

Electron Spin Resonance of Dipole-Coupled Anisotropic Pairs in Disordered Systems. Secular Approximation for Point Dipoles

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ESR spectra of pairs of paramagnetic centers with anisotropic g tensors are considered. The centers are assumed to be point magnetic dipoles with effective spins $\frac{1}{2}$. The dipole coupling Hamiltonian is discussed. Powder spectra are numerically calculated in the secular approximation for the dipole splitting. The temperature dependence of the spectral lineshape due to spin polarization is also studied. Special attention is paid to pairs containing an unobservable partner with $g_{\perp} = 0$. © 1995 Academic Press, Inc.

INTRODUCTION

The dipole-dipole interactions of paramagnetic centers have been the subject of a number of investigations. The changes in the magnetic-resonance spectra due to the dipole coupling contain important information on the structure and molecular dynamics of paramagnetic compounds (1-7). Usually when such interactions are treated, the centers are considered to have an isotropic g factor; this approach is valid for such species as organic radicals (1, 6, 7). Sometimes systems under study include highly anisotropic paramagnetic ions (3-5). Theoretical (8-10) and experimental (11, 12) investigations of the dipole line broadening of anisotropic centers in magnetically diluted solids were performed earlier. The present work is devoted to the description of the ESR spectra of pairs with anisotropic nonequivalent spin- $\frac{1}{2}$ partners and was initiated by an observation of a pair-like spectrum with unusual features (13). In papers (3, 4), theoretical treatments of the ion pair spectra were represented, but manifestations of the g tensor anisotropy in the dipole lineshape were not studied systematically, because specific systems were investigated and, thus, too many parameters would be involved.

In this paper, we first consider briefly one anisotropic paramagnetic center. In this case, Abragam's "dipole alphabet" should be modified. Powder spectral lineshapes using first-order perturbation determined by the secular term of the dipole Hamiltonian were calculated numerically and are

presented in the next section. The temperature dependence of these spectra is also considered. In the last section, pairs containing an unobservable partner with $g_{\perp} = 0$ are discussed.

AN ISOLATED PARAMAGNETIC CENTER WITH AN ANISOTROPIC g TENSOR

Paramagnetic centers such as metal ions, atoms, and stable and labile free radicals shift their energy levels when interacting with an external magnetic field due to the Zeeman effect. Here we consider only Kramers systems which can be treated as having (effective) spin $\frac{1}{2}$.

The Zeeman interaction of an external magnetic field \mathbf{B}_0 with a magnetic moment μ of the paramagnetic particle splits the lowest energy level into the Kramers doublet. The Hamiltonian for the interaction is

$$\mathcal{H} = -(\mathbf{B}_0, \mu). \quad [1]$$

The magnetic moment of the particle is proportional to its (effective) spin \mathbf{S} :

$$\mu = -\beta \hat{g} \mathbf{S}, \quad [2]$$

where β is the Bohr magneton and \hat{g} the so-called g tensor¹, the operator describing the interaction of an effective mechanical momentum \mathbf{S} with an external magnetic field. The properties of the g tensor as a diadic operator are discussed by Abragam and Bleaney (2).

Now we shall introduce some definitions useful for further discussions. Let all the vectors denoted simply by Latin or Greek letters in boldface type be columns [in contradiction to our previous treatment (10)]. In the coordinate representation,

$$\mathbf{x} = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}.$$

¹ In this article, an operator, including a tensor operator, is denoted by a circumflex, rather than by bold sans serif type.

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To obtain row vectors we shall use the Hermitian transposition operator $\mathbf{x}^+ = (x_1^*, x_2^*, x_3^*)$. Components of a three-dimensional vector \mathbf{x} , x_i , can contain spin operator combinations. The scalar product of two vectors \mathbf{a} and \mathbf{b}

$$(\mathbf{a}, \mathbf{b}) = \mathbf{a}^+ * \mathbf{b} = \sum_i a_i^* b_i \quad [3]$$

is symmetric if the components of both vectors contain Hermitian operators. The asterisks denote matrix multiplication.

In general, the operator \hat{g} for low-symmetry Kramers ions may have no symmetry elements (2), but this question is not very important as will be shown later.

Let us discuss the Zeeman Hamiltonian (Eq. [1]). It can be treated in two ways: (i) as an interaction of the magnetic moment μ with the external magnetic field \mathbf{B}_0 (it is written above in this way), and (ii) as an interaction of some magnetic moment μ_0 ,

$$\mu_0 = -\beta\mathbf{S}, \quad [4]$$

with an effective magnetic field \mathbf{B}_{eff} ,

$$\mathbf{B}_{\text{eff}} = \hat{g}^+ \mathbf{B}_0. \quad [5]$$

Using the second interpretation, one can rewrite the Hamiltonian [1],

$$\mathcal{H} = (\mathbf{B}_{\text{eff}}, \beta\mathbf{S}). \quad [6]$$

Let the unit vector along the external field be \mathbf{k}_1 ,

$$\mathbf{k}_1 = \mathbf{B}_0/B_0, \quad [7]$$

and that along the effective field \mathbf{k}_2 ,

$$\mathbf{k}_2 = \hat{g}^+ \mathbf{k}_1 / (\hat{g}^+ \mathbf{k}_1, \hat{g}^+ \mathbf{k}_1)^{1/2}. \quad [8]$$

We can transform Eq. [6] into

$$\mathcal{H} = B_{\text{eff}} \beta (\mathbf{k}_2, \mathbf{S}) = B_{\text{eff}} \beta \hat{S}_{k_2}, \quad [9]$$

where \hat{S}_{k_2} is an operator of the spin projection onto the \mathbf{k}_2 axis and B_{eff} is an absolute value of the effective magnetic field. For this quantity from Eqs. [5] and [7], we have

$$B_{\text{eff}} = g_{\text{eff}} B_0, \quad [10]$$

where

$$g_{\text{eff}} = (\hat{g}^+ \mathbf{k}_1, \hat{g}^+ \mathbf{k}_1)^{1/2}. \quad [11]$$

