPE in the case of the investigated odd quasilocal vibration can be represented in the form

$$a^2>\Delta\left[m\omega_q^2+\frac{\chi}{\omega_R}\operatorname{cth}\left\{\frac{\omega_R}{2kT}\right\}\right], \tag{8}$$

where aQ_q is the corresponding nondiagonal matrix element of the operator representing the electron–vibrational interaction between the electron states active in the JTPE. Here, a second-order local phase transition occurs when the unrenormalized frequency of a quasilocal vibration (6) does not reach the condensation point. The temperature of a second-order local phase transition is found from

$$a^2=\Delta\left[m\omega_q^2+\frac{\chi}{\omega_R}\operatorname{cth}\left\{\frac{\omega_q}{2kT_C{}^l}\right\}\right], \tag{9}$$

and the equilibrium displacement $Q_q(T)$ at temperatures $T<T_C^l$ is

$$Q_q{}^P(T)=\left[a^2\left(m\omega_q^2+\frac{\chi}{\omega_R}\operatorname{cth}\left\{\frac{\omega_R}{2kT}\right\}\right)^{-2}-\frac{\Delta^2}{a^2}\right]^{1/2}. \tag{10}$$

It therefore follows that the electron–vibrational interaction mixes various electron states and facilitate greatly the occurrence of local phase transitions as does the contribution of a soft vibrational mode.

We have investigated so far second-order local phase transitions. It is of considerable interest, particulary in connection with the experimental data on the ESR of Mn^+ in KCl, to discuss the case of first-order local phase transitions when the fourth-order anharmonic coefficients are negative. We shall consider this situation in the case of Mn^+ in KCl.

4. LOCAL FIRST-ORDER PHASE TRANSITION IN KCl:Mn$^+$

We shall begin by allowing for the circumstances that in the case of Mn^+ in KCl the electron–vibrational (vibronic) interaction which mixes the ground A and the excited T electron states in the case of polar distortions Q_q may give rise to the JTPE. As shown in the preceding section, this facilitates greatly local phase transitions. In fact, in this case the vibrational energy corresponding to the lower sheet of the adiabatic potential is

$$E=\Delta-\left[\Delta^2+a^2Q_q^2\right]^{1/2}+\frac{1}{2}\left[m\omega_q^2+\frac{\chi}{\omega_R}\operatorname{cth}\left\{\frac{\omega_q}{2kT}\right\}\right]Q_q^2+E_{\mathrm{anh}}. \tag{11}$$

Here, E_{anh} is the anharmonic contribution to the energy of polar quasilocal vibrations and the quantity Δ includes the contribution of the Jahn–Teller lowering of the energy of the excited T states. Bearing in mind the possible instability of a system when calculations are made allowing only for the fourth-order anharmonicity, typical of first-order phase transitions, we shall include in Eq. (11) the anharmonic contributions right up to the sixth order. Consequently, when Eq. (11) is expanded in powers of $(Q_q^x)^2$, $(Q_q^y)^2$, and $(Q_q^z)^2$, we obtain the following expression for the potential energy of polar quasilocal vibrations, which is similar in form to the expression for the free energy of a cubic ferroelectric considered as a function of the polarization[8]:

$$\begin{aligned}E={}&E_0+\alpha_0(T-T_C{}^l)Q_q^2+{}^1/{}_2\beta_1Q_q^4+\beta_2[(Q_q^x)^2(Q_q^y)^2\\&+(Q_q^z)^2(Q_q^x)^2+(Q_q^z)^2(Q_q^y)^2]+\frac{1}{3}\gamma_1(Q_q)^6\\&+\gamma_2\{(Q_q^x)^4[(Q_q^y)^2+(Q_q^z)^2]+(Q_q^y)^4[(Q_q^x)^2+(Q_q^z)^2]\\&+(Q_q^z)^4[(Q_q^x)^2+(Q_q^y)^2]\}+\gamma_3(Q_q^x)^2(Q_q^y)^2(Q_q^z)^2,\end{aligned} \tag{12}$$

where T_C^l is the temperature of condensation of a soft quasilocal mode found allowing for the JTPE and deduced from Eq. (9). An analysis of Eq. (12) carried out in the same way as in Ref. 8 shows that if $\gamma_2\approx\gamma_3$ and $\beta_2<0$, then the investigated centers can only have the point symmetries O_h,

