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High-temperature dipolar local field correlations in two-dimensional exchange-coupled systems

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Abstract. High-temperature local field correlations are needed to calculate the angular variation of the electron spin resonance (ESR) linewidth of exchange-coupled systems in the paramagnetic phase. In low-dimensional magnetic systems, these time correlations are usually calculated by appealing to arbitrary intermediate functions to interpolate between short- and long-time regimes. In this work, we calculate the correlation function of the dipolar field in a two-dimensional (2D) square lattice of spins $\frac{1}{2}$, for several orientations of an external magnetic field. Arbitrary interpolation functions are avoided by assuming that the normal modes of the spin correlations behave diffusively as soon as quantum coherence is broken. The effects of interlayer exchange in an actual system are considered by introducing a cut-off in the 2D diffusion. The angular variation of the resulting ESR linewidth is analysed as a function of the 'quantum coherence time' τ_0 and the cut-off time τ_c. Comparison with experimental data in layered Cu–amino acid crystals allows us to estimate $\tau_0 \leq 0.5\hbar/J$ and $\tau_c \simeq 200\hbar/J$, where J is the in-layer exchange.

1. Introduction and background

1.1. Electron spin resonance linewidth in exchange-coupled systems

Our purpose is to study the electron spin resonance (ESR) linewidth of systems in the paramagnetic phase (high temperatures), which are described by the Hamiltonian $H = H_0 + H'$, with $H_0 = H_Z + H_{ex}$, where H_Z is the electronic Zeeman interaction, $H_{ex} = \frac{1}{2}J\Sigma_{ij}\boldsymbol{S}_i \cdot \boldsymbol{S}_j$ is the nearest-neighbour isotropic exchange interaction between electronic spins ($S = \frac{1}{2}$) and H' includes other interactions, such as magnetic dipolar or hyperfine, which constitute a perturbation on H_0. These interactions, which verify $[H', H_0] \neq 0$, are the major source of ESR linewidth in these systems. Its effect can be illustrated as producing 'local fields' at each spin site, and the effect of the exchange interaction is to introduce a dynamics in these local fields, which can be described by the correlation function [1, 2]

$$\psi(t) = \langle [H'^0(t), S^+][S^-, H'] \rangle / \langle S^+ S^- \rangle \tag{1}$$

where $H'^0(t) = \exp(\mathrm{i}H_0 t/\hbar)H' \exp(-\mathrm{i}H_0 t/\hbar)$, S is the total spin of the system and the angular brackets indicate the statistical average of the quantum operator. In anisotropic

systems, ψ also depends on the angles θ, φ, which give the orientation of the applied magnetic field referred to x, y, z axes fixed on the magnetic system.

When the exchange energies are smaller than the Zeeman ones, (secular case [3]), the time dependence of ψ is determined only by H_{ex}, and the ESR linewidth can be expressed as [2]

$$\Delta H(\theta, \varphi) \propto \int \mathrm{d}t\, \psi(\theta, \varphi, t). \tag{2}$$

When H' is linear in electronic spin operators, as is the case for the hyperfine interaction, equation (1) tells us that $\psi(\theta, \varphi, t)$ involves two-site spin correlations $\langle S_i(t)S_j\rangle$. It can be shown that, in this case, angular and time dependences are separable, i.e. $\psi(\theta, \varphi, t) = \psi_1(\theta, \varphi)\psi_2(t)$, with $\psi_1(\theta, \varphi) = M_2(\theta, \varphi)$, the second moment of the corresponding interaction [3]. Using equation (2) it can be seen that in this case the angular variation of the ESR linewidth will be the same as that of M_2.

In the case that H' is quadratic in spin operators, as is the case for the magnetic dipolar interaction, ψ involves four-site spin correlations, and it can be separated only at short times, when under the usual decoupling approximations only self-site correlations are important [4–6]. In this short-time regime, $\psi_d^{st}(\theta, \varphi, t) = M_2^d(\theta, \varphi)\psi^{st}(t)$ is obtained. As time grows, pair correlations with more and more neighbours become important, the angular dependence evolves with time and ψ_d is no longer a separable function. The angular variation of the ESR linewidth will then depend on the relative weight of the different angular functions along the time integration in equation (2).