Expression [11] for the effective g factor value can be rewritten using the matrix multiplication operation

$$g_{\text{eff}} = \{\mathbf{k}_1^+ * \hat{g} * \hat{g}^+ * \mathbf{k}_1\}^{1/2}. \quad [12]$$

One can easily see from Eq. [12] that the Zeeman interaction Hamiltonian depends on the \hat{g} tensor convolution over spin indices. Abragam and Bleaney (2) introduced a rank 2 tensor \hat{G} ,

$$\hat{G} = \hat{g} * \hat{g}^+, \quad [13]$$

or in the coordinate form

$$G_{ij} = \sum_{\alpha} g_{i\alpha} g_{j\alpha}. \quad [14]$$

The tensor \hat{G} is symmetric and, thus, its principal axes can be easily found, all the principal values being nonnegative (2). The effective g factor value can be expressed using \hat{G} ,

$$g_{\text{eff}} = \{\mathbf{k}_1^+ * \hat{G} * \mathbf{k}_1\}^{1/2}. \quad [15]$$

Energy levels and eigenfunctions of the Hamiltonian [9] can be easily obtained. The eigenfunctions of the Hamiltonian are the operator \hat{S}_{k_2} eigenfunctions $|\alpha\rangle$ and $|\beta\rangle$ corresponding to $+\frac{1}{2}$ and $-\frac{1}{2}$ spin projections onto the quantization axis \mathbf{k}_2 . For the energy levels, we have

$$\epsilon_{\pm 1/2} = \pm \frac{1}{2} g_{\text{eff}} \beta B_0, \quad [16]$$

which also depend on \hat{G} .

There exists one more important vector characterizing an anisotropic PC. Let the secular part of the magnetic moment be a vector operator, which can be obtained from Eq. [2] by exchanging $\mathbf{S} \Rightarrow \mathbf{k}_2 \hat{S}_{k_2}$,

$$\mu^{\text{sec}} = -\beta \hat{g} \mathbf{k}_2 \hat{S}_{k_2}. \quad [17]$$

This operator does commute with the Zeeman Hamiltonian. Using Eqs. [8] and [13], we have from Eq. [17]

$$\mu^{\text{sec}} = -\beta \hat{g} \hat{S}_{k_2} \mathbf{k}_3, \quad [18]$$

where

$$\tilde{g} = \{(\mathbf{k}_1^+ * \hat{G}^2 * \mathbf{k}_1) / (\mathbf{k}_1^+ * \hat{G} * \mathbf{k}_1)\}^{1/2}, \quad [19]$$

and the direction \mathbf{k}_3 is the external magnetic field direction \mathbf{k}_1 transformed by the tensor \hat{G} ,

$$\mathbf{k}_3 = \hat{G} \mathbf{k}_1 / (\tilde{g} g_{\text{eff}}). \quad [20]$$

The operator μ^{sec} can be useful for calculations of the energy level shifts to first order if the perturbation is treated as a local distortion of the external magnetic field.

Using relationships [8], [13], and [15], we can modify expression [19] as

$$\tilde{g} = \{\mathbf{k}_2^+ * \hat{g}^+ * \hat{g} * \mathbf{k}_2\}^{1/2}. \quad [21]$$

In analogy to Eqs. [13] and [14], let us introduce a symmetric tensor \hat{G}' ,

$$\hat{G}' = \hat{g}^+ * \hat{g}. \quad [22]$$

For its components, we have (compare with Eq. [14])

$$G'_{\alpha\beta} = \sum_j g_{j\alpha} g_{j\beta}. \quad [23]$$

With its help, we obtain

$$\tilde{g} = \{ \mathbf{k}_2^+ * \hat{G}' * \mathbf{k}_2 \}^{1/2}. \quad [24]$$

The tensor \hat{G}' is constructed from \hat{g} by convolution over spatial indices (instead of spin indices for \hat{G}). Using definitions [13] and [22], one can write

$$\hat{G}^2 = \hat{g} * \hat{G}' * \hat{g}^+, \quad [25]$$

$$(\hat{G}')^2 = \hat{g}^+ * \hat{G}' * \hat{g}. \quad [26]$$

In general, \hat{G} and \hat{G}' may differ if the symmetric and antisymmetric parts of the operator \hat{g} do not commute. Their principal values must be the same, but principal axes may be different.

If the operator \hat{g} is symmetric

$$\hat{G}' = \hat{G}, \quad [27]$$

and, instead of Eq. [24], one can write

$$\tilde{g} = g_{\text{eff}}(\mathbf{k}_2). \quad [28]$$

In this case, \tilde{g} is equal to the g_{eff} value calculated not for the external field \mathbf{B}_0 but for the effective field \mathbf{B}_{eff} direction.

Vectors \mathbf{k}_3 and \mathbf{k}_1 coincide when the center is isotropic. If γ is an angle between them,

$$\cos \gamma = (\mathbf{k}_1, \mathbf{k}_3) = g_{\text{eff}} / \tilde{g}. \quad [29]$$

It is clear from Eq. [29] that

$$g_{\text{eff}} \leq \tilde{g}, \quad [30]$$

where both \tilde{g} and g_{eff} on the right side of Eq. [29] are nonnegative, and the angle between \mathbf{k}_3 and \mathbf{k}_1 is not more than $\pi/2$.

