Relaxation averaging of ESR spectrum broadened by spread in spontaneous polarization

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Near a coincidence of the resonant positions of two ESR transitions of a high-spin center, a new signal is observed in addition to these two transitions. This new signal is due to a relaxation averaging of some of the lines which are broadened as a result of a spread in the spontaneous polarization.

In the ferroelectric compound germanate, $Pb_5Ge_3O_{11}$ ($T_c \approx 450$ K, $P\bar{6} \leftrightarrow P3$), a narrow additional signal appears near a coincidence of the resonant positions H_{res} of the $-1/2 \leftrightarrow -3/2$ and $1/2 \leftrightarrow 3/2$ transitions of the trigonal Gd^{3+} center[1] (the polar angle is $\theta \approx 42°$). The additional signal appears between the signals corresponding to these two transitions (curve 2 in Fig. 1). It increases as the point of coincidence, H_{res}, is approached (by virtue of a change in orientation). The shape of the ESR spectrum does not depend on the microwave power level. The effect is not seen near coincidences in the positions of other signals, but between the $1/2 \leftrightarrow -1/2$ and

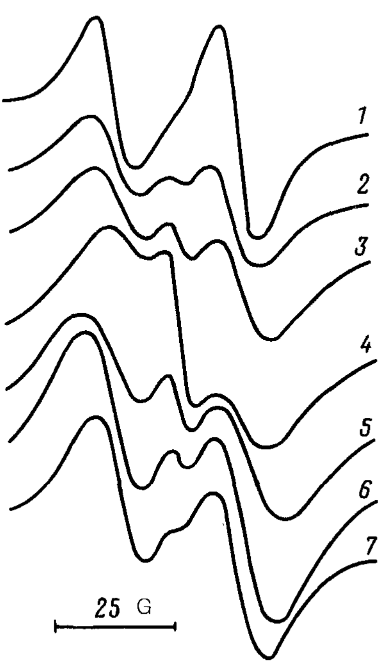

FIG. 1. Shape of the ESR transitions $1/2 \leftrightarrow 3/2$, $-1/2 \leftrightarrow -3/2$ (the first derivative of the absorption signal) of Gd^{3+} ions in lead germanate at $\theta = \theta_0 - 0.5$ (θ_0 is the polar angle at which the positions of the transitions are the same) at various temperatures: *1*—404; *2*—436; *3*—442; *4*—446; *5*—468; *6*—475; *7*—520 K.

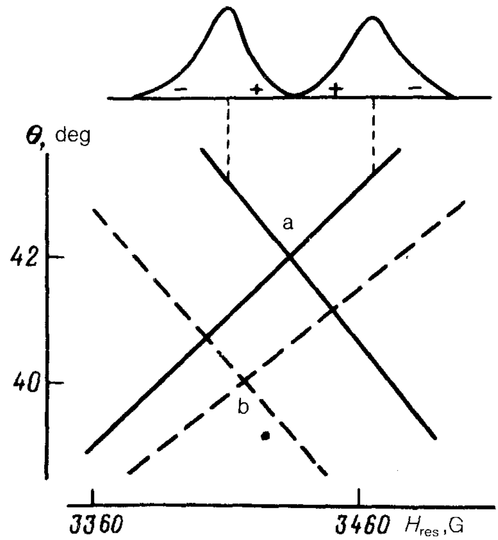

FIG. 2. Fragment of the polar-angle dependence of the positions of the $\pm 1/2 \leftrightarrow \pm 3/2$ transitions ($\varphi \approx 0°$) of ions in different domains (the solid and dashed lines). The + and − at the top show the positions of the spin packets in the ESR line corresponding to the maximum and minimum values of the spontaneous polarization.

$-1/2 \leftrightarrow -3/2$ transitions we do see some two-quantum transitions with a stronger dependence of the intensity on the microwave power. These transitions are easier to observe when the temperature is lowered.

The additional signal is not observed in a polydomain sample upon a coincidence of the positions of the $\pm 1/2 \leftrightarrow \pm 3/2$ transitions belonging to opposite domains (Fig. 2). The magnitude of the effect is different near crossings *a* and *b* in Fig. 2, reflecting a dependence on the azimuthal angle φ with a period of 120°. An increase in the concentration of the paramagnetic impurity (crystals doped with 0.0075%, 0.02%, and 0.1% Gd_2O_3 were studied) causes a slight increase in the angular interval $\Delta\theta$ in which the new signal is observed. Figure 1 shows the temperature dependence of the shape of the ESR spectrum of the $\pm 1/2 \leftrightarrow \pm 3/2$ transitions at a fixed disorientation from a coincidence of the H_{res} values. We see an anomalous behavior of the intensity of the additional signal near the ferroelectric transition.