C_{4v}, and C_{3v} in accordance with the experimental results (the phase with the point symmetry C_{2v} is unstable). We shall assume that $\beta_1 < 0$, $\gamma_1 > 0$, and $\gamma_2 \approx \gamma_3 > 0$, so that $T > T^l_C$. This situation is characteristic of first order phase transitions. A further analysis, carried out by analogy with the phenomenological theory of cubic ferroelectrics given in Refs. 8 and 9, and the minimization of Eq. (12) in terms of the variables Q^x_q, Q^y_q, and Q^z_q of a polar quasilocal vibration yields a sequence of two first-order local phase transitions. The high-temperature transition corresponds the appearance of a polar distortion along directions of the $\langle 100\rangle$ type, whereas the low-temperature transition produces a polar distortion along $\langle 111\rangle$ directions, in agreement with the experimental results. In particular, the high-temperature first-order phase transition point is

$$T_C^{\langle 100\rangle} = T_C{}^l + \frac{3}{16}\frac{\beta_1{}^2}{\gamma_1\alpha_0}. \tag{13}$$

Cooling to the temperature $T = T_C^{\langle 100\rangle}$ induces abruptly an equilibrium polar distortion of the centers along $\langle 100\rangle$ directions, so that the impurity ion is displaced from the lattice site and becomes noncentral. Further lowering of T to the temperature $T = T_C^{\langle 111\rangle}$ induces the second first-order local phase transition as a result of which the equilibrium polar distortion of the center changes abruptly not only in respect of its position but also in respect of the direction (from $\langle 100\rangle$ to $\langle 111\rangle$).

The experimentally observed coexistence of regions with a local symmetry C_{4v} and O_h (close to the high-temperature local phase transition) or C_{3v} and C_{4v} (close to the high-temperature local phase transition) can be explained if we allow for the contribution of the internal electric and elastic fields of crystal defects. In fact, the internal field of crystal defects alters the difference between the energies in the potential well with different symmetries (equality of these energies corresponds to a first-order local phase transition). This gives rise to a spatial distribution of the temperature of the first-order local phase transition induced by the defect fields. Therefore, in the region of this transition we both have the situation when $T < T^l_C$ in some part of the crystal and $T > T^l_C$ in other parts of a crystal.

Broadeninng of the ESR lines near first-order local phase transitions may be due to motional broadening of the lines because of the considerable acceleration of hopping tunnel transitions between potential wells of different local symmetries. Such an increase in the rate of tunnel transitions is due to an increase in the contribution of the hopping tunnel-controlled process[10] between the states active in first-order local phase transitions. In fact, the rate of the tunnel-controlled process[10] representing the coherent tunneling under conditions of homogeneously broadened and inequivaent (in respect of the energy) states in different potential wells is

$$1/\tau_{hop} = (2\Gamma)^2[1/\tau_0 + (\Delta U)^2\tau_0]^{-1}. \tag{14}$$

Here, Γ, ΔU, and $1/\tau_0$ are, respectively, the tunnel matrix element, the difference between the energies of the states, and the sum of the natural widths of the levels in potential wells with states between which a tunnel transition corresponding to a first-order local phase transition takes place. We can see that in the region of such a transition, where $\Delta U \approx 0$, the rate of the tunnel-controlled process between states with different local symmetry is maximal. This results in a dynamic increase in the width of the ESR line near a first-order local phase transition.

The coexistence of phases of different symmetry near a first-order local phase transition is also associated with thermal filling of inequivalent potential wells with similar energies ($\Delta U \lesssim kT$) but different local symmetries. Such an effect occurs even in the absence of a lattice defect field. The electric and elastic fields of lattice defects widen the temperature range of coexistence of phases of different symmetries.

5. CONCLUSIONS

Experimental results obtained in an investigation of the temperature dependences of the parameters of the ESR spectra of Mn^+ and KCl, carried out in the temperature range from 4 to 300 K, can be explained by postulating the occurrence of two successive first-order local phase transitions. Such transitions result in abrupt changes in the equilibrium polar distortion of clusters (each consisting of an impurity and ligands) both in respect of the magnitude and direction. If a polar quasilocal vibrations corresponds principally to the displacement of an impurity from a regular slit, then local phase transitions result in the assumption of noncentral positions by impurities. It is shown in the present paper that this effect may be associated with the harmonic interaction between quasilocal and resonance modes of an impurity center.

It should be pointed out that the absence of the effect corresponding to local phase transitions in the case of the Mn_c^{2+} and $\mathrm{Mn}_c^+ v_c$ centers is clearly due to the circumstances that in such cases the initial splitting of the electron states participating in the vibronic interaction is quite large and this gives rise to the JTPE and, therefore, to fairly high values of the effective frequencies of quasilocal vibrations. In fact, the Mn^{2+} ion which in the ground state has the $3d^5$ electron configuration is characterized by a large splitting of the electron spectrum. In the case of the $\mathrm{Mn}_c^+ v_c$ centers the presence of a vacancy in the immediate environment of Mn^+ again increases the splitting in the electron spectrum.

In conclusion, we must add that local phase transitions may be observed also for other types of radiation impurity defects characterized by closely spaced electron levels and a fairly low quasilocal vibration frequency.

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