THE HAMILTONIAN FOR THE DIPOLE-DIPOLE INTERACTION

The Hamiltonian for the magnetic dipole-dipole interaction is well known (I) and for point dipoles has the form

$$\mathcal{H}_d = (\mu_1, \mu_2) / r^3 - 3(\mathbf{r}, \mu_1)(\mathbf{r}, \mu_2) / r^5, \quad [31]$$

where μ_i is the magnetic moment of the i th particle, and \mathbf{r} denotes a vector that connects the two particles. For the isotropic paramagnetic centers, where \hat{g} is proportional to the unit operator, the Hamiltonian [31] is usually divided into six parts according to Abragam (I). These parts are known as a dipole alphabet:

$$\mathcal{H}_d = (\hat{A} + \hat{B} + \hat{C} + \hat{D} + \hat{E} + \hat{F}) g_1 g_2 \beta^2 / r^3. \quad [32]$$

Each "letter" possesses its own character:

$$\hat{A} = \hat{S}_z(1) \hat{S}_z(2) (1 - 3 \cos^2 \theta), \quad [33a]$$

$$\begin{aligned} \hat{B} = \{ & \hat{S}_+(1) \hat{S}_-(2) + \hat{S}_-(1) \hat{S}_+(2) \} \\ & \times [-\frac{1}{4}(1 - 3 \cos^2 \theta)], \end{aligned} \quad [33b]$$

$$\begin{aligned} \hat{C} = \{ & \hat{S}_z(1) \hat{S}_+(2) + \hat{S}_+(1) \hat{S}_z(2) \} \\ & \times [-\frac{3}{2} \sin \theta \cos \theta \exp(-i\phi)], \end{aligned} \quad [33c]$$

$$\hat{D} = \hat{C}^+, \quad [33d]$$

$$\hat{E} = \hat{S}_+(1) \hat{S}_+(2) [-\frac{3}{4} \sin^2 \theta \exp(-2i\phi)], \quad [33e]$$

$$\hat{F} = \hat{E}^+. \quad [33f]$$

Here the orientation of vector \mathbf{r} with respect to the laboratory frame with the Z axis coinciding with the external field direction is denoted by the angles θ and ϕ and

$$\hat{S}_{\pm}(j) = \hat{S}_x(j) \pm i \hat{S}_y(j), \quad [34]$$

j being the partner number.

The most important term for our purposes, \hat{A} , is called secular for clear reasons. When the paramagnetic centers are isotropic, their quantization axes coincide with the external field direction and the first-order level shifts depend on matrix elements of this operator. The pseudosecular term \hat{B} partially has an exchange-like character and is important from the energetic point of view only if $g_1 = g_2$ when both centers have the same resonance frequency. The other terms couple states with significantly different energies and influence the spectrum by permitting "forbidden" transitions.

The Hamiltonian [32] has the simplest form in the molecular frame where the Z -axis direction coincides with the vector \mathbf{r} . There it consists only of \hat{A} - and \hat{B} -type terms.

Note the symmetry of the operator part of each term in Eq. [33] with respect to exchange of the partner numbers $1 \leftrightarrow 2$.

Let us consider anisotropic paramagnetic centers. According to Abragam's logic, we should divide the Hamiltonian [31] into parts having symmetrical features and storing information about the directions of the quantization axes. To do it, let us use the spin operator in the form

$$\begin{aligned}\hat{S}(j) &= \mathbf{k}_2(j)\hat{S}_{\mathbf{k}_2}(j) + \hat{S}_-(j)\{\mathbf{l}(j) + i\mathbf{m}(j)\}/2 \\ &+ \hat{S}_+(j)\{\mathbf{l}(j) - i\mathbf{m}(j)\}/2.\end{aligned}\quad [35]$$

The vectors $\mathbf{l}(j)$, $\mathbf{m}(j)$, $\mathbf{k}_2(j)$ are unit vectors of the coordinate system associated with the j th center. The $\mathbf{k}_2(j)$ direction is given by expression [8]. Two other ones are perpendicular to it and each other, but their exact directions are not of great importance here.

Using relations [2] and [35], we can obtain from Eq. [31]

$$\begin{aligned}\mathcal{H}_d &= (\hat{A} + \hat{B} + \hat{C} + \hat{D} + \hat{E} \\ &+ \hat{F} + \hat{G} + \hat{H} + \hat{I})\beta^2/r^3.\end{aligned}\quad [36]$$

To prevent any confusion, we shall not use this version of the dipole alphabet in this paper after defining each letter except the term \hat{A} . Here (after some algebraic transformations)

$$\begin{aligned}\hat{A} &= \hat{S}_{\mathbf{k}_2}(1)\hat{S}_{\mathbf{k}_2}(2)\{(\hat{g}(1)\mathbf{k}_2(1), \hat{g}(2)\mathbf{k}_2(2)) \\ &- 3(\mathbf{n}, \hat{g}(1)\mathbf{k}_2(1))(\mathbf{n}, \hat{g}(2)\mathbf{k}_2(2))\}.\end{aligned}\quad [37a]$$

$$\begin{aligned}\hat{B} &= \{\hat{S}_+(1)\hat{S}_-(2) + \hat{S}_-(1)\hat{S}_+(2) \\ &\times (-\frac{1}{4})\{(\hat{g}(1)\mathbf{k}_2(1), \hat{g}(2)\mathbf{k}_2(2)) - 3(\mathbf{n}, \hat{g}(1)\mathbf{k}_2(1)) \\ &\times (\mathbf{n}, \hat{g}(2)\mathbf{k}_2(2)) - \text{Tr}[\hat{R}^+ * \hat{g}^+(1) * \hat{g}^+(2)] \\ &+ 3(\mathbf{n}, \hat{g}(1) * \hat{R} * \hat{g}^+(2)\mathbf{n})\},\end{aligned}\quad [37b]$$

$$\hat{C} = \{\hat{S}_{\mathbf{k}_2}(1)\hat{S}_+(2) + \hat{S}_+(1)\hat{S}_{\mathbf{k}_2}(2)\}C, \quad [37c]$$

$$\hat{D} = \hat{C}^+, \quad [37d]$$

$$\hat{E} = \hat{S}_+(1)\hat{S}_+(2)E, \quad [37e]$$

$$\hat{F} = \hat{E}^+, \quad [37f]$$

$$\begin{aligned}\hat{G} &= \frac{i}{4}\{\hat{S}_+(1)\hat{S}_-(2) - \hat{S}_-(1)\hat{S}_+(2)\} \\ &\times \{(\mathbf{l}(1), \hat{g}^+(1) * \hat{g}^+(2)\mathbf{m}(2)) \\ &- (\mathbf{l}(2), \hat{g}^+(2) * \hat{g}^+(1)\mathbf{m}(1)) \\ &- 3(\mathbf{k}_2(2), \hat{R}^+ * \hat{g}^+(1)\mathbf{n} \times \hat{g}^+(2)\mathbf{n})\},\end{aligned}\quad [37g]$$