We believe that the appearance of this new signal can be attributed to a cross-relaxation process which couples initial transitions which have been broadened nonuniformly by a spread in the magnitude of the spontaneous polarization. Since the spontaneous polarization is a macroscopic parameter, the interacting ions (which exchange excitation) are usually in identical local fields; i.e., they belong to a common spin packet. This situation does not arise in the case of a magnetic dipole broadening. Figure 2 shows the position of the spin packets corresponding to the extreme local fields. If the cross-relaxation probability W is nonzero, near an H_{res} coincidence, there will always be pairs of spin packets of two transitions for which W is greater than the spectral separation δH (in frequency units). These packets will form an exchange-narrowed line at the center. As the distance between the original signals decreases as a result of a change in θ, progressively more-intense spin packets experience narrowing

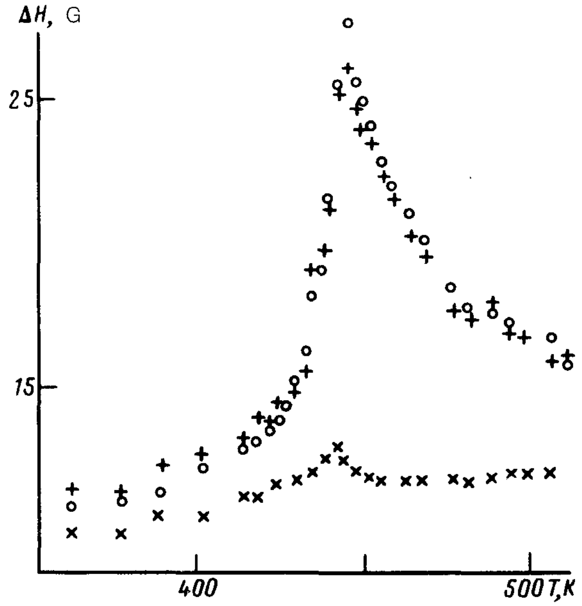

FIG. 3. Temperature dependence of the linewidth of Gd^{3+} transitions in lead germanate. ×—(− 1/2↔1/2); ●—(− 1/2↔ − 3/2); + —(1/2↔3/2) at $\theta \approx 39°$, $\varphi \approx 0°$.

conditions, so the intensity of the central signal increases. Spin packets for which the opposite inequality, $W < \delta H$, holds will be only slightly broadened and shifted toward the center.

One reason for the anomalous increase in the intensity of the additional signal near a ferroelectric transition (Fig. 1) is a pronounced nonuniform broadening of the $\pm 1/2 \leftrightarrow \pm 3/2$ transitions near T_c (Fig. 3) due to the spin-spin interaction of impurity Gd^{3+} ions through the field of soft optical phonons[2]

$$\sum_{j>i} R_{ij} O^i_{43} O^j_{43} ,$$

where O_{43} are the Stevens spin operators, and R_{ij} are functions of the temperature and of the angle between the coupling axis and C_3. This field arises because of the term $b_{43} O_{43}$, which is linearly related to the polarization, in the spin Hamiltonian of an isolated ion.[3] An increase in the nonuniform broadening at a fixed distance between the centers corresponding to the signals will understandably have the result that progressively more intense spin packets will become involved in the fast-relaxation regime. In the language of Ref. 4, the meaning is an increase in the probability for cross-relaxation due to an increase in the form factor. The absence of an additional signal near an H_{res} coincidence of the $1/2 \leftrightarrow -1/2$ and $\pm 1/2 \leftrightarrow \pm 3/2$ transitions both at room temperature and at T_c is a consequence of the small value of the nonuniform broadening of the $1/2 \leftrightarrow -1/2$ transition. The broadening is small because dH_{res}/dP_c is small and because the interactions through soft phonons have only a slight effect on it (Fig. 3). Observations near a coincidence of other transitions are complicated by an overlap of the signals and by a large difference in intensity.

Another reason for the anomalous behavior of this effect near T_c (Fig. 1) might be a structural feature on the temperature dependence of the cross-relaxation probability due to an increase in the parameters of the interaction which causes cross-relaxation transitions. The mechanisms for the transfer of excitation will be the subject of a following paper.

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Translated by Dave Parsons