Investigation of the local phase transition in $KTaO_3:Fe^{3+}$ by means of the temperature broadening of the EPR lines

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The temperature and angular dependences of the EPR lines of the Fe^{3+} impurity in $KTaO_3$ were investigated in the temperature interval 77–900 K. It turned out that the line width increases substantially in the range 200–400 K and is independent of temperature in the interval 400–900 K. This unusual behavior of the EPR line is attributed to a local phase transition at $T_c = 365$ K in the paramagnetic-impurity system. The temperature dependence of the frequency of the soft mode is obtained. Possible physical models of the phase transitions are discussed.

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INTRODUCTION

The possible onset of a local phase transition in an impurity system was predicted theoretically by Hock and Thomas[1] for ferroelectric crystals. Kristofel'[2] pointed out the possibility of the onset of a local soft mode in crystals of other types.

The ordering of the crystal lattice (phase transitions in crystals), which is connected with the condensation of the "soft" phonon mode, leads, as is well known, to singularities in the temperature dependences of the resonant-line widths. Thus, in $SrTiO_3$ near the structural phase transition at $T = 110$ K, Muller[3] observed a substantial broadening of the EPR of the Fe^{3+} impurity. Luders and Renk[4] observed anomalies in the temperature dependence of the half-width of the phononless line of the optical absorption of Eu^{3+} in $SrTiO_3$—a substantial broadening at $50 < T < 110$ K and a negligible one at $110 < T < 300$ K. This behavior of the width was attributed by them to the presence of a soft phonon mode of the entire crystal.

We have investigated the temperature dependence of the EPR line width of Fe^{3+} in $KTaO_3$. Potassium tantalate is a virtual ferroelectric, in which no phase transitions were observed. Therefore the anomalies in the temperature dependence of the width—the growth at $200 < T < 400$ K and the practically constant value in the interval 400–900 K—are attributed to the presence of a local phase transition in the paramagnetic-impurity system. Theoretical estimates have shown this assumption to be reasonable.

1. EXPERIMENT

The widths of the EPR lines of the Fe^{3+} impurity were measured with an RE-1301 microwave spectrometer. The temperature was varied by blowing a stream of nitrogen vapor (77–300 K) or air (300–900 K) through the resonator of the spectrometer. To prevent fogging of the resonator, a double quartz tube was used. The temperature was registered with a copper–constantan ($T < 300$ K) or a platinum–platinum–rhodium ($T > 300$ K) thermocouple. The thermoelectric power was measured with an R-348 dc potentiometer. The stability and the accuracy of the temperature measurements were not worse than 1 K.

The $KTaO_3$ single crystals were grown from the melt by the Czochralski method. The charge contained an excess of K_2CO_3 over the stoichiometric composition. The dopant amounted to 0.7 at. % relative to the Ta_2O_5 used in the charge.

The EPR spectrum of the impurity Fe^{3+} ($3d^5$, $^6S_{5/2}$) was investigated by Wessel[5] and is described by the spin Hamiltonian

$$\hat{\mathcal{H}}_0 = g\beta H(\hat{S}_z\cos\theta + \hat{S}_x\sin\theta) + D\hat{S}_z^2 \qquad (1)$$

with constants $D = 1.44$ cm^{-1} and $g = 2.00$.

We measured the angular dependences of the EPR line widths of the Fe^{3+} impurity (transition $\frac{1}{2} \longleftrightarrow -\frac{1}{2}$) at the temperatures 77 and 300 K (Fig. 1). The magnetic field rotates in the xz plane and makes an angle θ with the z axis. At $T = 77$ K there is a noticeable correlation with the angular dependence of the splitting of the EPR lines of Fe^{3+} in an external electric field, which was observed in Ref. 6. The observed correlation between the angular dependences of the EPR line widths and the electric-field effect offer evidence that the EPR line width at these temperatures is due to the internal electric fields of the defects.

The angular dependence of the EPR line width at $T = 300$ K (Fig. 1) correlates with the rate of change of the resonant magnetic field $dH_{res}/d\omega$. In fact, the observed angular dependence of $\Delta H(\theta)$ can be described by the formula

$$\Delta H_{\frac{1}{2},-\frac{1}{2}} = \frac{\hbar}{g\beta}\frac{1}{\tau}(\cos^2\theta - 9\sin^2\theta)^{-\frac{1}{2}}. \qquad (2)$$

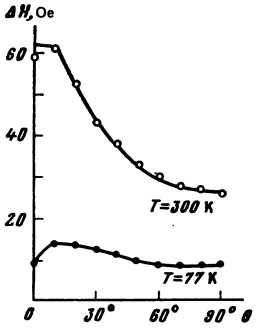

FIG. 1. Angular dependence of the line width of the EPR of Fe^{3+} in $KTaO_3$: points—experiment, solid line—theory.

