New type of ESR spectra in a partially-oriented matrix

I. V. Ovchinnikov, I. G. Bikchantaev, and N. E. Domracheva

Kazan' Physicotechnical Institute, USSR Academy of Sciences
(Submitted April 19, 1976)
Pis'ma Zh. Eksp. Teor. Fiz. **23**, No. 10, 584–587 (20 May 1976)

In addition to the lines typical of vitreous systems, the ESR spectra of partially oriented matrices have revealed additional lines with an angular dependence typica of single crystals. The conditions for the observation of these additional lines are explained.

PACS numbers: 61.30.+w, 61.50.Jr, 76.30.−v

It is known that the reason why ESR spectra of single crystals yield much information is that the line positions depend on the orientation of the single crystal in the external magnetic field. There is no such dependence, of cours for ESR spectra of systems with a random distribution of the particles (powde or high- and low-temperature glasses). With increasing degree of orientation paramagnetic particles in a partially oriented matrix, the spectrum typical of the vitreous system should be transformed into the spectrum that is characteristic of the single crystal, i.e., a certain intermediate situation should be realized. Oriented matrices of this type are liquid crystals. To our knowledg however, in oriented liquid crystals, under conditions when the translational

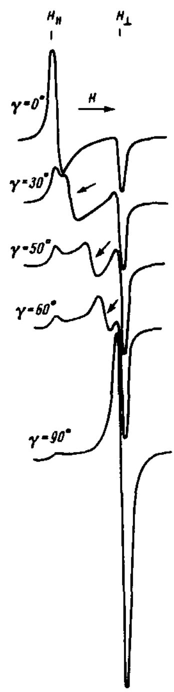

FIG. 1. ESR spectra of dimethyldithiocar bamate in an oriented lyotropic liquid cry tal (aqueous solution of sodium laurate), $T=180$°K.

ıd rotational motions of the paramagnetic particles are frozen, the spectra ›served to date differed from the spectra of randomly oriented systems only the dependence of the intensity (but not the position) of the individual lines ı the magnetic-field direction relative to the preferred orientation axis.[1,2]

We report here observation of an ESR spectrum of the "intermediate" type 'igs. 1 and 2) in oriented liquid-crystal matrices. Besides the lines typical the vitreous state, the positions of which are determined by the minimal ıd maximal values of the resonant magnetic field,[3] the spectrum reveals lditional lines whose position, just as in single crystals, depends on the orientation of the sample relative to the magnetic field.

The spectrum of the copper complex (Fig. 1) in the initial orientation (zero ıgle γ between the orientation axis and the magnetic field) consists of two exıange-narrowed lines typical of particles having axial symmetry with g factors $=2.103$ and $g_\perp = 2.023$. The position of the additional line, determined at the

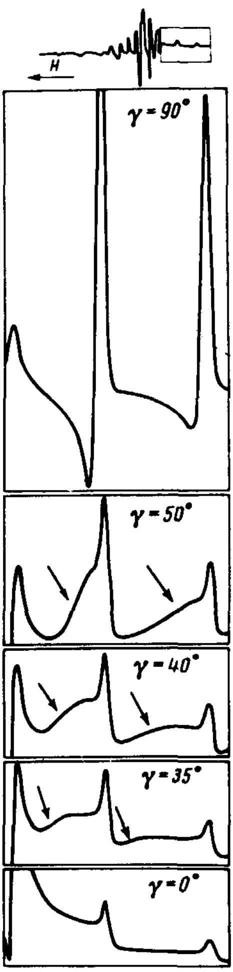

FIG. 2. Fragments of ESR spectra of vanadyl acetylacetonate in an oriented nematic liquid crystal (MBBA), $T=180\,°K$.

point of its intersection with the null line, depends on the angle via the relatio $g^2 = g_{\parallel}^2 \cos^2\gamma + g_{\perp}^2 \sin^2\gamma$. The intensity of the parallel component at $\gamma = 0$ is large than at $\gamma = \pi/2$, thus indicating a preferred orientation of the axial molecule axis along the orientation axis.