1.2. Case of dipolar interaction in two-dimensional systems

It is well accepted that in exchange-coupled systems, high-temperature spin dynamics at long times is governed by diffusive processes [7]. Then, the long-time dependence of spin-pair correlations appearing in ψ will obey $\langle S_i(t)S_j\rangle \propto t^{-d/2}$, where d is the dimensionality of the exchange network. Thus, in low-dimensional ($d < 3$) magnetic systems, ψ is expected to have a slow decay, having long-time tails that can weight strongly in the integral of equation (2).

A quasi-ideal magnetic 2D system is characterized by an exchange interaction J between in-plane nearest neighbours that is much larger than the exchange J' between out-of-plane neighbours, i.e. $J/J' \gg 1$. Richards [8, 9] has made the main contributions to the understanding of ESR data in low-dimensional systems, when dipolar interaction is the major source of linewidth. He showed that, owing to diffusive effects, the angular and time dependences of ψ_d become separable at long times, and that in this regime the angular dependence is constant in time and proportional to the $q = 0$ mode of the dipolar second moment, i.e. $\psi_d^{ll}(\theta, \varphi, t) = (M_2)_{q=0}(\theta, \varphi)\psi^{ll}(t)$. He also showed that in quasi-ideal 2D systems the contribution of the long-time regime of ψ_d is predominant in the time integral of equation (2) and thus $\Delta H(\theta, \varphi) \propto (M_2)_{q=0}(\theta, \varphi)$.

In non-ideal 2D systems, i.e. those with J' not negligible with respect to J, the 2D diffusion process becomes 3D at earlier times than in the quasi-ideal case, causing a much faster decay of the spin correlations. To simplify the calculations, it is usual to consider ψ_d as vanishing after a certain cut-off time τ_c, which at first sight can be thought as in [10], $\tau_c \simeq \hbar/J'$. The more elaborate reasoning of Hennessy *et al* yields the expression

$$\tau_c \simeq (J/J')^{\alpha}(\hbar/J') \tag{3}$$

where $\alpha = \frac{1}{3}$ in 1D systems [8, 11]. Using the arguments of these authors applied to 2D systems, $\alpha \simeq 1$ is obtained.

With the earlier transition to the 3D diffusive regime, the long-time angular dependence of ψ_d will have a smaller weight in the integral of equation (2), and the angular variation of the linewidth will depend on the short- and intermediate-time angular functions. In this context, it is important to establish the upper limit of validity of the short-time behaviour, and the lower time for the diffusive behaviour. Several approximations have been considered in previous works [9, 12], none of them considering the angular variation at intermediate times and interpolating arbitrarily between short- and long-time angular dependences in the calculation of ΔH.

In our group, we have studied by ESR layered Cu–amino acid systems [13] for which interlayer exchange interactions could be roughly estimated to verify $5 \leqslant J/J' \leqslant 15$ [13, 14]. Several interactions contribute to the linewidth in these systems. They can be isolated by analysing the angular variation of the linewidth in terms of the theoretically calculated angular dependence of each of the contributions [13]. Our usual practice was to include a term proportional to $(M_2)_{q=0}$ to take into account the dipolar contribution. Although this procedure gave reasonably good fits, we show in the present work that the dipolar contribution to the linewidth in these 2D systems, which are far from ideal, should have a smaller anisotropy than the one given by $(M_2)_{q=0}$. We apply the results obtained in this work to the experimental data in a Cu–amino acid system in which only dipolar interaction contributes significantly to the ESR linewidth.

To perform the calculation of the dipolar contribution to the linewidth in a system with non-negligible interlayer exchange, we need to know the precise way in which the angular dependence of ψ_d evolves from that of $M_2(\theta, \varphi)$ at short times to that of $(M_2)_{q=0}(\theta, \varphi)$ in the diffusive regime at long times. To have a picture of this evolution, we calculate the dipolar local field correlation function in a simple 2D system for several orientations of the external magnetic field. We then analyse the angular dependence of the resulting linewidth as a function of τ_c, which gives the degree of 'two-dimensionality' of the system. We also analyse the resulting anisotropy in the linewidth as a function of the time τ_0 at which it is assumed that quantum coherence is broken.

2. Theory

We will consider a square 2D lattice of N isotropic spins with $S = \frac{1}{2}$, having isotropic exchange and magnetic dipolar interactions, in the presence of an external magnetic field whose magnitude is such that Zeeman energy is greater than exchange. Thus, in the notation of the preceding section $H' = H'_d$, and the secular approximation [3] will be valid.