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The angle factor in (2) is connected with the function $dH_{res}/d\omega$ obtained on the basis of the results of Ref. 6.

When the temperature is raised from 77 K, the EPR lines of the Fe^{3+} impurities broaden noticeably, and at $T > 400$ K the width is practically independent of the temperature (Fig. 2). As will be shown below, the temperature broadening can be described by an exponential law with a temperature-dependent argument of the exponential.

We note that at temperatures 77–600 K an external electric field up to $E = 150$ kV/cm does not change the intensities of the EPR lines of the Fe^{3+} impurity.

The EPR line shape is close to Lorentzian in the entire temperature interval.

DISCUSSION OF RESULTS

The substantial broadening of the EPR lines in the interval 200 K $< T <$ 400 K might be, generally speaking, connected with the motion of the oxygen vacancies near the paramagnetic impurities. This motion would lead, with rising temperature, to an exponential broadening, and then to a motional narrowing.[7] Our estimates of the parameters of this mechanism have shown that owing to the large constant D, no motional narrowing should be observed, so that the width should increase in the entire investigated temperature interval $T < 900$ K. This contradicts the constant value of the width at 400 K $< T <$ 900 K.

That there is no motion of the vacancies is evidenced also by our investigation of the influence of the external electric field on the EPR spectrum. As indicated above, the intensities of the EPR lines of an Fe^{3+} impurity with oxygen vacancy do not change in fields up to 150 kV/cm. We note that in the case of a paramagnetic Mn^{2+} center with oxygen vacancy the intensities of the EPR lines change by a factor of 2 already at 40 kV/cm. It is shown in Ref. 6 that this is due to the reorientation of the vacancies in the external field.

A broadening of the zero-phonon line of the optical transition $^5D_0 \rightarrow {}^7\Gamma_1$ of the Eu^{3+} ion in $SrTiO_3$, which is qualitatively similar to the picture observed by us, was reported in Ref. 4. The temperature broadening was attributed there to the interaction of the impurity with a soft transverse optical mode that leads to a structural phase transition at 110 K.

We have assumed that in our case the main contribution to the temperature broadening of the line is made by the interaction of the paramagnetic center with the phonons. Favoring this assumption is the change of the character of the angular dependence of the EPR line width with increasing temperature. If the broadening is due to the interaction with optical or local oscillations of frequency ω, then the temperature dependence of the width for two-phonon processes is determined by the factors[9,10] $n(\omega)[n(\omega)+1]$ ($n(\omega) = [\exp(\hbar\omega/kT) - 1]^{-1}$ is the Bose-Einstein factor). Thus, the width of the EPR line can be written in the form

$$\Delta H = \Delta H_0 + B\frac{\exp(\hbar\omega/kT)}{[\exp(\hbar\omega/kT)-1]^2}, \tag{3}$$

where ΔH_0 is the temperature-independent part of the width at $T < 150$ K. A comparison of (3) with the experimentally measured dependence of the width of the EPR line on T leads to a temperature-dependent frequency ω with a minimum at $T_c = 365$ K for all B (Fig. 3). It is seen from this figure that ω^2 is a linear function of $T - T_c$ near T_c. The slope of this line at $T > T_c$ depends on the value of the parameter B; at $T < T_c$ the slope is constant. Thus, $\omega^2 = \omega_0^2 + A(T - T_c)$, where $A = A_1$ at $T < T_c$ and $A = A_2$ at $T > T_c$.

The appearance of a quasisoft mode in the vibrational spectrum of the crystal may be due either to a phase transition in the crystal itself or to ordering in the impurity system.

Since such specific singularities were observed only in the temperature dependence of the EPR line of the Fe^{3+} impurity (we investigated also the temperature behavior of the EPR line widths of the impurities Mn^{2+}, Ti^{3+}, Cd^{3+}), we have assumed that a local phase transition takes place in the impurity system. Favoring this assumption is the absence of changes in the temperature dependence of the spectrum of Cd^{3+} and of singularities in the dielectric susceptibility of the crystal.

It can thus be assumed that the frequency $\omega(T)$ obtained from the temperature dependence of the EPR line width of the impurity Fe^{3+} in $KTaO_3$ is evidence of a local phase transition. As usual, the ratio of the co-

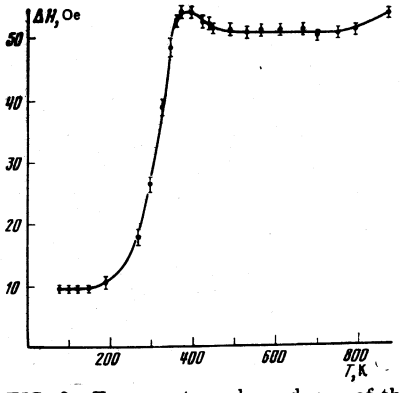

FIG. 2. Temperature dependence of the EPR line width of Fe^{3+} in $KTaO_3$.

