Simulation of the Orientation Ordering of Paramagnetics in Films on the Surface and in the Interlayer Space

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Abstract

A technique is proposed for quantitative description of partially oriented paramagnetic systems. The characterization is based on the assumption concerning the existence of one selected orientation for the major axis of the tensors of magnetic resonance parameters forming the angle α between the direction of the major axis z and the direction of the perpendicular to the substrate plane; another assumption is random scattering of the angle α with respect to this direction according to the Gauss law with the half-width equal to σ. The parameters α and σ are optimized by simulation of theoretical ESR spectra using a programme specially created for this model; the calculated and simulated spectra are then compared. The logic of this approach was applied to a series of experimental systems ($Cu(aa)_2$, $CuCl_2$ and $Cu(dpm)_2$ in the C_2F matrix).

INTRODUCTION

As a first approximation, solid substances can be divided into ordered (single crystal) and random (amorphous glass, polycrystal or powder) substances. With a more detailed view, we speak of texture which means partial ordering. This is the case when translation ordering is absent but the phase is characterized by more or less strict long-range orientation order of the fragments comprising the structure. This situation often occurs for the phases composed of the molecules with the dimensions substantially different with respect to three coordinates, or in thin layers organized on the surface (like pencils in a cup or lamella on a table). If the textures are organized from paramagnetic substances, it is not compulsory for magnetic axes of paramagnetic centres to coincide with macroscopic axes of the texture. Orientation ordering is sometimes exhibited also in liquids when in the presence of an external electric or magnetic field the molecules get arranged in a definite manner with respect to the lines of force of this field. This is the case of liquid crystals. The ordering of molecules leads to rather unusual properties exhibited under the action of light, magnetic field or electric current which can be used in definite technological developments.

On the other hand, when preparing oriented films the researchers have not too many possibilities to characterize and study them. Besides, the techniques available are rather poor. For example, methods based on X-ray diffraction cannot reveal amorphous phase on the surface even if it is well oriented. The method of polarization Raman spectroscopy follows lattice vibrations which also implies crystal character of the layer deposited.

So, it seems profitable to use ESR to develop the techniques for the characterization of surface and oriented bulk samples [1]. This method has some advantages with respect to the problem under consideration. First, it is sensitive to the orientation of the symmetry axes of the paramagnetic centres with respect to constant magnetic field. Other advantages that sometimes turn into shortcomings are the bulk character of samples, high sensitivity to paramagnetics and complete insensitivity to diamagnetics.

From the viewpoint of experimental technique of recording ESR spectra and simulation of the orientation ordering, paramagnetic centres in thin films do not differ from the centres that are in the solutions of oriented liquids or intercalated into he interlayer space of an oriented crystallite of fluorinated graphite. The molecules of the paramagnetic compound are captured between the macromolecules of the matrix and are to orient so that their longer dimension would go along the matrix planes. This position has also an effect on the movements of intercalated molecules when the rotation around a definite axis is possible but it is not possible around other axes. When temperature increases, the energy barrier can be overwhelmed, and the transition from anisotropic rotation to isotropic one occurs. This situation was observed earlier with the intercalate of a paramagnetic molecule NO_2 in C_2F matrix [2].

If the main magnetic axes of the paramagnetic centre do not coincide with the lines corresponding to minimum or maximum molecular dimensions, a molecule is forced to direct itself so that the main axes of g- and A-tensors form a definite angle with respect to the matrix plane.

These considerations served as the basis for numerical model describing ESR spectra of textured samples. Further on, this numerical model was organized as a programme allowing to simulate spectra, compare them with experimental ones (including quantitative comparison performed by calculating square mean deviation) and record them in a format accepted by the Bruker Co. (WinEpr programme). This programme works in dialogue regime and allows to change orientation and the reference spectrum without closing it and thus to fit all the parameters of the spin Hamiltonian and the orientation characteristics of the texture during one session. When working out the technique, we did not aim at the creation of a multipurpose programme but pay attention to the development of working capacity of the approach. The limitation connected with electron spin, the number of magnetic nuclei and the corrections of the order above the first one was accepted on purpose, so that we could speed up the calculations of specific systems in which the introduction of second-order corrections does not cause any substantial changes of the result.

