Electric-field effect in ESR and local fields in $KTaO_3$

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Splitting ΔH_E of the ESR line of Fe^{3+} in $KTaO_3$ was determined in electric fields at 77°K in the 3-cm and 8-mm wavelength ranges. The angular and electric-field dependences of the splitting were investigated. A correlation between the angular dependences ΔH_E and the rate of change of the resonance field on rotation of a sample in a magnetic field was observed experimentally and derived theoretically. This correlation was explained using a model allowing for the displacements of ions in an electric field. This made it possible to estimate the local field at an oxygen site from the electric field effect in ESR. The observed deviation of the electric-field dependence of ΔH_E from linearity was used to find the anharmonicity constant in the Landau phenomenological theory.

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INTRODUCTION

Investigations of the electric-field effects in ESR yield very valuable information on the physical properties of ferroelectric crystals. For example, determination of the nonlinear electric-field dependence of the shift of the ESR line of Gd^{3+} in $KTaO_3$ yielded the constants of the Landau phenomenological theory.[1] A study of the influence of the electric field on the ESR line intensities[2] was used to determine the local electric fields at sites in an ideal crystal lattice. The value of a local field was found at the Ta site.

In the present paper we shall use measurements of the angular dependences of the ESR line splitting in an electric field to show that the displacements of lattice ions and local fields can be determined. We shall estimate the field at an oxygen site. The essence of the method is as follows: the observed correlation between the angular dependences of ΔH_E and $dH_r/d\theta$ can be explained by a model involving ion displacements. These displacements are due to the local fields and are deduced from the splitting of the ESR line in an electric field. The observed deviation of the electric-field dependence from linearity yields an estimate of the anharmonicity constant in the Landau theory. This constant describes satisfactorily the electric-field dependences of the splittings of the ESR lines of Fe^{3+}, Mn^{2+}, and Gd^{3+} in $KTaO_3$.

1. EXPERIMENTAL METHOD

The ESR spectra of Fe^{3+} in $KTaO_3$ were determined in external electric fields (0–250 kV/cm) using ESR rf spectrometers operating in the 3-cm (RÉ-1301) and 8-mm ranges; this was done at liquid nitrogen temperature. The crystals employed were grown by the Czochralski method. The paramagnetic impurity concentration was $N = 3$ at.% in the original charge. The ESR spectra were also investigated at liquid nitrogen temperature by Wessel and Goldick,[3] who discovered the presence of several paramagnetic iron centers. Our investigation dealt with the ESR spectrum of the Fe^{3+} ($3d^5$, $^6S_{5/2}$) axial centers with an oxygen vacancy in its immediate environment, which can be 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 $g = 2.00$ and $D = 1.44$ cm^{-1}. The magnetic field was applied in the xz (010) plane and made an angle θ with the z [001] axis of the centers. The observed ESR line corresponded to a transition between the states of the lower Kramers doublet.

An external electric field E parallel to the y or z axis did not split or shift the ESR lines in magnetic fields of all orientations in the xz plane. A significant splitting of the ESR line was observed only in the $E \parallel x$ case. The angular dependences of the splitting are shown in Fig. 1 for the 3-cm and 8-mm ranges. The line shifts obtained for a fixed angle and in the same electric field are in the ratio of the corresponding microwave frequencies. The angular dependences of the ESR lines in an electric field (Fig. 1) are correlated with the angular dependences of the rate of change of the line position on rotation of the magnetic field in $E = 0$, i.e., they are correlated with the value of $dH_r/d\theta$. The electric field producing the splittings shown in Fig. 1 lies in the range of E which satisfies the condition $\Delta H_E \sim E$.

The influence of an external electric field on the ESR

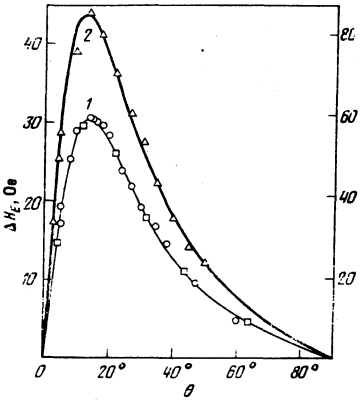

FIG. 1. Angular dependences of the splitting ΔH_E of the ESR line of Fe^{3+} in $KTaO_3$ in $E = 140$ kV/cm (○) and of the rate of change of the resonance field $dH_r/d\theta$ in the 3-cm range (□) (curve 1) and the angular dependence of ΔH_E in $E = 52$ kV/cm (△) in the 8-mm range (curve 2).