Following Kubo and Tomita's formalism [1] at high temperatures, the resonance absorption spectrum $I(\theta, \varphi, \omega)$ at the Larmor frequency ω_0 is given by the Fourier transform of the relaxation function Φ,

$$\Phi(\theta, \varphi, t) = \exp\left(-(1/\hbar^2)\int d\tau\,(t-\tau)\psi_d(\theta, \varphi, \tau)\right). \tag{4}$$

Here, ψ_d is given by equation (1), using $H' = H'_d$, and $H_0 = H_{ex}$ because of the neglect of non-secular contributions. Replacing H_{ex} and H'_d in equation (1), yields

$$\psi_d(\theta, \varphi, \tau) = \langle S^+ S^- \rangle^{-1} \sum_{i,j,k,l} F_{ij}F_{kl}\langle S_i^z(\tau)S_j^+(\tau)S_k^z S_l^- \rangle \tag{5}$$

where

$$F_{ij} = \tfrac{3}{2}(g\beta)^2(3\cos^2\theta_{ij} - 1)/r_{ij}^3. \tag{6}$$

Here, g is the gyromagnetic factor, β the Bohr magneton and θ_{ij} is the angle between the intersite vector $\boldsymbol{r}_{ij}$ and the magnetic field $\boldsymbol{H}$.

The next step to calculate ψ_d is to decouple the four-spin high-temperature correlation functions appearing in equation (5) [9, 15], and to transform equation (5) into reciprocal space,

$$\psi_d(\theta, \varphi, \tau) = 2\sum_q |F_q|^2 \langle S_q^+(\tau) S_{-q}^-\rangle \langle S_{-q}^z(\tau) S_q^z\rangle \tag{7}$$

where $\langle S_q^\sigma(\tau) S_{-q}^{-\sigma}\rangle = (1/N)\Sigma_{i,j}\langle S_i^\sigma(\tau) S_j^{-\sigma}\rangle \exp(i\boldsymbol{q}\cdot\boldsymbol{r}_{ij})$, where $\sigma = +, -$ or z, $|F_q| = (1/\sqrt{N})\,\Sigma_j F_{ij}\exp(i\boldsymbol{q}\cdot\boldsymbol{r}_{ij})$, and $\boldsymbol{q}$ runs over the first Brillouin zone.

The behaviour of the spin correlation functions $\langle S_i^\sigma(\tau) S_j^{-\sigma}\rangle$ at high temperatures and short times is well described by a Gaussian decay [1, 6], i.e. only self-correlations are important while quantum coherence is preserved, and this regime will be valid up to a certain time τ_0. In $\boldsymbol{q}$-space,

$$\langle S_q^\sigma(\tau) S_{-q}^{-\sigma}\rangle_{st} \simeq \langle S_q^\sigma(0) S_{-q}^{-\sigma}\rangle \exp(-\omega_e^2\tau^2/2) \qquad (\tau < \tau_0). \tag{8}$$

Here, ω_e is the exchange frequency, calculated from a short-time expansion [6] as $\omega_e^2 = (1/2\hbar^2)zJ^2$, where z is the number of nearest neighbours.

For times longer than τ_0, we assume that the local fields at different sites can 'see' each other. Thus, the spin correlations are no longer restricted to self-correlations, different site pair correlations begin to grow, and the spin dynamics may be associated with the first steps of a diffusive process, described by the hydrodynamic equation [16]

$$\langle S_q^\sigma(\tau) S_{-q}^{-\sigma}\rangle_{ll} \simeq \langle S_q^\sigma(\tau_0) S_{-q}^{-\sigma}\rangle \exp[-Dq^2(\tau - \tau_0)] \qquad (\tau > \tau_0) \tag{9}$$

where D is the spin diffusion constant.