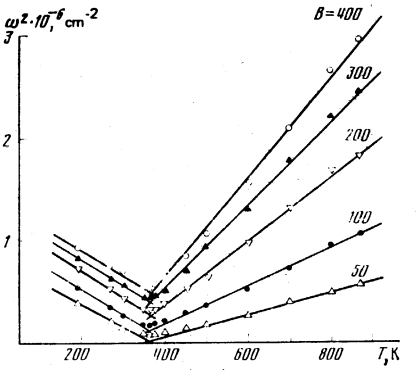

FIG. 3. Family of temperature dependences of the squares of the frequencies of the soft mode at different values of the parameter B.

efficients of $T-T_c$ in the ferroelectric and paraelectric phases should be equal to 2. This ratio is obtained at $B=50$, $\omega_0=9.7$ cm^{-1}, and $A_1=2280$ cm^{-2}/deg. It is probable that this amplitude is connected with the paramagnetic center. Using the obtained values of ω_0 and A_1 we can estimate the frequency at other temperatures. Thus at $T=77$ K we have $\omega=700$ cm^{-1}. This agrees in order of magnitude with estimates obtained in the oscillator model on the basis of experimental results on the influence of external electric fields on the EPR spectra in $KTaO_3$:

$$\omega^2=\frac{(z_1/M_1)E_{loc}^{(1)}-(z_2/M_2)E_{loc}^{(2)}}{u_1-u_2} \quad (1\text{–}Fe^{3+}, 2\text{–}O^{2-}); \tag{4}$$

the local fields E_{loc} and the difference u_1-u_2 of the displacements of the atoms were taken from Refs. 6 and 8.

The rather large values we obtained for the frequencies of the local oscillations at $T\gg T_c$ fall in the gap between the frequencies of the natural oscillations in $KTaO_3$, namely $\omega_{LO_4}=837$ cm^{-1} and $\omega_{TO_4}=547$ cm^{-1}.[11] This possibility is connected with the fact that the dispersion of the phonon branches in crystals of this type is usually small. If it is recognized that the mass of the iron ion is less than the mass of the tantalum ion, then the observed local oscillations can be split off from the branch $\omega_{TO_4}=547$ cm^{-1}. On the other hand, one should not exclude the possibility of local oscillations with a higher-frequency branch $\omega_{LO_4}=837$ cm^{-1}, since the presence of a vacancy in a site adjacent to the impurity can cause a decrease in the elastic-coupling constants.

The local phase transition can be due to displacement of the Fe^{3+} ion at $T=365$ K in the direction of the axis joining the paramagnetic Fe center and the vacancy. In the case of displacement in a perpendicular direction, a splitting of the EPR lines, proportional to $dH_{res}/d\theta$ (i.e., maximal at $\theta=15°$) should be observed if $T<T_c$.

The criterion given in Ref. 1 for the appearance of a local phase transition for a displacement-type impurity is of the form

$$3\gamma kT_c+V_0K<V_0^2. \tag{5}$$

Here K and γ are the constants of the harmonic and anharmonic terms, respectively, in the vibrational energy of the impurity;

$$V_0=\sum_{ll_1}V_{ll_1},$$

where V_{ll_1} characterizes, as usual, the interaction of the ions in different unit cells of a crystal. Using for $KTaO_3$ the values $\gamma=1.5\cdot10^{19}$ J/m^4 (Ref. 12), $V_0=z^2\gamma_0/3\varepsilon_0a^3$ (Ref. 13), and $K=M_{Fe}\omega_1^2$, where z is the charge of the ion, a^3 is the volume of the unit cell, γ_0 is the Lorentz factor, and ω_1^2 is the unrenormalized frequency of the harmonic oscillator (assumed equal to the Debye frequency for the estimates), we verify that the criterion (5) is indeed satisfied. Recognizing that $3\gamma kT_c\ll V_0K$, we reduce expression (5) to the requirement $K<V_0$, i.e., it is necessary that the polarization that displaces the ion from the site be stronger than the repulsion that tends to keep in in the site.

For a transition of the order-disorder type (impurity of the Ising type) the criterion for the appearance of a soft local mode[1] is also satisfied. In this case one can speak of "freezing" of the motion of the vacancies near the paramagnetic impurities. However, the observed temperature dependence of the frequency of the soft mode is poorly described by a function of the type[1] $(T-T_c)/T$. In addition, as indicated above, no change is observed in the intensities of the EPR lines in an electric field not only at low temperatures, but also at $T>T_c$.

We note in conclusion that the nonzero frequency ω_0 can be due, for example, to the fact that the soft mode is damped and has "memory." In this case, as shown in Ref. 14, the frequency of the soft mode is not equal to zero at T_c if the relaxation is slow enough.

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