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spectrum of the investigated paramagnetic center (point symmetry C_{4v}) can be described by adding to Eq. (1) the spin Hamiltonian $\hat{\mathcal{H}}_E$ of the type

$$\begin{aligned}\hat{\mathcal{H}}_E=&T_{zzz}E_{lz}H_z\hat{s}_z+T_{xxz}E_{lz}(H_x\hat{s}_x+H_y\hat{s}_y)\\&+T_{zxx}(E_{lx}H_x+E_{ly}H_y)\hat{s}_z+T_{xzx}H_z(E_{lx}\hat{s}_x+E_{ly}\hat{s}_y)\\&+R_{zzz}E_{lz}\hat{s}_z^2+R_{xxz}[E_{lz}\{\hat{s}_x\hat{s}_z\}+E_{ly}\{\hat{s}_y\hat{s}_z\}],\end{aligned}\qquad(2)$$

where E_l is the local electric field acting on this center:

$$E_l=E+4\pi\gamma P/3.\qquad(3)$$

Here, P is the dipole moment per unit volume and γ is the factor allowing for the deviation of the environment symmetry from cubic. In the case of ferroelectric crystals the local field E_l is usually dominated by the second term.

In general, P is a nonlinear function of the external field. However, in weak fields we have $P\propto E_l$. Since curve 1 in Fig. 1 belongs to this range, we shall assume that $E_l\propto E$ and we shall include the constant of proportionality in the tensors T and R.

The observed line splittings are considerably less than the resonance field and, therefore, $\hat{\mathcal{H}}_E$ can be regarded as a perturbation to the Hamiltonian $\hat{\mathcal{H}}_0$. The eigenvalue spectrum of $\mathcal{H}_0$ was calculated on a computer and analytically. In the latter case the Zeeman energy Hamiltonian was regarded as a perturbation, which was reasonable in the 3-cm range.

Calculations of ΔH_E carried out using exact wave functions and their approximations gave similar results. We shall give the expressions obtained in the perturbation theory and we shall try to make them clear.

In the second order of the perturbation theory the lower Kramers doublet is characterized by

$$H_r=\frac{h\nu}{g\beta}(\cos^2\theta+9\sin^2\theta)^{-1/2},\qquad(4a)$$

$$\frac{dH_r}{d\theta}=-\frac{4h\nu}{g\beta}\frac{\sin 2\theta}{(\cos^2\theta+9\sin^2\theta)^{3/2}}\qquad(4b)$$

where ν is the klystron frequency.

The angular dependence $dH_r/d\theta$ plotted on the basis of Eq. (4b) is represented by a continuous curve in Fig. 1. We can see that the approximation employed is sufficiently accurate to describe the experimental results.

The resonance field (4a) describes the position of the ESR line for two types (I, II) of the Fe^{3+}–$V(O^{2-})$ paramagnetic centers (Fig. 2). In an external electric field the Hamiltonian $\hat{\mathcal{H}}_E$ of the I and II centers differs by the sign of Eq. (2). This difference is responsible for the ESR line splitting. The magnitude of the splitting, calculated in the first order of the perturbation theory in the operator $\hat{\mathcal{H}}_E$, can be represented in the form

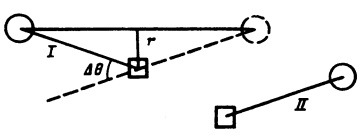

FIG. 2. Rotation of the paramagnetic centers in an electric field: □) impurity ion; ○) oxygen vacancy.