CALCULATIONS

The observed phenomena are interpreted on the basis of spin Hamiltonian (SH) technique. The algorithm of the determination of SH constants is based on the following scheme: starting from the assumed structure of the sample and literature data on g-factors and hyperfine splitting constants typical for such a case, we select initial values for the calculation which are then corrected by comparing theoretical ESR spectra with experimental ones. In case of rather good agreement in the positions and relative intensities of lines in the spectra, the interpretation of spectra is accepted as successful. Some discrepancy can often be explained by the approximate character of the model which, for example, does not take account of the isotope composition of atoms in the paramagnetic centre or the scattering of some SH parameters due to the sample nonhomogeneity. Sometimes, in order to achieve better agreement, it is important to take account of higher-order corrections. If the discrepancy is rather large and fitting of parameters does not help to improve the agreement, then the model of the structure assumed initially is neglected. It is natural that the unambiguity of the solution obtained according to this algorithm is limited by the imagination of experimenters.

At the present stage, we shall be interested only in the Zeeman and hyperfine interactions in the paramagnetic centre with the spin $1/2$ (the basis of spin functions with the projections m_s equal to $+1/2$ and $-1/2$). Hyperfine interaction will be limited only to one magnetic nucleus. The solution of the secular equation for the case of anisotropic g-factor gives the position of the line of resonance transition for a single centre [3]:

$$H_{res}(\theta, \varphi) = (h\nu/\beta)/\{(g_{xx}^2\cos^2\varphi + g_{yy}^2 \sin^2\varphi) \sin^2\theta + g_{zz}^2 \cos^2\theta\}^{-1/2}$$

The probability of transition varies from one orientation to another within the limits of g-factor anisotropy. This means that when the direction of the magnetic field is changed, the position of the line of magnetic resonance will change from the point corresponding to the orientation with maximum g-factor to the point

corresponding to the minimum g with insignificant change of intensity.

In order to obtain the ESR spectrum of the sample, it is necessary to integrate the lines of all the orientations taking into account the probabilities for each orientation. Small changes of the probabilities of transitions caused by the anisotropy of g-factor can be neglected. The change of the probability $P(\theta)$ due to the change of solid angle proportional to $\sin\theta$ is more substantial.

In textured samples, the probability for the paramagnetic centre to occur with some definite magnetic field orientation with respect to its main values can be substantially different. In the general case, it is determined by the structure of paramagnetic centre and the method of sample preparation. There is a complete randomness in the selection of a function to describe the distribution of paramagnetic centres. It is principally impossible to obtain an unambiguous result in this case, however, it is possible to start from general assumptions and to build up a model which would allow to calculate some quantitative parameters of the subject.

In the present work the model is built up assuming that the crystallites or paramagnetic centres, due to their geometric features, are oriented preferentially with one of their main axes (designated as z) at a definite angle α with respect to the perpendicular to the plane of substrate or C_2F crystallite. The scattering of orientations of the major axis z with respect to the perpendicular is random and can be described by the Gauss distribution with half-width σ. The distribution of probabilities is normalized which depicts the conservation of the number of paramagnetic centres in the sample:

$$W(\psi,\,\alpha,\,\sigma) = N\exp(-\ln 2\,(\psi-\alpha)^2/\sigma^2)$$

In order to obtain the probability function $P(\theta,\varphi)$ which is required to simulate the ESR spectrum of the sample, it is necessary to prescribe the orientation of texture in the magnetic field of spectrometer. Considering paramagnetic particle on the substrate plane oriented at an angle γ with respect to the magnetic field, we can connect the orientation (θ,φ) with the angle γ and calculate ψ determining the probability to
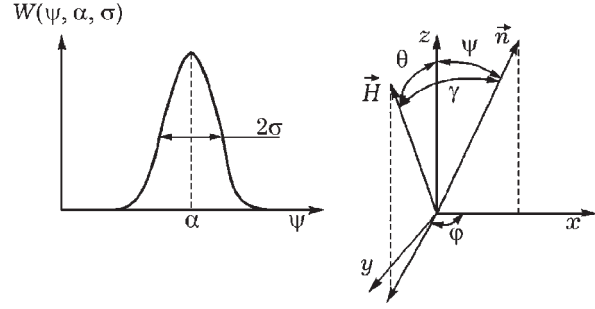

