ANGULAR DEPENDENCES OF THE EPR LINE WIDTHS OF Cr^{3+} *IN* $ZnWO_4$

A. A. BUGAĬ, M. D. GLINCHUK, M. F. DEĬGEN, P. T. LEVKOVSKIĬ, V. M. MAKSIMENKO, and V. A. SEN'KIV

Institute for Semiconductors, Ukrainian Academy of Sciences

Submitted July 22, 1968

Zh. Eksp. Teor. Fiz. 56, 111–114 (January, 1969)

The angular dependences of the EPR line widths during the rotation of an external static magnetic field in three mutually perpendicular planes were studied experimentally. A theoretical analysis was carried out of the spin-phonon mechanism of line broadening. A satisfactory agreement between theory and experiment was obtained.

THE angular dependences of the EPR line widths and the influence of external electric fields on the profile and width of the EPR lines have been investigated experimentally and theoretically.[1-4] A theory has been developed on the assumption that the line broadening is due to the spin-phonon interaction. An explanation exists[1] of the experimentally observed correlation between the angular dependences of the splitting of a line in an external electric field and the line width. A dependence of the EPR line profile on an external electric field was predicted in[4] and detected experimentally in[3]. A qualitative explanation of the angular dependence of the line width and of the correlation effect was also given in[5,6] on the assumption that the line broadening is due to the electric fields of impurities in crystals.

An experimental investigation of the angular dependence of the line width of the EPR of Cr^{3+} in $ZnWO_4$ was carried out in[1,2,6] using a magnetic field rotating in a plane perpendicular to a symmetry axis. A theoretically calculated half-width[2] has three free parameters, which have been determined by comparison with experiment.

It has seemed necessary to carry out new experiments and to compare results with the theory so as to reduce the number of free parameters. Such a comparison should make it possible to determine the role of the spin-phonon mechanism in the line broadening. With this purpose in mind, we investigated experimentally and theoretically the angular dependences of the EPR line width during the rotation of a magnetic field in three mutually perpendicular planes.

The measurements of the EPR half-width were carried out using an EPR spectrometer working in the 3-cm range at room temperature. We used single-crystal samples of $ZnWO_4$ with admixtures of Cr^+ ions and compensating Li^+ impurities. The concentration of the Cr ions was approximately 0.1% in the original charge. The samples were oriented in the resonator in such a way that when a magnet was rotated, the orientation of the magnetic field was varied in one of the three planes: xz, yz, xy (the y axis was assumed to coincide with the C_2 symmetry axis of a crystal). We investigated the EPR line corresponding to a transition between levels of the lower Kramers doublet. The experimental results are presented in Figs. 1-3.

A theoretical analysis was carried out using the quantum transport equation method, similar to that described

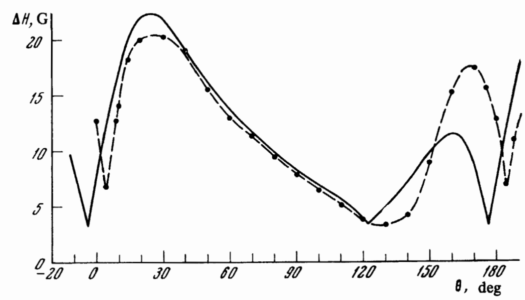

FIG. 1. Angular dependence of the EPR line half-width (transition $-3/2 \rightarrow -1/2$) during the rotation of **H** in the xz plane. The continuous curve is theoretical ($A_0 = 10$, $A_1 = 33$, $A_2 = -5.8$); the points and the dashed curve represent the experimental results.

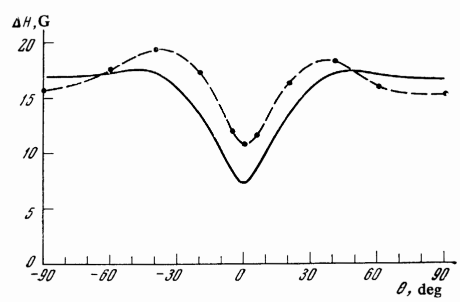

FIG. 2. Angular dependence of the EPR line half-width (transition $-3/2 \rightarrow -1/2$) during the rotation of **H** in the yz plane. The continuous curve is theoretical ($B_0 = 27$, $B_2 = -23$); the points and the dashed curve represent the experimental results.

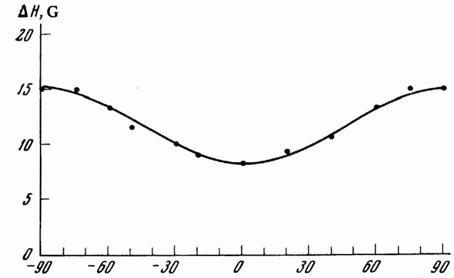

FIG. 3. Angular dependence of the EPR line half-width (transition $-3/2 \rightarrow -1/2$) during the rotation of **H** in the xy plane. The continuous curve is theoretical $C_0 = 8.4$, $C_2 = -3.4$); the points represent the experimental.

in[2]. The solution of a system of transport equations for the components of the density matrix with a Hamiltonian including the pure spin part (the Zeeman component and the crystal field), the phonon part, and the spin-phonon interaction, made it possible to determine the dynamic magnetization and the EPR line profile.