$$\begin{aligned}\Delta H_E=-\frac{h\nu}{g\beta}\frac{1}{(\cos^2\theta+9\sin^2\theta)^{3/2}}\Big\{&E_x\sin 2\theta\Big[\frac{T_{xxz}}{g\beta}+\frac{9T_{zzz}}{g\beta}-\frac{8R_{xxz}}{D}\Big]\\&+2E_z\Big(\frac{T_{zzz}}{g\beta}\cos^2\theta+\frac{9T_{zzz}}{g\beta}\sin^2\theta\Big)\Big\}.\end{aligned}\qquad(5)$$

In agreement with the experimental results, we can see from Eq. (5) that $\Delta H_E=0$ for $E\|y$. Calculations indicate that this result is associated with the absence of the H_y component of the magnetic field. Within the limits of the experimental error, there is no splitting for $E\|z$ in magnetic fields for all orientations in the xz plane. Consequently, we may conclude that $T_{zzx}=T_{xxx}=0$.

Equations (4b) and (5) also demonstrate clearly a correlation between the angular dependences of ΔH_E for $E\|x$ and of $dH_r/d\theta$ for $E=0$, which is in agreement with the experimental results.

The continuous curve 1 in Fig. 1 is the angular dependence of the ESR line splitting calculated from Eq. (5) for $E=E_x$ in the 3-cm range using just one theoretical parameter

$$\frac{T_{xxz}}{g\beta}+\frac{9T_{zzz}}{g\beta}-\frac{8R_{xxz}}{D}=2.5\cdot10^{-4}\text{cm/kV}.$$

The theory describes satisfactorily the experimental results.

Figure 3a gives the dependence of the splitting of the ESR line of Fe^{3+} in $KTaO_3$ on an external electric field. The corresponding dependences for Mn^{2+} and Gd^{3+} (Ref. 1) are shown in Figs. 3b and 3c. It is clear from these figures that there is a deviation from the expected linear (Fe^{3+}, Mn^{2+}) and quadratic (Gd^{3+}) dependences.

The correlation between the angular dependences of ΔH_E and $dH_r/d\theta$ has been found also experimentally in the range where ΔH_E varies nonlinearly with E. Allowance for small nonlinear corrections obtained in various orders of the perturbation theory alters the

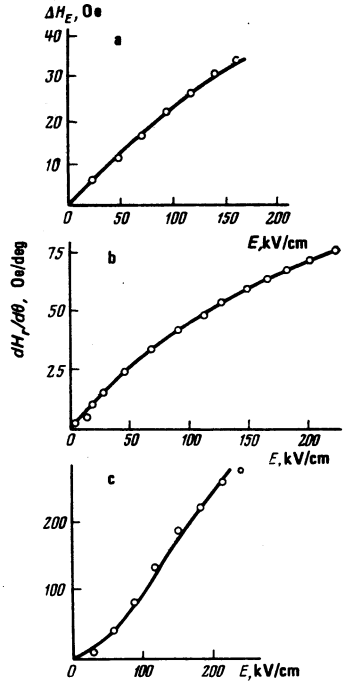

FIG. 3. Electric-field dependences of the splitting of the ESR line of Fe^{3+} for $\theta=15°$ (*a*) and of the displacements of the ESR lines of Mn^{2+} ($|-3/2\longleftrightarrow-1/2|_\perp$ transition) (*b*) and of Gd^{3+} ($|-7/2\longleftrightarrow-5/2|_\parallel$ transition) (*c*) in $KTaO_3$. The points are the experimental values.

angular dependence of ΔH_E and, therefore, disturbs the correlation. In view of this, we may assume that throughout the investigated range of electric fields (up to 200 kV/cm) we can use Eq. (5) in which $E_i = E_{1i}$.

By analogy with our earlier paper,[1] we shall attribute the dependence of ΔH_E on E to the nonlinear dependence of the local field on E. The latter is associated with the contribution of the anharmonic terms to the free energy. The continuous curves in Fig. 3 are plotted including such terms and assuming that $\xi = 0.5 \times 10^{10}$ $V \cdot m^5 \cdot C^{-3}$ (ξ is the anharmonicity parameter). The experimental results for all the impurities Fe^{3+}, Mn^{2+}, and Gd^{3+} are described satisfactorily by the theory (Fig. 3).