Fig. 1. Angle transformation scheme.

find such a particle in the sample, $i.\,e.$ to obtain the $P(\theta,\varphi)$ function with the parameters α,σ,γ (Fig. 1):

$$\cos\psi = \cos\theta\cos\gamma + \sin\theta\cos\varphi\sin\gamma$$

$$P(\theta,\,\varphi,\,\alpha,\,\sigma,\,\gamma) = W(\psi,\,\alpha,\,\sigma)\sin\theta$$

The developed mathematical model does not pose any substantial limitations on the sample structure since the Gauss function does not limit the width of distribution; at rather large σ, the model describes the spectra of unoriented powders quite satisfactorily. The deviation of real function from the Gaussian approximation would not have a strong effect on the resulting theoretical spectrum if the real distribution is more or less smooth. However, if for some reasons the real sample will exhibit more than one sharply preferred directions, the model would be unacceptable.

In the systems where the magnetic moment of electron interacts with the magnetic nucleus, for example copper ion, an anisotropic hyperfine splitting can be observed. Usually, the energy of hyperfine interaction is much less than the Zeeman interaction energy and is taken into account as the perturbation in the first or second order of the perturbation theory. Orientation dependence can be expressed in the first order as follows [3−5]:

$$A_2(\theta,\,\varphi) = \{(A_{xx}^2 g_{xx}^2\cos^2\varphi + A_{yy}^2 g_{yy}^2\sin^2\varphi)\sin^2\theta$$
$$+ A_{zz}^2 g_{zz}^2\cos^2\theta\}/g_2(\theta,\,\varphi)$$

The programme to model ESR spectra calculates the position and intensity of the resonance transition for each orientation, splits it into the corresponding number of hyperfine splitting lines and imparts the Gaussian or Lorentzian shape. The spectrum is recorded as a massif of points corresponding to the magnetic field
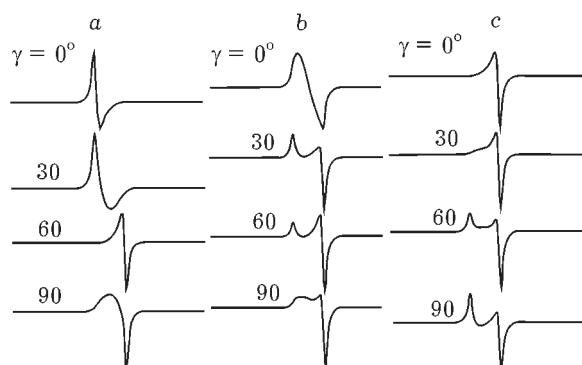
Fig. 2. Results of the simulation of ESR spectra of the hypothetical textures with different distribution parameters for $\sigma = 20^\circ$ and $\alpha = 0$ (*a*), 45 (*b*), and 80° (*c*).

sweep. The resulting ESR spectrum is obtained after the accumulation of the spectra of separate orientations after the whole grid of θ and ϕ angles is scanned. The line shape function is used as a derivative to simplify the comparison with experimental spectra recorded with a ESR spectrometer. The massif accumulated is normalized per its second integral, so that the intensity of spectrum would be independent of the density of the integration grid.

The result of simulation is shown on the screen together with the reference spectrum. If necessary, both spectra can be integrated and compared in the integral form. This representation is sometimes more clear. The programme also calculates the square mean deviation for the experimental and thus accumulated spectra, as well as for their integrals. The final spectrum meeting the demands of the experimenter can be saved in the computer memory in the WinEpr format for further use.

In order to demonstrate the programme operation, we accumulated the spectra of oriented hypothetical films with different α, β, γ parameters. The results are shown in Fig. 2.