Using equations (8) and (9) in equation (7), the dipolar local field correlation function may be written

$$\psi_d^I(\theta, \varphi, \tau) = \tfrac{1}{4}\exp(-\omega_e^2\tau^2)\sum_q |F_q|^2 \qquad (\tau < \tau_0) \tag{10a}$$

$$\psi_d^{II}(\theta, \varphi, \tau) = \tfrac{1}{4}k\sum_q \exp[-2Dq^2(\tau - \tau_0)]|F_q|^2 \qquad (\tau_0 < \tau < \tau_c) \tag{10b}$$

$$\psi_d^{III}(\theta, \varphi, \tau) = 0 \qquad (\tau > \tau_c) \tag{10c}$$

where $k = \exp(-\omega_e^2\tau_0^2)$ to satisfy continuity, and we have assumed for simplicity that, at the cut-off time τ_c introduced in equation (3), ψ goes abruptly to zero. It can be shown easily that $\frac{1}{4}\Sigma_q|F_q|^2$ coincides with the dipolar second moment $M_2(\theta, \varphi)$, thus yielding the familiar expression $\psi_d^I(\theta, \varphi, \tau) = M_2(\theta, \varphi, \tau)\exp(-\omega_e^2\tau^2)$ for $\tau < \tau_0$ [2].

Replacing equations (10) into (4) and assuming that we only need to know $\Phi(t)$ for $t > \tau_c$, the Fourier transform yields a Lorentzian ESR line [1], with a peak-to-peak linewidth calculated from equation (2) as

$$\Delta H(\theta, \varphi) \simeq \frac{2}{\sqrt{3}}\left(M_2(\theta, \varphi)\int_0^{\tau_0} d\tau \exp(-\omega_e^2\tau^2) + \int_{\tau_0}^{\tau_c} d\tau\, \psi_d^{II}(\theta, \varphi, \tau)\right). \tag{11}$$

Thus, the linewidth is expressed as the sum of a short-time contribution, having the angular variation of the dipolar second moment M_2, plus a contribution whose angular variation is not easy to establish, because $\psi_d^{II}(\theta, \varphi, \tau)$ is not separable, except for long times where it is proportional to $(M_2)_{q=0}$. We may ask what we mean by 'long times', i.e. when is the angular variation $\psi_d \propto (M_2)_{q=0}$ established, and what will be the resulting

angular variation of the linewidth for non-ideal 2D systems, for which τ_c is much smaller than in quasi-ideal ones.

3. Model and calculations

We calculate the local field correlation function $\psi_d(\theta, \varphi, \tau)$ given by equations (10), for a 2D 21×21 square lattice of spins $\frac{1}{2}$, coupled by exchange and magnetic dipolar interactions. The cell parameter, called a, is arbitrary, with the only restriction that it should lead to a dipolar interaction much smaller than the exchange interaction, to justify our perturbative approach. Only secular contributions [3] are retained.

As was discussed in the previous section, we assume that only self-site correlations are important in the calculation of ψ_d^L (short-time regime). Two relevant questions may be asked: Up to what time does this regime persist? When do correlations with other sites begin to be non-negligible? We propose that after a 'quantum coherence time' τ_0, which should be of the order of $\hbar/2J$ [17] and could be taken as the upper limit of the short-time behaviour, the first steps of a diffusive process take place. This assumption leads to the continuity of ψ_d at $\tau = \tau_0$ in a natural way, without resorting to arbitrary intermediate functions. Thus, it is possible to follow the time evolution of the angular variation of ψ_d.

In order to perform the calculations, it is necessary to know the relationship between the spin diffusion constant D and the isotropic in-layer exchange parameter J. Several authors [5, 16–18] have obtained

$$D/a^2 \simeq \delta J/\hbar \tag{12}$$

where δ depends on dimensionality and effective spin, taking values in the range $0.2 \leqslant \delta \leqslant 0.5$ for 2D systems and $S = \frac{1}{2}$. Here, the two extreme values will be taken into account in order to determine their influence on the final results.

Using equation (12) in equation (10) and introducing the dimensionless variables $X = J\tau/\hbar$ and $Q = aq$, the dipolar local field correlation function $\psi_d(\theta, \varphi, \tau)$ can be written as

$$\psi_d(\theta, \varphi, X) = \frac{1}{4}\sum_{Q} |F_Q|^2 E(X, Q) \tag{13}$$

with

$$E(X, Q) = \begin{cases} \exp(-2X^2) & X \leqslant X_0 \\ \exp(-2X_0^2)\exp[-2\delta(X - X_0)(Q_x^2 + Q_y^2)] & X_0 < X \leqslant X_c \\ 0 & X > X_c \end{cases}$$

