Determination of the orientation distribution function of anisotropic paramagnetic species from the angular dependence of the ESR spectra

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A method for determination of the orientation distribution function of anisotropic paramagnetic species from the angular dependence of the ESR spectra based on simulation of the spectra was developed. The orientation distribution function is represented as a sum of orthonormal functions. The weight coefficients are determined by minimizing the deviations of the theoretical spectra from experimental ones. The method was numerically tested. The method is relatively insensitive to the presence of noise and foreign ESR signals not related to the sample orientation in the magnetic field.

Key words: molecular orientation, orientation distribution function, ESR spectroscopy, angular dependence, simulation of the ESR spectra, nonlinear least-squares method.

The properties of many materials (drawn polymers, liquid crystals, Langmuir—Blodgett films, *etc*.) are determined by the orientation ordering of molecules of the medium. The orientation distribution function $\rho(\alpha,\beta,\gamma)$ is the most accurate measure of the species ordering, which shows the number (or the fraction) of species oriented in the range of angles $\alpha + d\alpha$, $\beta + d\beta$, and $\gamma + d\gamma$ (α, β, and γ are the Euler angles that relate the coordinate system of a separate species to the sample coordinate system). No generally accepted methods currently exist that would allow one to find the orientation distribution function for partially oriented molecules. Usually, the partial ordering of species is characterized[1—3] by averaged values: the degree of orientation, the order parameters, *etc*. This approach is natural if optical methods[2] or X-ray absorption spectroscopy[3] are used to determine the degree of orientation of molecules, because these methods provide just parameters averaged over the whole species ensemble. The ESR method is free from this drawback. The position of the resonance signal of each separate species in the ESR spectrum depends on the orientation of this species relative to the magnetic field strength vector. Thus, from the ESR spectra one can derive a more detailed information on the orientation distribution of molecules.

A number of publications[4—14] have been devoted to analysis of the ESR spectra in order to extract data on the orientation distribution of species. The angular dependence of the amplitude of the parallel component of the ESR spectrum of vanadyl acetylacetonate in the liquid crystalline medium has been considered.[4] It was assumed that the amplitude of this component is proportional to the number of species oriented parallel to the vector of the magnetic field strength. Theoretical analysis shows[5,6] that the higher the degree of orientation of paramagnetic centers, the greater the difference between the orientation distribution function of species obtained in this way and the true function. It should be noted that the studies cited[4—6] consider the paramagnetic species with axially anisotropic magnetic characteristics. This approach is inapplicable in the case where the three principal values of the [*g*]-tensor and the HFS tensor are different. A drawback of these procedures[4—6] is that analysis of angular dependences of the ESR spectra is performed only at characteristic points of the spectrum and much information on the orientation distribution of species, which would be derived from the whole spectrum, is thus lost.

In other studies,[7—12] the whole ESR spectrum has been analyzed but the orientation distribution of paramagnetic species was determined by a trial-and-error method. In this procedure, suggestions concerning the form of the distribution function to be found are made and the ESR spectra corresponding to this function are simulated. The suggestion made is either confirmed or disclaimed based on a qualitative comparison of the simulated and experimental spectra. The agreement is considered satisfactory if the positions and intensity ratios of the spectral components approximately coincide.

The more accurate orientation distribution function of species was determined[13,14] in a study of the orientation distribution in the muscle fibers of myosinic fragments labeled by iminoxyl radicals. The distribution function was represented as a sum of orthonormal functions with coefficients that were called[13,14] order parameters. In conformity with the proposed distribution function, the theoretical ESR spectra were simulated, the order parameters being adjusted to ensure coincidence of the simulated

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spectra with experimental ones. The data obtained from analysis of the ESR spectra were considered together with the polarization fluorescence data. It was concluded that the number of order parameters that can be determined by ESR is greater than the number of these parameters determined by polarization fluorescence. It should be noted that the method proposed[13–15] for determination of the orientation distribution function has been developed for a particular biological system and cannot be used in the general case. In addition, the unambiguity of the solution obtained in this way was not discussed in these studies.[13,14]

Generally, it can be stated that currently there is no method for determination of the orientation distribution function of paramagnetic species from the angular dependence of the ESR spectra applicable to systems with different degrees of ordering and paramagnetic species of different symmetries. The goal of this study is to develop such a method.