In the ESR spectrum of the vanadyl complex (Fig. 2), each pair (parallel an perpendicular) of hyperfine-structure components with definite value of the projection of the nuclear magnetic moment ($I_{V^{51}} = 7/2$) corresponds to an additional line that moves when the sample rotates in antiphase compared with the preceding case. The intensity of the parallel components in the initial orientation $\gamma = 0$ is less than at $\gamma = \pi/2$, thus indicating a predominant distribution of th axial axis of the molecules in a plane perpendicular to the orientation axis. Th additional lines are in the case more weakly pronounced and do not cross the null line. For this reason, they were not noted in the earlier investigations carried out on nematic-type crystals.

A theoretical computer calculation of the absorption line shape of a model system (Fig. 3) not only confirms fully the very possibility of the existence of

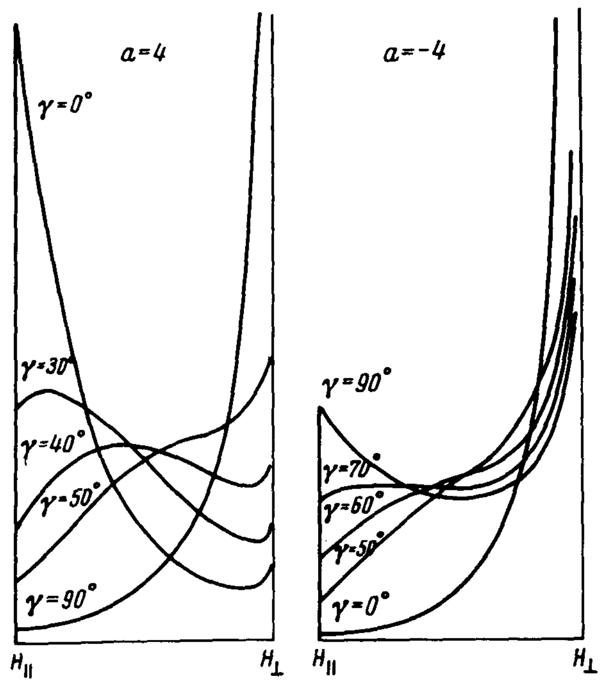

FIG. 3. Theoretical integral absorption lines of particles with $g_{\parallel} = g_{\perp} = 0.08$, th axial axes of which are distributed relative to the preferred direction with probability $P(\beta) \sim \exp(a \cos^{2\beta})$.[1] The cases $a > 0$ and $a < 0$ correspond to the tw distribution methods obtained in the experiments.

the unusual additional lines, but also explains the different positions, intensities, and shapes of these lines in the spectra shown in Figs. 1 and 2. As follows from the figures, the best conditions for the observation of the additional lines are realized in the case when the axial axes are distributed about the eferred direction. These conditions depend on the anisotropy of the g factor. the anisotropy of the g factor is appreciable then, other conditions being ual, the line is more clearly pronounced at $g_{\parallel} > g_{\perp}$ than at $g_{\parallel} < g_{\perp}$.

Owing to the observed singularity, more information is contained in e ESR spectra and, by the same token, additional extensive possibilities of vestigating partially oriented systems are uncovered.

The authors are deeply grateful to B. M. Kozyrev and S. A. Al'tshuler for terest in the work and for a useful discussion.

J. Bulthuis, C. W. Hilbers, and C. Maclean, Magnetic Resonance 4, 201 (1974).
J. H. Freed, Annual Rev. Phys. Chem. 23, 265 (1972).
S. A. Al'tshuler and B. M. Kozyrev, ÉPR soedineniĭ élementov promezhutochnykh grupp (ESR of Intermediate-Group Elements), Moscow, 1972, p. 358.