$$\hat{H} = \{\hat{S}_{\mathbf{k}_2}(1)\hat{S}_+(2) - \hat{S}_+(1)\hat{S}_{\mathbf{k}_2}(2)\}H, \quad [37h]$$

$$\hat{I} = \hat{H}^+, \quad [37i]$$

$$\mathbf{n} = \mathbf{r}/r. \quad [37j]$$

The coordinate parts are specified only for the terms \hat{A} , \hat{B} , and \hat{G} . We use the sign \times in expression [37g] to denote vector multiplication. \hat{R} denotes the transformation that rotates the coordinate system of the second spin into that of the first one,

$$\{\mathbf{l}(1), \mathbf{m}(1), \mathbf{k}_2(1)\} = \hat{R}\{\mathbf{l}(2), \mathbf{m}(2), \mathbf{k}_2(2)\}. \quad [38]$$

Let us note the antisymmetry of the operator part of the terms \hat{G} , \hat{H} , and \hat{I} with respect to the exchange of the partner numbers $1 \leftrightarrow 2$. These terms seem to have tensor rank 1 (14), but the question of the rank is more complex because the quantization axes of the partners do not in general coincide. The term \hat{G} is also called the spiral exchange or Dzialoshinski Hamiltonian (3). The matrix elements of the Hamiltonian in the form [36] and [37] can be easily obtained in the basis diagonalizing the Zeeman interaction of both centers.

ESR SPECTRA OF THE DIPOLE-COUPLED PAIRS IN THE SECULAR APPROXIMATION

The secular part of the dipole-dipole interaction between anisotropic centers is given by the term \hat{A} (Eq. [37a]). In a previous work (10), several representations were derived. Here we use a variant obtained after substitution of Eqs. [8] and [13] into Eq. [37a],

$$\hat{A} = \hat{S}_{\mathbf{k}_2}(1)\hat{S}_{\mathbf{k}_2}(2)A, \quad [39]$$

where

$$\begin{aligned}A &= \{(\hat{G}(1)\mathbf{k}_1, \hat{G}(2)\mathbf{k}_1) - 3(\mathbf{n}, \hat{G}(1)\mathbf{k}_1) \\ &\times (\mathbf{n}, \hat{G}(2)\mathbf{k}_1)\} / \{g_{\text{eff}}(1)g_{\text{eff}}(2)\}.\end{aligned}\quad [40]$$

The Hamiltonian of the coupled pair in the secular approximation can be written as

$$\begin{aligned}\mathcal{H} &= \{g_{\text{eff}}(1)\hat{S}_{\mathbf{k}_2}(1) + g_{\text{eff}}(2)\hat{S}_{\mathbf{k}_2}(2)\}\beta B_0 \\ &+ A\beta^2/r^3\hat{S}_{\mathbf{k}_2}(1)\hat{S}_{\mathbf{k}_2}(2).\end{aligned}\quad [41]$$

Its energy levels are

$$\begin{aligned}\epsilon(m_1, m_2) &= \beta B_0\{g_{\text{eff}}(1)m_1 + g_{\text{eff}}(2)m_2\} \\ &+ m_1m_2A\beta^2/r^3,\end{aligned}\quad [42]$$

where m_i is the spin projection of the i th particle onto its quantization axis direction $\mathbf{k}_2(i)$. Four ESR transitions are allowed: $|\frac{1}{2}, m_2\rangle \leftrightarrow |-\frac{1}{2}, m_2\rangle$, $|m_1, \frac{1}{2}\rangle \leftrightarrow |m_1, -\frac{1}{2}\rangle$; $m_1, m_2 = \pm\frac{1}{2}$. The value B_{01} of external resonance field for the first center depends on its orientation, pair geometry, and quantum number m_2 ,

$$B_{01}(m_2) = \{\hbar\omega - m_2A\beta^2/r^3\} / \{g_{\text{eff}}(1)\beta\}, \quad [43]$$

ω being the working frequency of the ESR spectrometer. The dipole interaction splits the ESR line of each partner into a Pake doublet (we consider the case $S_1 = S_2 = \frac{1}{2}$). The splitting value Δ depends on the geometry of the system in question,

$$\Delta = A\beta/[r^3g_{\text{eff}}(1)]. \quad [44]$$

If the particles are isotropic, the mean value of Δ is equal to zero and the centers of the doublet components coincide.

Let us consider the results of numerical simulations of ESR spectra. We have performed the calculations for a simple model. The pair had a fixed structure (see Fig. 1), its orientation in space being random with respect to the laboratory frame. The first paramagnetic center was treated as isotropic and its powder (or glassy) spectrum was calculated.

Figures 2–5 show dipole shapes of the ESR line of the isotropic center, depending on the pair geometry and the degree of anisotropy of the second-partner g tensor. The contribution of the second partner to the ESR spectrum is negligible because of the large width of its spectral line due to the g -tensor anisotropy. All the doublets are symmetric and have the features of spin-1 ion spectra. But the centers of the doublet components do not coincide. For this reason, in some cases the amplitudes of the outer extremes exceed that of the intermediate ones (Fig. 5).