Substantiation of the method for determination of the orientation distribution function of paramagnetic species

The method for determination of the orientation distribution function of paramagnetic species that we propose is as follows. The ESR spectra corresponding to different positions of the sample with respect to the magnetic field strength vector are simulated, the orientation distribution function being represented as a sum of orthonormal functions with variable coefficients. The weight coefficients are determined by minimizing the deviations of the simulated spectra from experimental ones. The angular dependences of all points of the spectrum are analyzed simultaneously and, hence, the information on the orientation distribution of paramagnetic species contained in the spectra is fully utilized.

The representation of the orientation distribution function as a sum of orthonormal functions. Depending on the degree of ordering of the system and the symmetry of paramagnetic centers, the orientation distribution function can be represented in different ways. If axially anisotropic paramagnetic species form an axially symmetric sample, the orientation of each separate species in the sample is determined unambiguously by the angle between the anisotropy axis of this species and the symmetry axis of the sample. In this case, the orientation distribution function is a function of only one angle $\rho = \rho(\beta)$, which can be represented as an expansion in terms of the Legendre polynomials.

If axially anisotropic paramagnetic species are arbitrarily distributed in the sample, the orientation of each species is determined by two angles that describe the position of the axis of anisotropy of this species in the coordinate system related to the sample. In this case, the orientation distribution function is a function of two angles $\rho = \rho(\beta,\gamma)$. The distribution function of species characterized by three different principal values of the [*g*]-tensor and/or the HFS tensor in a sample with an axial symmetry is also a function of two angles. In this case, the β and γ angles describe the position of the symmetry axis of the sample in the coordinate system related to a separate paramagnetic species. It is known that in these two cases, the orientation distribution function can be represented as an expansion in terms of spherical harmonics:

$$\rho(\beta,\gamma) = \sum_{j=0}^{\infty}\left\{\frac{1}{2}a_{j0}P_j(\cos\beta) + \sum_{k=1}^{j}P_j^k(\cos\beta)[a_{jk}\cos(k\gamma) + b_{jk}\sin(k\gamma)]\right\}, \quad (1)$$

where P_j are the *j*th-power Legendre polynomials, P_j^k is the *j*th-power added Legendre functions of the first kind and the *k*th order.

If paramagnetic species having three different principal values of the [*g*]-tensor and/or the HFS tensor are distributed arbitrarily in the sample, the orientation distribution function is a function of three angles and can be represented as an expansion in terms of the Wigner function. This case is beyond the scope of this work.

Note that the distribution function derived from analysis of the ESR spectra is always symmetrical relative to the center of coordinates. Indeed, upon rotation of the magnetic field strength vector by 180°, the effective magnetic parameters of the paramagnetic species do not change; thus, some information on the orientation of species in the sample is inevitably lost. The symmetry of the distribution function imposes certain restrictions on the coefficients of the expansion. In particular, if the distribution function is represented as an expansion in terms of spherical harmonics, all the a_{jk} and b_{jk} coefficients for odd *j* are equal to zero.

Unambiguity of the determination of the orientation distribution function of species from the ESR spectra. In the general case, it is impossible to determine the orientation distribution function of species in a sample from one ESR spectrum, because the positions of the resonance signals of species with different orientations in the magnetic field may coincide. It is necessary to analyze several spectra recorded at different positions of the sample with respect to the magnetic field. The orientation distribution function cannot be determined unambiguously from the spectra recorded with sample turning around an arbitrary axis normal to the magnetic field strength vector (in the coordinate system connected to the sample, the magnetic field strength vector rotates in the plane). This is due to the fact that a paramagnetic species cannot be distinguished from its reflection in the plane where the magnetic field strength vector rotates. This ambiguity (we call it the reflection problem) arises with every paramagnetic species, therefore, the angular dependence of the ESR spectra recorded in this way is matched by an infinite

number of orientation distribution functions ranging from the true function to its reflection in the plane of rotation of the magnetic field strength vector and including any their combination with retention of the common norm.

In Appendix 1, it is shown that the ambiguity in determining the orientation distribution of species can be avoided by recording the ESR spectra with sample turning around three mutually perpendicular axes (in the sample coordinates system, the magnetic field strength vectors lie in three mutually perpendicular planes).