EXPERIMENTAL PROCEDURE

The goal of the experimental study was to demonstrate the operation capacity of the model under the conditions of real films and textures. We studied the films of copper (II) acetylacetonate obtained by the deposition of volatile complexes onto the surface of Dacron substrates. The films were polycrystal coatings with sharply exhibited anisotropy of ESR spec-

tra. No hyperfine structure was observed in the spectra which corresponded to magnetoconcentrated phase.

Paramagnetic molecules are present in the C_2F intercalates at substantial distances from each other which corresponds to magnetodiluted phase. The probe molecules were intercalated into the interlayer space according to the techniques worked out earlier [1]. The samples with intercalated molecules $Cu(aa)_2$, $Cu(dpm)_2$ and $CuCl_2 \cdot nH_2O$) were obtained.

In order to obtain texture, the intercalate powder was mixed with a small amount of vaseline oil. The paste was pressed between two layers of Dacron film under small vibrations. The excess of vaseline oil was pressed out of the sample while the C_2F crystallites got well ordered. The change of spectra obtained as a result of ordering is clearly exhibited when comparing the ESR spectra of texture and powder of $Cu(dpm)_2$ intercalate in C_2F (Fig. 3).

DISCUSSION

It became possible to put forward the problem of fine analysis of film and texture spectra due to the use of modern means to record and treat ESR spectra. The initial spectrum is accumulated till the required single-to-noise ratio, then the background line with the refence
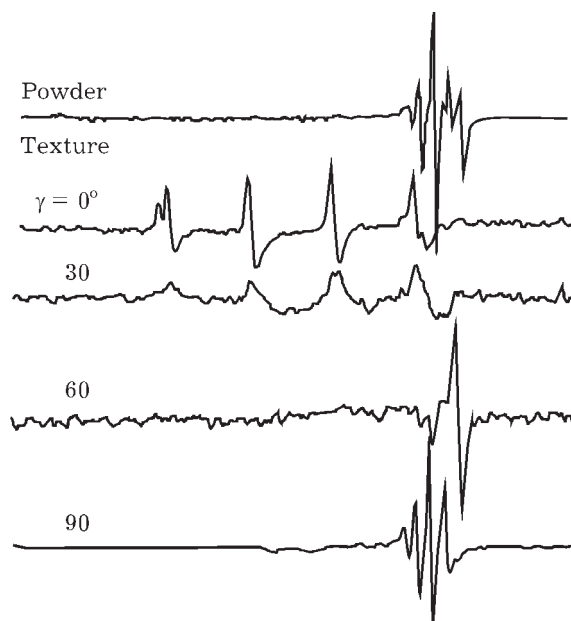

Fig. 3. Changes of ESR spectra obtained as a result of the sample ordering.

spectrum are subtracted. If necessary, an additional correction of the background line is performed and noise is filtered. Then the spectrum is used for comparison with the initial one.

Textured intercalates, unlike paramagnetic complexes deposited onto film surface, exhibit the presence of exchange interaction in the magnetoconcentrated polycrystal phase of films. This interaction leads to the disappearance of hyperfine splitting structure in ESR spectra and to the averaging of signals from differently oriented paramagnetic centres while the main axes of the observed g-factor are brought to the crystal symmetry axes. Now the main values of g-tensor do not correspond to an individual paramagnetic centre but represent a combination of them determined by the manner of molecule packing in the crystal. To the contrary, in textured intercalates the main values of g-tensor and the tensor of hyperfine interaction are due to the structure of the individual paramagnetic centre and possibly to its distortions during intercalation into the inter- layer space. The function of the orientation ordering of the samples is given by the combination of the function of paramagnetic centre ordering in the inter-layer space of the matrix and the ordering of crystallites in the structure. The latter is determined by the technique of sample preparation. In the present study we do not separate these contributions. It can be assumed that the order-

ing of crystallites in all the samples is similar and the contribution from crystallite disordering into σ does not exceed σ for the maximally ordered samples.