The positions of the specific points (see Fig. 6) of a doublet component can be approximated by the expressions

$$B(p_1, m_2) \approx B_{1c} + 2m_2\beta \times \{g_{\parallel}^{5/2} \cos^2\theta + g_{\perp}^{5/2} \sin^2\theta\}^{2/5} / r^3, \quad [45]$$

$$B(p_2, m_2) \approx B_{1c} - m_2(\beta/r^3) \begin{cases} \{g_{\perp}^{9/2} \cos^2\theta + g_{\parallel}^{9/2} \sin^2\theta\}^{2/9}, & \text{if } g_{\perp} > g_{\parallel}, \\ g_{\perp}, & \text{if } g_{\perp} < g_{\parallel} \end{cases} \quad [46]$$

$$B(p_3, m_2) \approx B_{1c} - m_2(\beta/r^3) \begin{cases} f, & \text{if } g_{\perp} < g_{\parallel}, \\ \max(f, g_{\perp}), & \text{if } g_{\perp} > g_{\parallel}, \end{cases} \quad [47]$$

where

$$B_{1c} = \hbar\omega/(g_{\parallel}\beta) \quad [48]$$

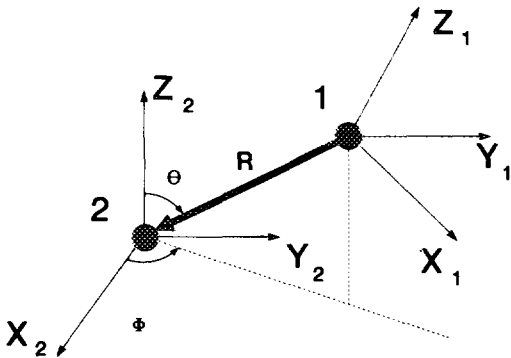


FIG. 1. The geometry of a pair of paramagnetic centers. Principal axes of the G tensors are denoted by numbers with indices corresponding to partner number. The first partner is assumed to be isotropic for the spectra in the figures below (the only exception is Fig. 8).

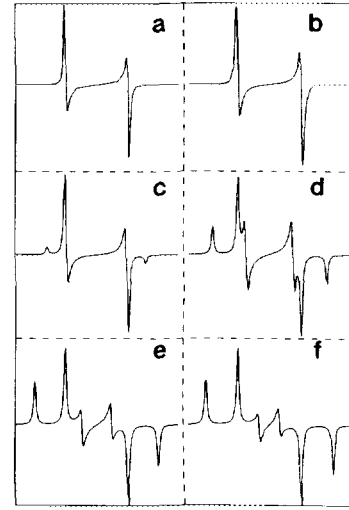


FIG. 2. The dependence of the isotropic partner spectral contour on the pair geometry and g -tensor axial anisotropy of the second partner. Each spectrum is characterized by the corresponding value of the angle θ specified in Fig. 1: (a) $\theta = 0$, (b) $\theta = \pi/6$, (c) $\theta = \pi/4$, (d) $\theta = \pi/3$, (e) $\theta = 5\pi/12$, (f) $\theta = \pi/2$. Spectra were numerically calculated for $G_{\parallel}/G_{\perp} = (g_{\parallel}/g_{\perp}) = 0.1$; $G_{\parallel} = 0.5$, suitable isotropic homogeneous broadening being included.

is the center of the ESR line of the first partner, and

$$f = \left\{ \frac{g_{\parallel}^4 \cos^2\theta + g_{\perp}^4 \sin^2\theta}{g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta} \right\}^{1/12} \times \left\{ \frac{g_{\perp}^{12/5} \cos^2\theta + g_{\parallel}^{12/5} \sin^2\theta}{g_{\perp}^{6/5} \cos^2\theta + g_{\parallel}^{6/5} \sin^2\theta} \right\}^{5/6}. \quad [49]$$

A comparison of the approximated values with the numerically obtained ones is given in Fig. 7. The smaller the anisotropy, the better the approximation.

When a small axial anisotropy of the first-partner g tensor is introduced, its spectrum becomes asymmetric. Certain examples of such spectra are presented in Fig. 8. Their form is rather sensitive to the orientation of the symmetry axes of the observed partner with respect to the molecular frame of the highly anisotropic center.

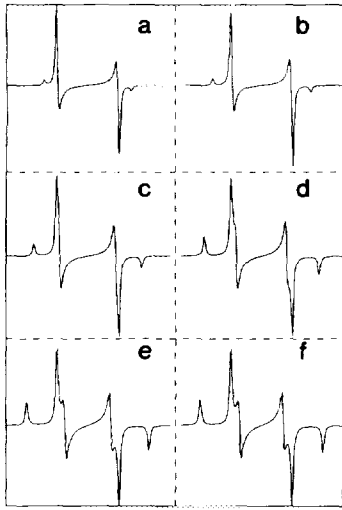


FIG. 3. The same as described in the legend to Fig. 2, $G_{\parallel}/G_{\perp} = 0.2$; $G_{ij} = 2.35$.

TEMPERATURE DEPENDENCE OF THE PAIR SPECTRA

The temperature dependence of the ESR spectra is determined mainly by the frequency changes in molecular motions which modulate the system Hamiltonian and, thus, cause transformations of the spectra. In this section, we do not consider such processes. Here we deal with the "static" temperature influence caused by the Boltzmann distribution of the energy level populations. This distribution is

$$n(m_1, m_2) = Z^{-1} \exp \{ -[\beta B_0 (g_{\text{eff}}(1)m_1 + g_{\text{eff}}(2)m_2) + m_1 m_2 A \beta^2 / r^3] / (k_B T) \}, \quad [50]$$

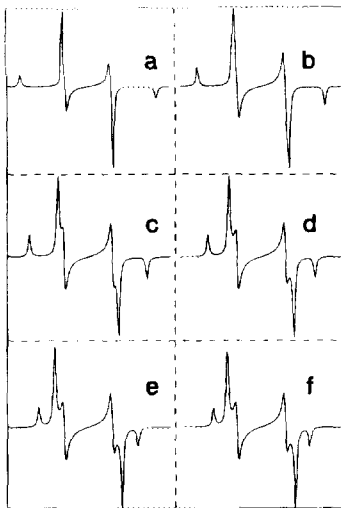


FIG. 4. The same as described in the legend to Fig. 2, $G_{\parallel}/G_{\perp} = 2$; $G_{ij} = 5.74$.