The number of spectra needed for unambiguous determination of the orientation distribution function, obviously, does not exceed the number of the sought-for expansion coefficients. Thus, to find all second-order coefficients, it is necessary to record five ESR spectra and finding fourth-order coefficients requires nine spectra. Since second- and fourth-order coefficients are determined independently from each other, all second- and fourth-order coefficients can be derived unambiguously from nine spectra.

If the required distribution function is known to possess an axial symmetry, its unambiguous determination requires fewer ESR spectra. There always exists a sample coordinate system ($X^*Y^*Z^*$) such that the axial distribution function depends in this system only on one angle. Thus, the coefficients of the expansion of the function in terms of spherical harmonics (1) will be designated by $\{a^*_{jk}\}$ and $\{b^*_{jk}\}$, only the $\{a^*_{j0}\}$ coefficients being nonzero. Since the spherical harmonic coefficients of different orders are determined independently, it is sufficient to consider one ESR spectrum for finding the axial distribution function in the $X^*Y^*Z^*$ coordinate system. The coefficients of this expansion function in terms of spherical harmonics in an arbitrary system of sample coordinates XYZ depend on the $\{a^*_{j0}\}$ coefficients and two angles, χ and ω, which describe the position of the anisotropic axis of the distribution function in the XYZ system of coordinates. In is shown in Appendix 2 that unambiguous determination of all expansion coefficients of the axial function in an arbitrary system of coordinates of the sample requires only four ESR spectra recorded at fixed positions of the sample relative to the magnetic field strength vector $\mathbf{H}$ ($\mathbf{H}_1$, $\mathbf{H}_2$, $\mathbf{H}_3$ are located in one plane, while the $\mathbf{H}_4$ neither lies in this plane nor is normal to the plane).

If the orientation distribution function has symmetry elements, it is of interest to find the symmetry axes of this function in the experimental system of coordinates of the sample. This search can be done in the following way. Let the orientation distribution function depend on not more than two angles. In the Cartesian coordinates, imagine a sphere with a unit radius and with an inertial mass being distributed over its surface according to the required distribution function. The spatial orientation of the principal axes of the inertia tensor of such a quasi-physical object would coincide with the orientation of the symmetry axes of the required distribution function. If the distribution function is represented as the expansion of spherical harmonics, the inertia tensor corresponding to this function takes the form

$$I = 4\pi \begin{bmatrix} \frac{a_{00}}{3} + \frac{a_{20}}{30} - \frac{2a_{22}}{5} & -\frac{2b_{22}}{5} & -\frac{a_{21}}{5} \\ -\frac{2b_{22}}{5} & \frac{a_{00}}{3} + \frac{a_{20}}{30} + \frac{2a_{22}}{5} & -\frac{b_{21}}{5} \\ -\frac{a_{21}}{5} & -\frac{b_{21}}{5} & \frac{a_{00}}{3} - \frac{a_{20}}{15} \end{bmatrix}. \quad (2)$$

Relation (2) shows that the position of the symmetry axes of the distribution function in the coordinate system connected to the sample is determined by the first six coefficients of this expansion function of spherical harmonics. The system of sample coordinates in which the inertia tensor is diagonal will be called the proper coordinate system of the distribution function.

Software implementation of the method

The software implementation of the method is based on the program that allows simulation of the ESR spectrum[16] and the minimizer program executing the nonlinear least-squares method.[17] On this basis, we developed the software that provides combined analysis of the ESR spectra corresponding to different orientations of the sample in the magnetic field. The program minimizes the sum of squared deviations of the simulated ESR spectra from the experimental spectra with variation of the weight coefficients of the distribution function in terms of orthonormal functions.

Since the required function should acquire only positive values over the whole domain of definition, the minimizer program was designed to include the operation that sharply increases the deviation of the simulated spectra from the experimental ones if some set of weight coefficients results in a negative range of values for the distribution function.

If the search of the distribution function takes place in the proper coordinate system of the sample, the set of the weight coefficients is chosen in such a way that the inertia tensor has a diagonal form.

In the experimental ESR spectra, the half-width of a signal often depends on the orientation of the paramagnetic species in the magnetic field. To take this into account, the program provides the option of specifying the half-width of a signal as a second-rank tensor. The shape of the signal is specified by a convolution of the Lorentz and Gauss functions.