2. DISCUSSION OF RESULTS

The correlation between the angular dependences of the shift ΔH_E linear in respect of E_i and of $dH_r/d\theta$ may occur in all systems characterized[1)] by $D \gg g\beta H$. This follows from Eqs. (4) and (5). Such a situation occurs, for example, in some perovskite ferroelectrics with paramagnetic centers that have a vacancy in their immediate environment.

The splitting of the ESR line correlated with $dH_r/d\theta$ can be understood on the basis of the following model. Let us assume that a crystal contains axial paramagnetic centers of two types and that their axes meet at an angle of $\Delta\theta$ but their D constants and g factors are identical. If the angle between the axis of the center I and the magnetic field is θ, then for the center II the same angle is $\theta + \Delta\theta$. If $\Delta\theta \ll \theta$, the resonance field H_{rII} can be expanded as the series

$$H_{r\,II} = H_{r\,I} + \frac{dH_r}{d\theta}\Delta\theta + \dots .$$

It is clear that, in general, the ESR spectrum consists of two lines and the separation between them in the approximation linear in $\Delta\theta$ is

$$\Delta H_x = H_{r\,II} - H_{r\,I} = -\frac{dH_r}{d\theta}\Delta\theta. \qquad (6)$$

In this model the ESR line splitting in an electric field correlated with $dH_r/d\theta$ can be explained by different displacements of the Fe atoms and the oxygen vacancy in a field. This causes the axes of the investigated centers to deviate by an angle $\Delta\theta/2$ from the [001] direction.

If the ESR line splitting ΔH_E observed in $E \| x$ is written in the form of Eq. (6), it then follows from Eqs. (4) and (5) that the angle between the axes of the centers I and II (Fig. 2) can be expressed in the form

$$\Delta\theta = \frac{E_x}{4}\left(\frac{T_{xxz}}{g\beta} + \frac{9T_{xxx}}{g\beta} - \frac{8R_{xxz}}{D}\right). \qquad (7)$$

The angle $\Delta\theta$ is related to the tensors T and R and to the spin Hamiltonian constants. The values of the tensors T and R depend on the electronic and ionic polarizabilities of the defects and, as shown above, on the ratio $\delta = E_{1oc}/E$. It is shown in Ref. 2 that at the Ta site this ratio is large: $\delta \approx 1600 = \gamma(\varepsilon - 1)/3$. This is typical of ferroelectrics with the perovskite structure (ABO_3). In such crystals the angle between the axes of centers of two types may be sufficient for the experimental observation.

A calculation based on Eq. (7) gives $\Delta\theta = 0.0087 = 0.5°$ for $E = 140$ kV/cm. The value $\Delta\theta$ deduced from measurements in the 3-cm range makes it possible to describe, with the aid of Eq. (6), the angular dependences of the splitting also in the 8-mm range without introducing any adjustable parameters (curve 2 in Fig. 1). An elementary geometric construction (Fig. 2) gives the relative displacement $r = 0.0088$ Å.

It is clear from the measurements that the permittivity depends weakly on the paramagnetic impurity concentration in the range $N \leq 3$ at.%. For a cubic crystal, we have

$$\Delta P_i = E_i \Delta\varepsilon_{ii}/4\pi, \qquad (8)$$

where $\Delta\varepsilon$ and ΔP are the changes in the permittivity and dipole moment per unit volume due to the addition of an impurity. If we assume that the displacements of Fe and Ta in $KTaO_3$ are similar, we obtain from Eq. (8)

$$2e(u^O - u^{Fe}) \approx \alpha^O E_{lx}^O,$$

where E_{lx}^O is the local field at an O″ site; u^O and u^{Fe} are the displacements of the oxygen and iron ions in an electric field; α^O is the electronic polarizability of oxygen. Substituting the above displacement for $r = u^O - u^{Fe}$, we obtain $E_{lx}^O \approx 80E$. The local field estimated in this way is in agreement with that calculated by us for $KTaO_3$ in the Slater model.[4]

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[1)] If the terms with the T tensor are dropped from ΔH_E, the correlation is retained for arbitrary relationships between D and $g\beta H$.

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