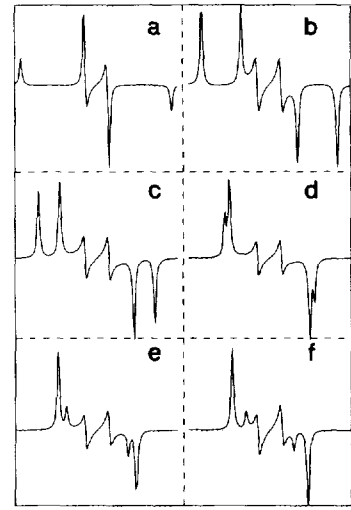


FIG. 5. The same as described in the legend to Fig. 2, $G_{\parallel}/G_{\perp} = 10$; $G_{ij} = 7$.

where T is the absolute temperature and k_B is the Boltzmann constant. Z is the statistical sum

$$Z = \sum_{m_1, m_2} \exp \{ -[\beta B_0 (g_{\text{eff}}(1)m_1 + g_{\text{eff}}(2)m_2) + m_1 m_2 A \beta^2 / r^3] / (k_B T) \}. \quad [51]$$

ESR usually deals with the high-temperature limit. For X band, the temperature at which the Zeeman and thermal energies become equal is about 0.4 K. Even liquid-helium temperature seems to be high from this point of view. The use of 2 mm band devices makes it possible to polarize spins

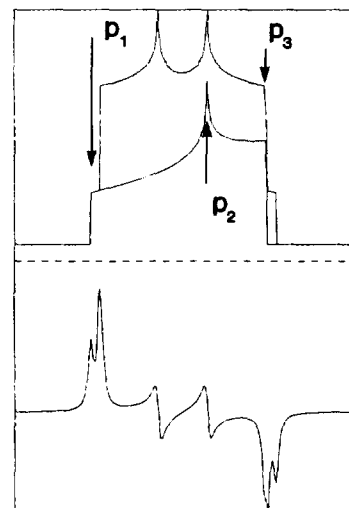


FIG. 6. Positions of the specific points of a Pake-doublet component. The doublet components are symmetric with respect to B_{1c} , the center of the first-partner ESR line.

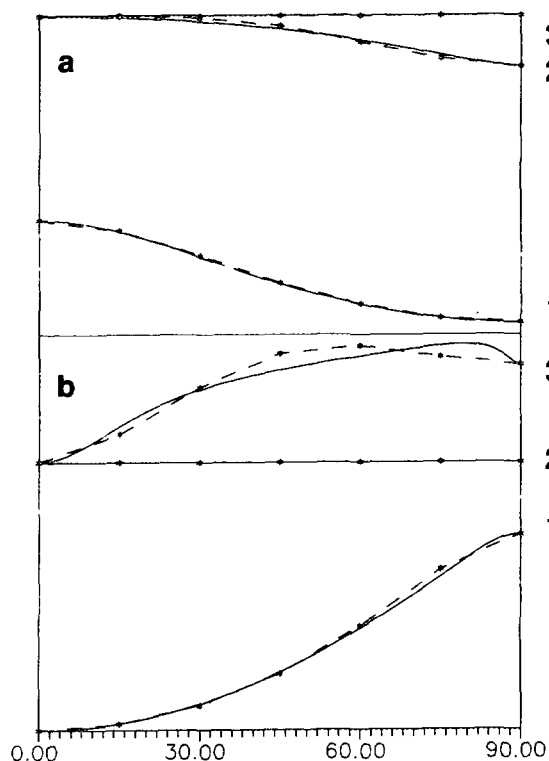


FIG. 7. Comparison of approximated (solid lines) and numerically obtained (asterisks and dashed lines) positions of the specific points of the pair spectra. Lines are numbered as corresponding specific points. (a) $g_{\parallel}/g_{\perp} = \frac{1}{2}$, (b) $g_{\parallel}/g_{\perp} = 5$.

sufficiently at helium temperatures (15). With energies of the spin levels obtained above to the first order in the perturbation, the following relation must hold,

$$B_0 \min\{g_{\text{eff}}(1), g_{\text{eff}}(2)\} \gg \max|A|\beta/r^3. \quad [52]$$

The above notes and expression [52] allow us to simplify formulas [50] and [51] by excluding the influence of the dipole interaction on the level populations

$$n(m_1, m_2) = Z^{-1} \exp\{-\beta B_0 [g_{\text{eff}}(1)m_1 + g_{\text{eff}}(2)m_2]/(k_B T)\}, \quad [53]$$

$$Z = 4 \text{ch}\{\beta B_0 g_{\text{eff}}(1)/(2k_B T)\} \times \text{ch}\{\beta B_0 g_{\text{eff}}(2)/(2k_B T)\}, \quad [54]$$

as the summation in Eq. [51] is easily performed for spins $\frac{1}{2}$.

Now we can compare the relative intensities of the Pake-doublet components, with their positions being given by Eq. [43]. These intensities are proportional to the difference in the population of the appropriate levels:

$$I_1(m_2) \propto \text{th}\{\beta B_0 g_{\text{eff}}(1)/(2k_B T)\} \times \exp\{-\beta B_0 g_{\text{eff}}(2)m_2/(k_B T)\}. \quad [55]$$

Taking into account relation [43] and neglecting any dipole influence on the level populations once more, one can obtain from Eq. [55]

$$I_1(m_2) \propto \text{th}\{\hbar\omega/(2k_B T)\} \times \exp\{-\hbar\omega g_{\text{eff}}(2)m_2/[g_{\text{eff}}(1)k_B T]\}. \quad [56]$$

Equation [56] shows that, if $g_{\text{eff}}(2) \gg g_{\text{eff}}(1)$, the influence of the second-partner polarization would be sufficient even at helium temperatures for X band. An experiment of this kind was performed by Altshuler and co-authors (16) for the dipole line-broadening studies of diluted species.