Testing of the procedure

In order to verify the proposed procedure and the developed software, a series of computer experiments was

performed. For a given orientation distribution function of radicals in the sample ρ_i, the ESR spectra corresponding to different orientations of this sample in the magnetic field were simulated and the resulting set of spectra was used to determine the orientation distribution function ρ_f, which was compared to the initial one. The difference between these two functions was characterized by the value

$$\Delta = \int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi} \left|\rho_i - \rho_f\right| d\alpha d\beta d\gamma. \qquad (3)$$

It was found experimentally that at $\Delta \le 0.05$, the functions ρ_i and ρ_f do not virtually differ.

The numerical experiments were carried out for orientation distribution functions of different symmetry and for paramagnetic species with different anisotropy of magnetic parameters. As an illustration, we will choose two distribution functions substantially differing in symmetry. The function ρ_1 (Fig. 1, *a*) has three planes of symmetry. The expansion in terms of spherical harmonics involves only second-order terms. The function ρ_2 (Fig. 1, *b*) does not have any symmetry elements. The expansion of ρ_2 in terms of spherical harmonics contains nonzero fourth-order terms.

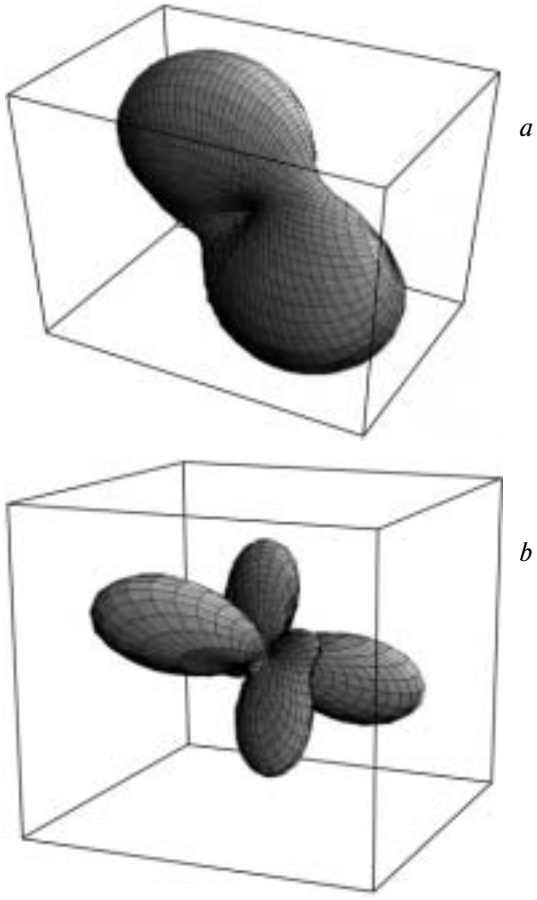

Fig. 1. Orientation distribution functions of axially anisotropic species ρ_1 (*a*) and ρ_2 (*b*).

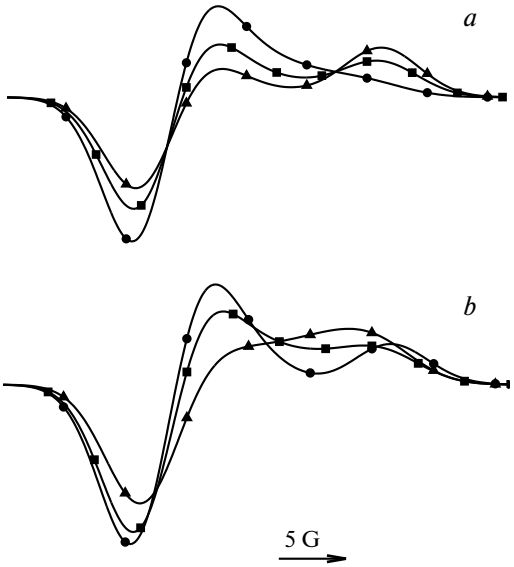

Fig. 2. Simulated ESR spectra corresponding to different orientations orientation in the magnetic fields of samples with axially anisotropic paramagnetic species oriented according to functions ρ_1 (*a*) and ρ_2 (*b*).