Textured intercalate of $Cu(aa)_2$ in C_2F was obtained earlier and its spectra were reported. In the present study we reproduced these results to test the programme in simulating the spectra of textures (Fig. 4). Simulation parameters α and σ are obtained by minimizing the square mean deviation over all the points of the spectrum. To what extent we can rely on them is a separate question. The splitting of the edge components of the spectrum which is observed in experimental spectra when the film is oriented perpendicularly to the magnetic field but is absent from the calculated spectra is not an error. This is conditioned by the occurrence of two natural copper isotopes with slightly different magnetic moments. The programme does not take this fact into account. This agreement between the experiment and calculation can be considered as a good one. To achieve further improvement, second-order corrections can be added in the frames of the perturbation theory and isotope composition can be taken into account.

The $Cu(aa)_2$ film obtained by the deposition of $Cu(aa)_2$ vapour onto Dacron or glass sub-

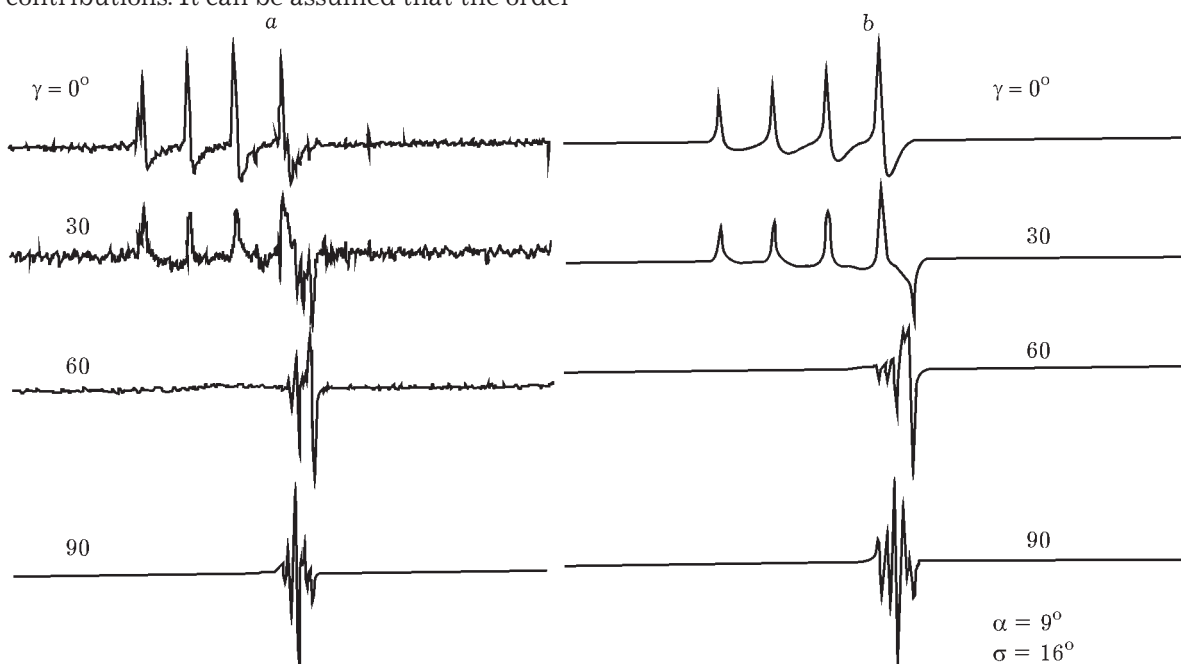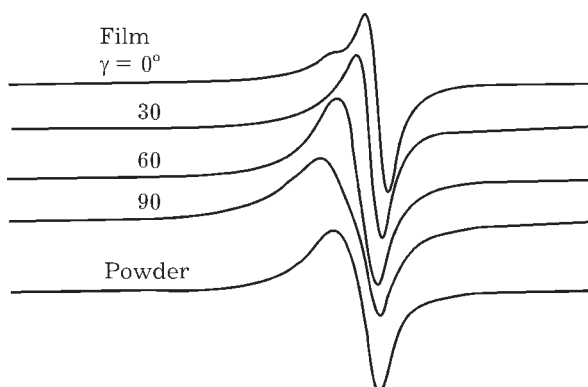Fig. 4. Experimental (*a*) and calculated (*b*) ESR spectra of the $Cu(aa)_2$ intercalate in the C_2F texture.