and $X_0 = J\tau_0/\hbar$, $X_c = J\tau_c/\hbar$. In this way, $\psi_d(\theta, \varphi, X)$ is expressed as a sum of normal-mode contributions satisfying the matching condition between short-time and diffusive regimes. Each term of the sum is 'weighted' by the function $E(X, Q)$, which contains the time dependence. As can be seen in equation (13), the time variation is Q-independent in the short-time regime, but for the diffusional regime, $E(X, Q)$ acts as a 'filter', producing a faster decay of the larger-Q contributions. Consequently, for times long enough, only the $Q = 0$ mode survives, yielding the dominant contribution to ψ_d. This is essentially the same result as Richards [9] obtained, but our procedure also yields information about the intermediate-time regime of ψ_d.

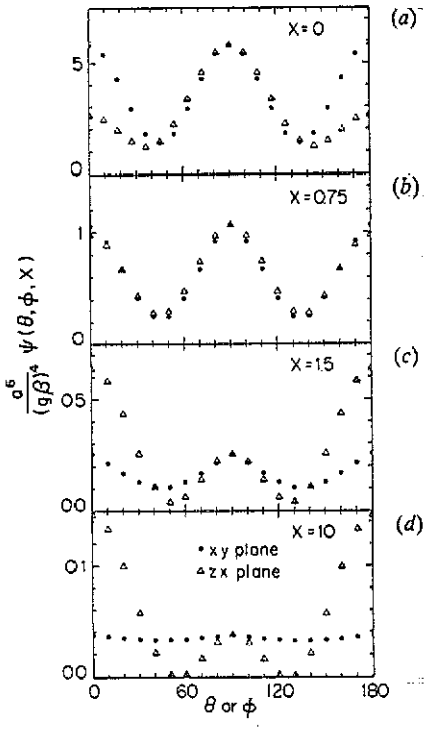

Figure 1. Angular dependence of the dimensionless high-temperature dipolar field correlation function calculated at different dimensionless times $X = J\tau/\hbar$, for $X_0 = 0.5$ and $\delta = 0.5$, in a square lattice of spins $\frac{1}{2}$ and cell parameter a: (*a*) $X = 0$; (*b*) $X = 0.75$; (*c*) $X = 1.5$; (*d*) $X = 10$. $H \| \hat{z}$ ($\theta = 0°$) corresponds to the magnetic field normal to the layer of spins.

The orientation of the magnetic field H is given relative to an orthogonal system where $\hat{x}$ and $\hat{y}$ are coincident with the square lattice axes. The fast decay of $E(X, Q)$ as a function of Q_x and Q_y allows us to limit the calculation of ψ_d to the interval $Q_x, Q_y \leq \pi$. This results in an error less than 1%, except in the limited range $X_0 < X < 1$. For each orientation (θ, φ) of H and for a 21×21 grid in the range $0 \leq Q_x, Q_y \leq \pi$, the $|F_Q|^2$ were calculated considering spins at distances not greater than $5a$. To test the validity of our approximations, we calculated $\frac{1}{4}\Sigma_Q |F_Q|^2$, which agreed within 5% with the exact calculation of M_2.

We calculate the values of the linewidth ΔH, using equation (11). The integration could be performed analytically by inserting equation (13) into (11), which yields

$$\Delta H(\theta, \varphi) \simeq \frac{2\hbar}{\sqrt{3}J}\Bigg[|F_0|^2[(\pi/8)^{1/2}\,\mathrm{erf}(\sqrt{2}X_0) + \exp(-2X_0^2)(X_c - X_0)] + \sum_{Q \neq 0} |F_Q|^2 \Bigg((\pi/8)^{1/2}\,\mathrm{erf}(\sqrt{2}X_0) + \frac{\exp(-2X_0^2)}{(2\delta Q^2)} \times \{1 - \exp[-2\delta Q^2(X_c - X_0)]\} \Bigg) \Bigg] \tag{14}$$

where $Q^2 = Q_x^2 + Q_y^2$.