The calculated angular dependences of the ESR spectra of substances in which the axially anisotropic paramagnetic species are oriented in conformity with the functions ρ_1 and ρ_2 are shown in Fig. 2. The difference between the spectra corresponding to different positions of the sample in the magnetic field is determined by both the anisotropy of distribution of the species in the sample and the degree of magnetic anisotropy of these species. The magnetic parameters used in the calculation (g_x = g_y = 2.1000, g_z = 2.0900, half-width of a single line h = 5 G) were such that the difference between different spectra of the angular dependence was smaller than the difference observed in known experimental works.[4,15]

The orientation distribution functions determined from analysis of the spectra in terms of the proposed method fully coincide with the initial functions ρ_1 and ρ_2, which demonsrtates the feasibility of the method.

The real experimental ESR spectra can contain noises and signals independent of the sample orientation in the magnetic field, for example, the signals of standards. To elucidate the role of these errors in recording the spectra on determination of the orientation distribution function, the simulated spectra were intentionally distorted by adding noises and foreign signals of various intensities. One of the angular dependence spectra and the spectra obtained by adding a noise and a foreign signal are presented in Fig. 3. In the analysis of the set of distorted spectra, the coefficients of the distribution function were first determined in an arbitrary system of coordinates of the sample and then in the proper coordinate system of this function.

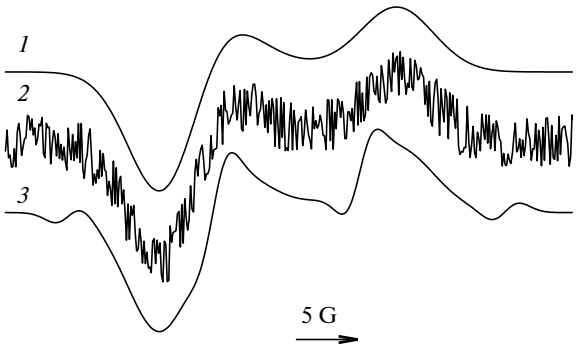

Fig. 3. One ESR spectrum of the angular dependence (*1*) and the spectra obtained by adding noise (*2*) and an isotropic quartet of lines with an intensity ratio of 1 : 3 : 3 : 1 (*3*).

The orientation distribution functions found from noised spectra and from the spectra in the presence of an isotropic paramagnetic impurity are similar to the initial functions. The deviations of the resulting distribution functions from the initial functions ρ_1 and ρ_2, calculated from relation (3) are summarized in Tables 1 and 2. It can be seen that the deviation of the symmetrical distribution function found from the spectra from the true function ρ_1 does not exceed 5% in the case where the noise intensity does not exceed 1/3 and the amplitude of the foreign signal is not higher than 1/4 of the intensity of the main signal. In the case of orientation distribution ρ_2 having a more complex pattern, random errors are more significant. To ensure that the difference between the function ρ_2 found from noised spectra and the true one is no more than 5%, the noise intensity should not exceed 1/5 of the intensity of the main signal.

It also follows from Tables 1 and 2 that in the case of the symmetrical distribution function, repeated analysis of the ESR spectra in the proper coordinate system of the sample allows one to correct the coefficients for this expansion function, whereas for a non-symmetrical distribution function, this procedure does not result in more precise determination of the coefficients.

Table 1. Deviation (Δ) of the orientation distribution functions obtained from noised spectra from the true ones calculated by relation (3)

Signal/noise ratio	Δ* (%)			
	for the function ρ_1		for the function ρ_2	
	I	II	I	II
10	1.3	1.0	1.3	2.1
7	1.9	0.3	1.8	1.2
5	4.2	3.5	4.1	4.2
4	3.0	2.0	6.5	4.0
3	5.2	3.0	9.9	9.6
2	7.6	1.1	12.7	40.4
3/2	9.2	6.6	—	—

* The calculation was performed in an arbitrary (I) and in the proper coordinate system (II).

Table 2. Deviation (Δ) of the orientation distribution functions obtained from spectra with addition of an isotropic signal from the true function ρ_1

Ratio*	Δ** (%)	
	I	II
10	1.9	1.6
7	2.7	2.3
5	3.8	3.1
4	4.7	3.9
3	6.1	5.1
2	8.9	7.3
3/2	11.4	9.5

* Ratio of the anisotropic to isotropic signal amplitudes.
** The calculation was performed in an arbitrary (I) and in the proper coordinate system (II).

