Acceleration of spin-lattice relaxation of tunneling $[AlO_4]^0$ centers in quartz by an electric field

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Experiments show that the rate of spin-lattice relaxation of tunneling paramagnetic centers can be controlled by means of a low-frequency, nonresonant, external electric field.

1. Studies of effects induced by electric fields at tunneling paramagnetic centers can yield detailed information on the processes by which charged particles tunnel in solids and on how these processes are affected by external electric and magnetic fields.[1]

Among the tunneling paramagnetic centers which have received the most study are the $[AlO_4]^0$ aluminum centers in quartz.[1–5] A steady-state cooling of these centers by means of external electric fields was described in Refs. 3–5. A reduction of the rate of spin-lattice relaxation of these centers induced by a static electric field was described in Ref. 6. The energy structure of these centers was calculated in Refs. 1 and 7. In the present letter we are describing a new electric-field-induced effect at $[AlO_4]^0$ centers in quartz.

2. The experiments were carried out at $T=4.2$ K on a 3-cm-range superheterodyne ESR spectrometer. The procedure for applying the electric field to the sample was similar to that described in Refs. 1, 4, and 5.

We studied samples of synthetic pleochroic quartz with relative aluminum-center concentrations $c=N/N_{max}$ of 0.05, 0.11, 0.18, 0.40, 0.70, and 1.0 (N_{max} corresponds to roughly 10^{18} cm^{-3}). The samples with the various concentrations were prepared by annealing in a muffle furnace.

In the samples with a low concentration of $[AlO_4]^0$ centers ($c<0.18$) we detected a sharp increase in the intensities of the ESR signal from the centers upon the application of an alternating electric field $E_\sim$ (curve *1* in Fig. 1). Curve *2* in this figure shows for comparison the effect described in Refs. 3–5, which is observed in samples with a high concentration of centers. The effect represented by curve *1* (in contrast with the effect represented by curve *2*) is observed only upon saturation of the ESR signals by the microwave field. We detected this effect at frequencies of the electric field in the range $200\leqslant\nu_E\leqslant800$ Hz and at microwave power levels $P>0.01$ mW.

To determine the mechanism for the observed effect, we studied the influence of the field $E_\sim$ on the extremum of the ESR-signal saturation curves. It was found that in samples with a concentration of aluminum centers $c>0.7$ the field $E_\sim$ has essentially no effect on the saturation curves, while in samples with $c<0.4$ it shifts the extremum of these curves toward higher power levels. For the experimental conditions corresponding to curve *1* in Fig. 1 this shift was ~15 dB. We detected this effect in

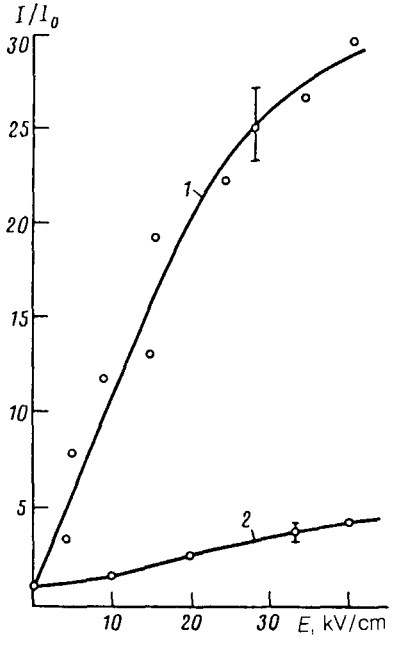

FIG. 1. Increase in the intensity of the ESR signals versus the amplitude of the alternating electric field. *1,2*—Samples with relative concentrations of aluminum centers $c=0.11$ and 1.0, respectively. The intensity I_0 is the signal intensity under the conditions $E=0$, $T=4.2$ K, $\mathbf{H}\| \mathbf{E}\| L_3$, $\nu_E=300$ Hz, and $P\approx 0.1$ mW.

two orientations of the electric and magnetic fields, namely $\mathbf{H}\| \mathbf{E}\| L_2$ and $\mathbf{H}\| \mathbf{E}\| L_3$, where L_2 and L_3 are the twofold and threefold axes of the crystal. We found no significant differences in the effect in these two orientations.

3. Studies of the rf-spectroscopic and structural characteristics of $[AlO_4]^0$ centers were described in Refs. 1–8. Associated with these centers in addition to the magnetic moment is an electric dipole moment **d**, formed by the Al^{3+} ion and O^- ion, at which a paramagnetic hole is localized.[2–5] The hole can undergo a tunneling between different sites of the oxygen ions (we will call these sites *1* and *2*). This tunneling corresponds to a reorientation of the electric dipole from $\mathbf{d}_1$ to $\mathbf{d}_2$ (Refs. 2 and 3).