Fig. 5. ESR spectra of the Cu(aa)$_2$ on the film surface and in powder.

strate is a magnetoconcentrated oriented polycrystal. The orientation dependence of ESR spectra of such a sample is shown in Fig. 5. The simulation of the spectra according to the technique described does not allow to reproduce the main features of the orientation-induced changes in the position and relative intensity of spectral lines at the same parameters of SH and the function of probability distribution. The spectra of separate orientations were reproduced with rather good accuracy but when the angle between the magnetic field direction and the perpendicular to the substrate plane was changed, it was necessary, besides changing the angle γ in the programme, to vary the parameters α and σ, as well as the main values of g-tensor (the latter should be independent of the magnetic field direction). Another warning is the substantial difference between the ESR spectrum of Cu(aa)$_2$ powder and that simulated using the obtained main values of g-tensor. ESR spectra of powder were modelled both according to this programme by taking σ equal to 360° and according to the Simfonia programme of the Bruker Co. The results were similar. The reason of the failure is the real distribution function which is much different from that used in the model.

The intercalate of CuCl$_2 \cdot n$H$_2$O in the C$_2$F texture was obtained by the diffusion of copper salt from the solution in chloroform. In the resulting texture, copper ions are rather mobile at room temperature which is exhibited in strong broadening of lines in ESR spectra. The broadening of lines causes the disappearance of hyperfine structure; however, the spectra remain asymmetric; their width and line shape are different in the parallel and perpendicular orientations of the texture plane with respect to magnetic field direction. This fact is the evidence of anisotropy of the movement of paramagnetic centre. The re-orientation rate is insufficient to provide the averaging of the anisotropy of g-factor and hyperfine splitting constants.

When temperature is decreased to 77 K, the movement is frozen, and hyperfine structure from copper nuclei appears in the spectra. Simulated spectra of the textured sample according to the programme described above exhibited the best correspondence with the experimental ones for the preferable orientation $\alpha = 53^\circ$ and half-width $\sigma = 30^\circ$ (Fig. 6).

The sensitivity of the ESR line shape to the change of orientation parameters is the higher the better is the model fitted to the real structure of the sample. The programme proposed allows to estimate numerically the deviation between the spectra using the least squares method and to minimize the square mean deviation. Minimization can be performed at an accuracy of a degree. However, this minimization can be devoid of real physical sense. In order to clear up this question, it is necessary to estimate the reproducibility of the result in the case of multiple treatment of one and the same sample with different signal-to-noise ratio and different versions of separating the background constituent.

A separate important problem is the possibility to vary the distribution function. In the frames of the available Gaussian function we did not succeed in achieving the acceptable result when modelling the ESR spectra of copper acetylacetonate films. According to X-ray diffraction data, acetylacetonate microcrystals can
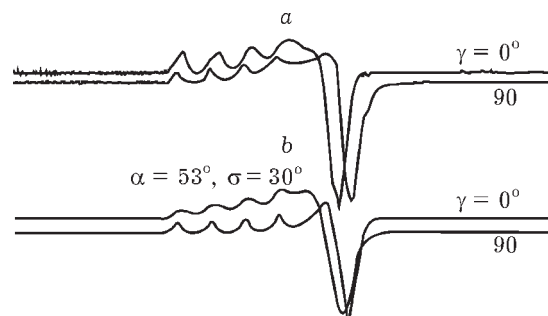

Fig. 6. Experimental (*a*) and calculated (*b*) ESR spectra of the CuCl$_2$ intercalate in C$_2$F texture.

be placed over the substrate surface in two manners orienting either one or another of the major axes of *g*-factor along the normal to the substrate. Quantitative relation between these two versions depends on specific features of film preparation technique and differs from sample to sample. From the viewpoint of developing the calculation technique, it is desirable to foresee the consideration of an arbitrary distribution function, though the arbitrarity and unambiguity are thus increased substantially.

CONCLUSION

The technique proposed is promising to characterize partially oriented paramagnetic films and textures, to determine spatial structure of paramagnetic molecules and attribution to magnetic axes of the paramagnetic centre. The change of orientation parameters α and σ can be used as a criterion of surface modification or change of the ordering degree.

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