Figure 2 and Tables 1, 2 illustrate the following, rather simple rules. The orientation distribution function is determined reliably if the difference between different spectra of the angular dependence is greater than the experimental error of recording the spectra, *i.e.*, the amplitudes of noise and foreign signals. It can also be seen that the finer the details of the orientation distribution function to be elucidated, the stricter the requirements to the accuracy of recording the spectra.

Thus, the method we proposed allows one to derive information on subtle features of the orientation distribution of species from the ESR spectra and is rather stable against errors not related to the sample orientation in the magnetic field in the ESR spectra.

Appendix 1

Let us consider at which sample positions relative to the magnetic field the ESR spectra are to be recorded for their analysis to provide unambiguous determination of the orientation distribution function of the paramagnetic species in the sample.

The true distribution function can be represented in the sample coordinate system *XYZ* as the expansion of spherical harmonics (1) with the $\{a_{jk}\}$ and $\{b_{jk}\}$ coefficients. The reflection of this function from the *YZ* plane gives $\beta_{\text{refl}} = \beta$, $\gamma_{\text{refl}} = -\gamma$ and, hence, $(a_{jk})_{\text{refl}} = a_{jk}$, $(b_{jk})_{\text{refl}} = -b_{jk}$. The ESR spectra recorded with the magnetic field strength vector located in the *YZ* plane do not change upon this reflection. Any distribution function can be represented by a sum of an infinite number of functions; for each of these, $\{a_{jk}\}$ are determined unambiguously and $\{b_{jk}\}$ are determined to within a sign from analysis of the spectra recorded with rotation of the magnetic field strength vector in the *YZ* plane. Thus, for the summarized distribution function, the $\{a_{jk}\}$ coefficients can also be determined unambiguously from this set of spectra, while each b_{jk} coefficient can be varied over a broad range.

Let us consider the $X'Y'Z'$ and $X''Y''Z''$ systems of coordinates of the sample. The $XYZ \rightarrow X'Y'Z'$ and $X'Y'Z' \rightarrow X''Y''Z''$

transitions are accomplished through cyclic transposition of the coordinate axes. The coefficients of the distribution function in the $X'Y'Z'$ and $X''Y''Z''$ systems are related unambiguously to the coefficients of this function in the XYZ system

$$
\begin{aligned}
a'_{20} &= -a_{20}/2 + 6a_{22} & a''_{20} &= -a_{20}/2 - 6a_{22},\\
a'_{21} &= -2b_{22}, & a''_{21} &= b_{21},\\
b'_{21} &= -a_{21}, & b''_{21} &= -2b_{22},\\
a'_{22} &= -a_{22}/8 - a_{20}/8, & a''_{22} &= -a_{22}/2 + a_{20}/8,\\
b'_{22} &= b_{21}/2, & b''_{22} &= -a_{21}/2,\\
a'_{40} &= 3a_{40}/8 - 15a_{42} + 210a_{44}, & a''_{40} &= 3a_{40}/8 + 15a_{42} + 210a_{44},\\
a'_{41} &= 3b_{42}/2 - 42b_{44}, & a''_{41} &= -3b_{41}/4 - 21b_{43}/2,\\
b'_{41} &= 3a_{41}/4 - 21a_{43}/2, & b''_{41} &= 3b_{42}/2 + 42b_{44},\\
a'_{42} &= a_{40}/48 - a_{42}/2 - 7a_{44}, & a''_{42} &= -a_{40}/48 - a_{42}/2 + 7a_{44},\\
b'_{42} &= -b_{41}/12 + 7b_{43}/2, & b''_{42} &= a_{41}/12 + 7a_{43}/2,\\
a'_{43} &= b_{42}/4 + b_{44}, & a''_{43} &= b_{41}/24 - 3b_{43}/4,\\
b'_{43} &= a_{41}/24 + 3a_{43}/4, & b''_{43} &= -b_{42}/4 + b_{44},\\
a'_{44} &= a_{40}/384 + a_{42}/16 + a_{44}/8, & a''_{44} &= a_{40}/384 - a_{42}/16 + a_{44}/8,\\
b'_{44} &= -b_{41}/48 - b_{43}/8, & b''_{44} &= -a_{41}/48 + a_{43}/8.
\end{aligned}
$$