Since the crystal contains internal oriented electric fields E_i, which are associated with lattice defects, the two-well potential in which a hole moves is distorted[2,4–6] by an amount $2\Delta_i=(\mathbf{d}_1-\mathbf{d}_2)E_i$. The distribution function of these distortions can be approximated by[5]

$$f(\Delta_i)=\frac{1}{\sqrt{\pi}\Delta_0}\exp\left[-\left(\frac{\Delta_i}{\Delta_0}\right)^2\right], \tag{1}$$

where Δ_0 is the width of the distribution function. When an external electric field $E_\sim$ is applied to a crystal, the distortion of the two-well potential is given by $2\Delta_j=2\Delta_i+2\Delta_E$, where $2\Delta_E=(\mathbf{d}_1-\mathbf{d}_2)E_\sim$. The external electric field $E_\sim$ thus causes a periodic shift of the distribution function of the distortions of the two-well potentials (Fig. 2a).

The spin-lattice relaxation of $[AlO_4]^0$ centers in quartz is caused[6] by rapidly relaxing centers, for which (Fig. 2b) the Stark energy is roughly equal to the Zeeman energy: $2\Delta_j\approx g\beta H$. For these rapidly relaxing centers, the Zeeman levels with different

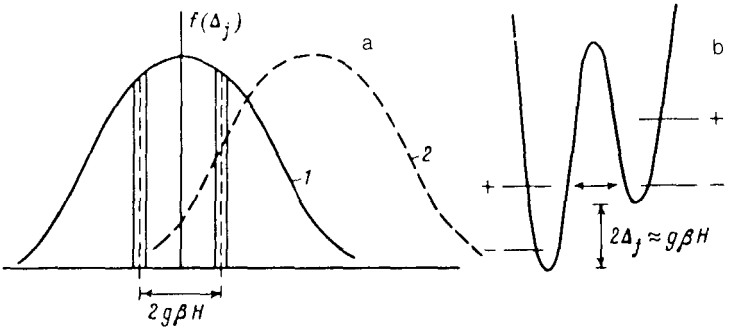

FIG. 2. a: Distribution function of the distortions of two-well potentials in the absence (1) and presence (2) of an external electric field. The hatched regions are the regions of distortions corresponding to rapidly relaxing centers. b: Two-well potential in the case $g\beta H \approx 2\Delta_j$. The plus and minus signs indicate the projection of the spin onto the magnetic field.

spin projections onto the magnetic field of the centers in the different wells are degenerate (Fig. 2b). As a result, the tunneling is intensified, and the spin-lattice relaxation of the centers is accelerated.[6]

In the samples with a high concentration of aluminum centers the spin-lattice relaxation of the bulk of the centers occurs through a spin diffusion to the rapidly relaxing centers.[5,6] In samples with a low concentration of centers, this spin diffusion is evidently hindered. When an alternating electric field is imposed on a sample, however, the different centers play the role of the rapidly relaxing centers in different parts of the period of this field (Fig. 2a). As a result, there is an effective acceleration of the spin-lattice relaxation of the centers, since the different centers relax in specifically those time intervals in which they are playing the role of the rapidly relaxing centers. In this case the time scale of the spin-lattice relaxation of the $[AlO_4]^0$ centers is a function of the external electric field: $T_1 - T_1(E_\sim)$. In the simplest case, the intensity of the ESR signal can be described as a function of the microwave field intensity H_1 by[3]

$$I = H_1 \Delta N (1 + 2T_1 W)^{-1}, \tag{2}$$

where ΔN is the difference between the populations of the Zeeman levels when the spins are at equilibrium with the lattice, and W is the probability for transitions induced by the microwave field. Here[9] $W \sim H_1^2$. When the field $E_\sim$ is imposed, the quantity T_1 in (2) should be understood as $T_1(E)$. We can then write the following expression for the ratio of the ESR signal intensities in the cases with and without the field:

$$\frac{I(E)}{I_0} = \frac{1 + 2T_1 W}{1 + 2T_1(E) W}. \tag{3}$$

At saturation of the ESR signals, i.e., under the conditions $2T_1 W \gg 1$ and $2T_1(E) W \gg 1$, expression (3) can be written in the form

$$I(E)/I_0 = T_1^{-1}(E)/T_1^{-1}. \quad (4)$$

The intensification of the ESR signals is thus determined by the ratio of the relaxation rates of the centers in the presence and absence of the field $E_{\sim}$.

The model described above is obviously too simplified for making a quantitative comparison with experiment. Expressions (3) and (4), along with the comments above regarding the mechanism for the relaxation of the $[AlO_4]^0$ centers, make it a simple matter to understand the shape of curve *1* in Fig. 1.

The symmetry characteristics of the standard electric-field-induced effects in the intensities of ESR signals are determined by the symmetry of the piezoelectric tensor of the crystal.[10,11] Since in our case the effect also occurs when $\mathbf{E}\| L_3$ (there is no piezoelectric effect in this case), the effect which we have been discussing here differs qualitatively from the standard effects in terms of symmetry characteristics.

In addition to its obvious use for intensifying ESR signals in low-concentration samples, the effect described here may find use for extracting detailed information on tunneling processes and spin-diffusion processes in a system of paramagnetic centers.

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