The examples of the influence of low-temperature spin polarization on the dipole lineshape of ESR powder pair spectra in X band are shown in Fig. 9. One can note that, for a pair of isotropic centers (Fig. 9B), one component is suppressed uniformly with decreasing temperature, but when the second partner is anisotropic (Fig. 9A), such suppression becomes inhomogeneous (compare intensities at the positions of the arrows).

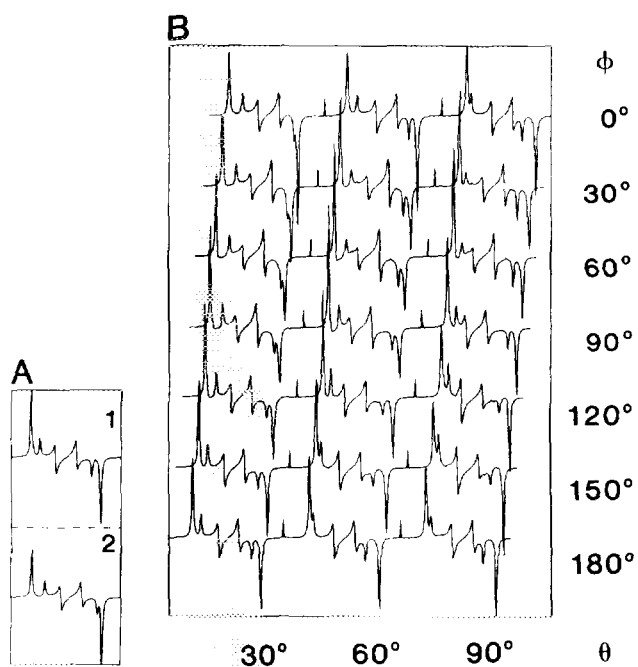


FIG. 8. Manifestations of a small axial anisotropy of the first-partner g tensor ($g_{\parallel}(1) = 2.000$, $g_{\perp}(1) = 1.9975$) in the ESR spectral contour. G_{\parallel}/G_{\perp} of the second partner equals 10. The angle θ between the vector \mathbf{r} and the molecular axis Z is 70° , $r = 7.94 \text{ \AA}$. (A) Spectrum 1 corresponds to the isotropic partner, spectrum 2 to $\theta = 0$. (B) The dependence of the line form of the first partner on the orientation of its symmetry axis with respect to the molecular frame of the second partner (θ, ϕ —polar and azimuthal angles, respectively); the vector \mathbf{r} is assumed to be in the X-Z plane.

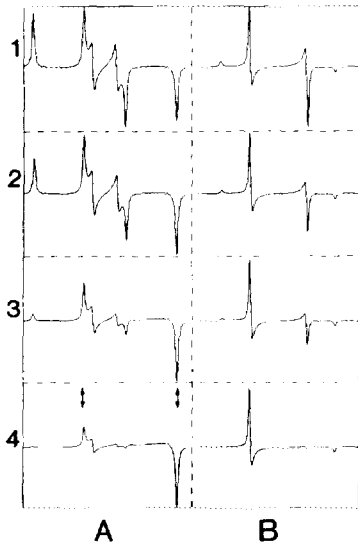


FIG. 9. Examples of the temperature dependence of the isotropic partner ESR spectra in the dipole coupled pair. The second-partner anisotropies are: (A) $G_{\parallel}/G_{\perp} = 10$ ($G_{\parallel} = 7$, $\theta = \pi/9$); (B) $G_{\parallel}/G_{\perp} = 1$ ($G_{\parallel} = 4$). (1) The high-temperature limit; (2) $T = 1$ K; (3) $T = 0.25$ K; (4) $T = 0.125$ K.

PAIRS WITH AN ESR-UNOBSERVABLE PARTNER WITH $g_{\perp} = 0$

When a paramagnetic center has an axially symmetric g tensor with $g_{\perp} = 0$, it does not absorb microwave power (2) because the transition probability for the particle is equal to zero. Thus, direct ESR investigations are impossible. The dipole-dipole interaction of the center in question with a more normal one, denoted here as the first partner, contains information about the unobservable partner.

The consideration of the dipole interactions above is not valid for a system with one partner having $g_{\perp} = 0$ since, for the orientations of the pair where the g tensor symmetry axis is perpendicular to the magnetic-field direction, $g_{\text{eff}}(2) = |g_{\parallel} \cos \theta| \approx 0$ and relation [52] is not fulfilled.

To solve this problem, we write the system Hamiltonian in the form

$$\mathcal{H} = g_{\text{eff}}(1)\beta B_0 m_1 + \beta(\mathbf{H}_{\text{eff}}, \hat{g}(2)\mathbf{S}(2)). \quad [57]$$

The \mathbf{H}_{eff} value can be obtained in the secular approximation by summing up the Zeeman term of the second partner (Eq. [1]) and the dipole term (Eq. [31]), substituting μ^{sec} defined by Eqs. [17] and [18] instead of μ_1 in the dipole Hamiltonian:

$$\mathbf{H}_{\text{eff}}(m_1) = \mathbf{B}_0 + m_1(\beta/r^3)\hat{g}(1) \times \{\mathbf{k}_3(1) - 3(\mathbf{n}, \mathbf{k}_3(1))\mathbf{n}\}. \quad [58]$$

The fact of the \mathcal{H}_{eff} dependence on the quantum number of

the first partner is underlined in the above expression. The quantization axis direction of the second-partner spin now can be easily obtained,

$$\mathbf{k}_2(2, m_1) = \hat{g}^{\dagger}(2)\mathbf{H}_{\text{eff}}(m_1)/B(2, m_1), \quad [59]$$

and using definition [13], we have

$$B(2, m_1) = \{\mathbf{H}_{\text{eff}}^{\dagger}(m_1) * \hat{G}(2) * \mathbf{H}_{\text{eff}}(m_1)\}^{1/2}. \quad [60]$$

The energy levels of our system are

$$\epsilon(m_1, m_2) = \beta\{g_{\text{eff}}(1)B_0 m_1 + B(2, m_1)m_2\}. \quad [61]$$