The high-temperature approximation was used to obtain the following formulas for the EPR line half-width, corresponding to a transition between levels in the lower Kramers doublet in those cases when a magnetic field was rotated in the xz, yz, and xy planes [Eqs. (1), (2), and (3), respectively]:

$$\frac{1}{\tau}=\frac{1}{\sqrt{1+3\sin^2\theta}}\left[A_0+A_1\frac{\sin 2\theta}{1+3\sin^2\theta}+A_2\frac{\cos^2\theta}{1+3\sin^2\theta}\right], \quad (1)$$

$$A_0=4\Phi_1^{1,1}(0)+12\Phi_1^{1,-1}(0)+{}^1\!/_2\Phi_1^{0,0}(0)+6\Phi_1^{1,-1}(\omega_0),\quad A_1=4\Phi_1^{0,1}(0), \quad (1a)$$

$$A_2={}^1\!/_2\Phi_1^{0,0}(0)-4\Phi_1^{1,1}(0)-4\Phi_1^{1,-1}(0);$$

$$\frac{1}{\tau}=\frac{1}{\sqrt{1+3\sin^2\theta}}\left[B_0+B_2\frac{\cos^2\theta}{1+3\sin^2\theta}\right], \quad (2)$$

$$B_0={}^1\!/_2\Phi_1^{0,0}(0)+12\Phi_1^{1,-1}(0)+6\Phi_1^{1,-1}(\omega_0)-4\Phi_1^{1,1}(0), \quad (2a)$$

$$B_2={}^1\!/_2\Phi_1^{0,0}(0)-4\Phi_1^{1,-1}(0)+4\Phi_1^{1,1}(0);$$

$$\frac{1}{\tau}=C_0+C_2\cos 2\varphi, \quad (3)$$

$$C_0={}^1\!/_4\Phi_1^{0,0}(0)+6\Phi_1^{1,-1}(0)+3\Phi_1^{1,-1}(\omega_0),$$
$$C_2=2\Phi_1^{1,1}(0). \quad (3a)$$

Here, θ and φ are, respectively, the polar and azimuthal angles; $\Phi_1^{\lambda,\mu}$ is the Fourier transform of the correlation function (cf.[2]); $\omega_0 = 2D$, where D is the crystal field constant.

Eqs. (1)—(3) take into account only those terms of the spin-phonon Hamiltonian

$$\mathscr{H}_{\text{s-p}}=F_1{}^0\hat{S}_z+F_1{}^{-1}(\hat{S}_x+i\hat{S}_y)+F_1{}^1(\hat{S}_x-i\hat{S}_y)$$

which are linear in spin.

It is evident from Eqs. (1a)—(3a) that the parameters A_i, B_i, and C_i are related by three expressions, for example,

$$A_0+A_2=B_0+B_2,\quad {}^1\!/_2A_0=C_0+C_2,\quad {}^1\!/_2B_0=C_0-C_2. \quad (4)$$

Comparison of the theory and experiment was carried out for the anisotropic part of the half-width, found as the difference between the observed value and the average "background". This background was evidently due to approximately isotropic interaction mechanisms, which were not allowed for in the theory.

It is evident from Eqs. (2) and (3) that the half-widths of the lines in the case when the magnetic field rotates in the yz and xy planes are even functions of the angle. Figures 2 and 3 show that the experimental values of the half-widths are indeed represented by curves which are symmetrical with respect to the origin of the coordinates.

Comparison of the theoretical predictions with the experimental results for the three planes makes it possible to obtain good agreement by a suitable selection of parameters (cf., for example[2] for the xz plane). However, in this case one of the relationships between the parameters given in Eq. (4) is satisfied less well than the other two. This is probably due to the fact that the theory allows only for one of the possible broadening mechanisms, i.e., the phonon mechanism. In fact, other mechanisms, including those producing a nonuniform line broadening (effect of electric fields of impurities, mosaic structure, scatter of values of the crystal field constants, etc.), also result in angular dependences of the line width. Moreover, the use of an isotropic average "background" may give rise to errors in estimates of the parameters. Therefore, we should expect only a qualitative agreement between the theory and experiment.

Use of the relationships given in Eq. (4) to compare the theoretical predictions with the experimental results (determination of two parameters by "joining" the half-width in the xy plane, and of one parameter by the same procedure in the yz plane, and use of the parameters determined in this way in plotting the curve in the xz plane) gives the results shown in Figs. 1—3.

It is evident from Eqs. (1a)—(3a) that the knowledge of the coefficients A_i, B_i, and C_i makes it possible to carry out approximate estimates of some Fourier transforms of the correlation functions.

In conclusion, we must mention that it would be desirable to investigate the temperature dependences of the line widths in order to separate the various broadening mechanisms.

[1]M. D. Glinchuk and M. F. Deĭgen, Zh. Eksp. Teor. Fiz. 53, 1657 (1967) [Sov. Phys.-JETP 26, 952 (1958)].

[2]A. A. Bugaĭ, P. T. Levkovskiĭ, V. M. Maksimenko, M. V. Mashkovskiĭ, and A. B. Roĭtsin, Zh. Eksp. Teor. Fiz. 50, 1510 (1966) [Sov. Phys.-JETP 23, 1007 (1966)].

[3]A. A. Bugaĭ, M. D. Glinchuk, M. F. Deĭgen, and P. T. Levkovskiĭ, ZhETF Pis. Red. 6, 790 (1967) [JETP Lett. 6, 247 (1967)].

[4]M. D. Glinchuk, M. F. Deĭgen, and G. V. Korobko, Fiz. Tverd. Tela 9, 3198 (1967) [Sov. Phys.-Solid State 9, 2519 (1968)].

[5]W. B. Mims and R. Gillen, Phys. Rev. 148, 438 (1966).

[6]B. F. Jones, W. S. Moore, and J. Neal, Brit. J. Appl. Phys. (J. Phys. D) Ser. 2, 1, 41 (1968).

Translated by A. Tybulewicz
16