As shown above, from the ESR spectrum recorded while rotating the magnetic field strength vector in the YZ plane, the $\{a_{jk}\}$ coefficients can be determined unambiguously and the $\{b_{jk}\}$ coefficients cannot be determined. From the spectra recorded while rotating the magnetic field strength vector in the $Y'Z'$ plane normal to the YZ plane, the $\{a'_{jk}\}$ coefficients are determined unambiguously, while the spectra recorded with rotation of the magnetic field strength vector in the $Y''Z''$ plane normal to YZ and $Y'Z'$ planes give unambiguous values of the $\{a''_{jk}\}$ coefficients. In view of the fact that $a''_{21} = b_{21}$, $a'_{21} = -2b_{22}$, $a''_{41} = -3b_{41}/4 - 21b_{43}/2$, $a''_{43} = b_{41}/24 - 3b_{43}/4$, $a'_{41} = 3b_{42}/2 - 42b_{44}$, and $a'_{43} = b_{42}/4 + b_{44}$, it can be concluded that by recording the ESR spectra with sample turning around three mutually perpendicular axes (in the sample coordinate system, this implies rotation of the magnetic field strength vector in three mutually perpendicular planes), one can determine unambiguously all the coefficients of the distribution expansion function of the spherical harmonics up to the fourth order.

Appendix 2

The coefficients of the axial expansion function of spherical harmonics in an arbitrary sample coordinate system XYZ depend on the expansion coefficients in the proper coordinate system $X^*Y^*Z^*$ and two angles χ and ω, which determine the position of the anisotropic axis of the function in the system of coordinates XYZ:

$$
\begin{aligned}
a_{00} &= a^*_{00},\\
a_{20} &= a^*_{20}[1 + 3\cos(2\chi)]/4,\\
a_{21} &= -a^*_{20}(\cos\chi\sin\chi\cos\omega)/2,\\
b_{21} &= -a^*_{20}(\cos\chi\sin\chi\sin\omega)/2,\\
a_{22} &= a^*_{20}[\cos(2\omega)\sin^2\chi]/8,\\
b_{22} &= a^*_{20}[\sin(2\omega)\sin^2\chi]/8,\\
a_{jk} &= a_{jk}(a^*_{j0},\chi,\omega),\\
b_{jk} &= b_{jk}(a^*_{j0},\chi,\omega).
\end{aligned}
$$

By analyzing three ESR spectra recorded in such a way that the magnetic field strength vectors $\mathbf{H}_1$, $\mathbf{H}_2$, and $\mathbf{H}_3$ lie in one plane in the sample coordinate system, one can determine unambiguously the a_{20}, a_{21}, and a_{22} coefficients and, hence, the a^*_{20}, $\cos\chi$, and $\cos\omega$ values. Since $0 \le \omega \le 2\pi$, $\cos(-\omega) = \cos\omega$, in the analysis of the spectra, the true position of the anisotropic axis of the function in the XYZ system cannot be distinguished from its reflection in the plane accommodating $\mathbf{H}_1$, $\mathbf{H}_2$, and $\mathbf{H}_3$. Recording one more ESR spectrum in such a way that the $\mathbf{H}_4$ vector does not lie in this plane and is not normal to it allows one to determine unambiguously the position of the anisotropic axis of the distribution function in the sample coordinate system XYZ, *i.e.*, to find χ and ω. The a^*_{20}, χ, and ω values can be used to calculate all second-order coefficients. To calculate the fourth-order coefficients, it is necessary to determine a_{40}. With known χ and ω, the a_{40} value is determined unambiguously by analyzing one ESR spectrum. Thus, unambiguous determination of all the coefficients of the axial expansion function in an arbitrary system of coordinates of the sample requires four ESR spectra recorded for definite positions of the sample relative to the magnetic field strength vector $\mathbf{H}$ ($\mathbf{H}_1$, $\mathbf{H}_2$, $\mathbf{H}_3$ lie in one plane, $\mathbf{H}_4$ does not lie in this plane and is not perpendicular to it).

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