In this situation, when the quantization axis direction of the second partner depends on the quantum number of the first one, forbidden transitions with simultaneous spin flips of both partners are allowed. The intensities of the transitions with (I_F) and without (I_A) changing quantum number m_2 depend upon the cosine of the angle χ between vectors $\mathbf{k}_2(2, m_1 = \frac{1}{2})$ and $\mathbf{k}_2(2, m_1 = -\frac{1}{2})$,

$$I_A \propto g_{\parallel}^2(1)[1 + \cos(\chi)], \quad [62]$$

$$I_F \propto g_{\parallel}^2(1)[1 - \cos(\chi)], \quad [63]$$

where $g_{\parallel}^2(1)$ is the so-called Bleaney factor (2) appearing due to the anisotropy of the single center transition probability, and

$$\cos(\chi) = [B_0^2 g_{\text{eff}}^2(2) - \beta^2 \hat{g}^2(1) \times [\mathbf{q}^{\dagger} * \hat{G}(2) * \mathbf{q}]/(4r^6)]/[B(2, \frac{1}{2})B(2, -\frac{1}{2})], \quad [64]$$

where

$$\mathbf{q} = \mathbf{k}_3(1) - 3(\mathbf{n}, \mathbf{k}_3(1))\mathbf{n}. \quad [65]$$

Appropriate equations for the determination of the resonance field values are

$$g_{\text{eff}}(1)\beta B_{01A}(m_2) = \hbar\omega - m_2[B(2, \frac{1}{2}) - B(2, -\frac{1}{2})], \quad [66]$$

$$g_{\text{eff}}(1)\beta B_{01F}(\pm) = \hbar\omega \pm [B(2, \frac{1}{2}) + B(2, -\frac{1}{2})]/2. \quad [67]$$

One can see clearly from Eqs. [62]–[64] that peculiarities in ESR spectra appear only when the first (Zeeman) term of Eq. [64] has the same order of magnitude as the second (dipole).

The above consideration is general enough and valid for the cases when the Zeeman interaction of the first partner is stronger than the dipole one. In our particular situation, $g_{\perp}(2)$ is equal to zero, and the above formulas become sim-

pler, the g tensor of the second partner in the molecular frame having the form

$$\hat{g}(2) = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & g_{\parallel}(2) \end{bmatrix}. \quad [68]$$

In this coordinate system, the direction of the vector $\mathbf{k}_2(2, m_1)$ does coincide with the symmetry axis of the g tensor (Z axis of the molecular frame) and may have projection value ± 1 onto this direction. For this reason, $\cos(\chi)$ also may have only two values ± 1 . Let \mathbf{a} be a unit vector along the symmetry axis of the second partner. One can rewrite expression [60] using Eqs. [65] and [68]:

$$B(2, m_1) = g_{\parallel}(2) |(\mathbf{B}_0, \mathbf{a}) + m_1(\beta/r^3)\tilde{g}(1)(\mathbf{q}, \mathbf{a})|. \quad [69]$$

And so

$\cos(\chi)$

$$= \begin{cases} +1, & \text{if } |(\mathbf{B}_0, \mathbf{a})| > (\beta/2r^3)\tilde{g}(1)|(\mathbf{q}, \mathbf{a})|, \text{ "weak dipole"} \\ -1, & \text{if the dipole interaction is "strong."} \end{cases} \quad [70]$$

When the dipole-dipole interaction is weaker than the Zeeman interaction, only "allowed" transitions take place, and their resonance-field values can be easily obtained:

$$B_{01A}(m_2) = \{ \hbar\omega - m_2 g_{\parallel}(2)\beta\tilde{g}(1)(\mathbf{q}, \mathbf{a}) \\ \times \text{sign}(\mathbf{B}_0, \mathbf{a})/r^3 \} / [g_{\text{eff}}(1)\beta]. \quad [71]$$

In another case, only forbidden transitions can be observed,

$$B_{01F}(\pm) = \{ \hbar\omega \pm g_{\parallel}(2)\beta\tilde{g}(1)|(\mathbf{q}, \mathbf{a})|/(2r^3) \} / \\ (g_{\text{eff}}(1)\beta). \quad [72]$$

One can note that the resonance-field values do not change with the inversion of the vector \mathbf{a} : $\mathbf{a} \rightarrow -\mathbf{a}$. The results of our numerical calculations are shown in Fig. 10. The first partner is assumed to be isotropic. All the high-temperature spectra in the integral form look like the Greek letter Π .

CONCLUSION

We have finished our description of the situation where the only significant factor forming the ESR lineshape is the dipole-dipole interaction in a pair of paramagnetic centers. Such a situation seems to be rather exotic but does allow us to look at the problem systematically.

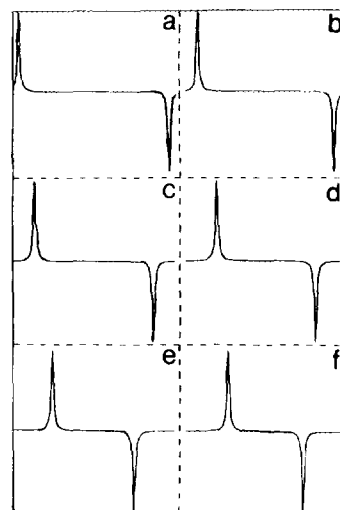


FIG. 10. The same as described in the legend to Fig. 2, $G_{\parallel} = 7$, $G_{\perp} = 0$.

Three letters are added to the Abragam's "dipole alphabet."

It is shown that centers of Pake-doublet components do not coincide due to the g tensor anisotropy. The component lineshape is determined by three specific points and, thus, is similar to spectra of paramagnetic centers with nonaxial g tensors. Intensities of the components are shown to change inhomogeneously in comparison with the isotropic case.

Pairs with ESR unobservable partners with $g_{\perp} = 0$ are found to have a Π -like integral ESR lineshape.

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