4. Results and discussion

Figure 1 displays the angular variation of ψ_d calculated at different dimensionless times X, considering $X_0 = 0.5$ and $\delta = 0.5$. In the figure ψ_d is multiplied by the factor $a^6/(g\beta)^4$

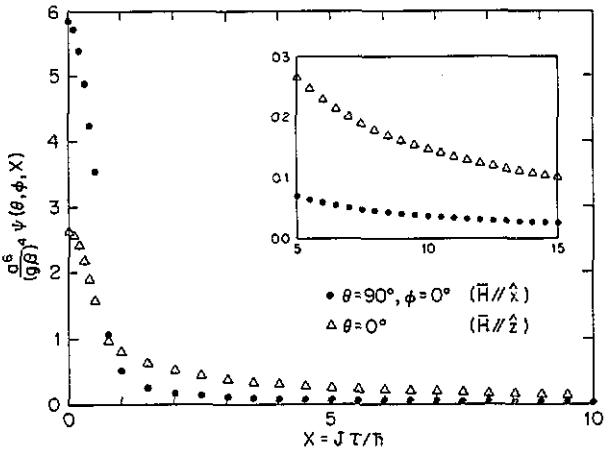

Figure 2. Dimensionless dipolar field correlation function versus the dimensionless time X, for $X_0 = 0.5$ and $\delta = 0.5$, for two different directions of the external magnetic field: along the layer ($\boldsymbol{H} \| \hat{x}$) and normal to the layer ($\boldsymbol{H} \| \hat{z}$).

to give a dimensionless result. Figure 1(*a*) shows that for $\psi_d(\theta, \varphi, 0) = M_2(\theta, \varphi)$, the maximum value of ψ_d is reached at the $\hat{x}$ and $\hat{y}$ axes, i.e. when $\boldsymbol{H}$ lies along the layer (xy plane). This angular variation remains constant over the short-time regime ($X \leqslant X_0$). At $X = X_0$, the beginning of a diffusive process is assumed, and for subsequent times the angular variation evolves as shown in figures 1(*b*)–(*d*). For $X = 10$, figure 1(*d*), the angular variation of ψ_d fits well the $(3\cos^2\theta - 1)^2$ behaviour calculated by Richards [9] for $(M_2)_{q=0}$. If we consider the case $\delta = 0.2$, the process is more sluggish, and it is found that this angular variation is established at $X \simeq 23$. Thus, it can be stated that the decoupling between angular and time dependences proposed in [9] is already valid in our case for times $\tau \geqslant 10\hbar/J$ if we take $\delta = 0.5$, or $\tau \geqslant 23\hbar/J$ if $\delta = 0.2$. It should be noted that the main characteristics of the angular variation at long times (such as maximum ψ_d for $\boldsymbol{H} \| \hat{z}$, and minimum near the 'magic angle' in the zx plane) can be observed even at times as short as $X - X_0 = 1$ (figure 1(*c*)) for $\delta = 0.5$, or $X - X_0 = 2.5$ if $\delta = 0.2$ (not shown in the figure). The effect of considering different values of X_0 will be to shift the beginning of the diffusive process, yielding the same angular variations of figure 1 as a function of $X - X_0$, i.e. figure 1(*b*) should be considered as corresponding to $X - X_0 = 0.25$, 1(*c*) to $X - X_0 = 1$ and 1(*d*) to $X - X_0 = 9.5$.

In figure 2 we have chosen two representative orientations of the magnetic field, $\boldsymbol{H} \| \hat{x}$ ($\theta = 90°$, $\varphi = 0°$) and $\boldsymbol{H} \| \hat{z}$ ($\theta = 0°$, normal to the layer), to show the time evolution of $\psi_d(\theta, \varphi, X)$, with $X_0 = 0.5$ and $\delta = 0.5$. It can be observed that for $X \geqslant X_0 = 0.5$, ψ_d is strongly damped when $\boldsymbol{H}$ is along the layer ($\boldsymbol{H} \| \hat{x}$), while its decay is slow for $\boldsymbol{H}$ along the normal to the layer ($\boldsymbol{H} \| \hat{z}$). In order to determine the effects of these different decay rates on the ESR linewidth, we calculated ΔH for these two orientations, using equation (14). Figure 3 shows the resulting dimensionless linewidths, plotted as a function of the dimensionless cut-off time X_c. We have considered also the cases $\delta = 0.2$ and $X_0 = 0.3$. It can be seen that the lower X_0 increases the linewidth for $\boldsymbol{H} \| \hat{z}$, while the linewidth for $\boldsymbol{H} \| \hat{x}$ remains practically the same, for the same cut-off times. For the lower δ, instead, it is observed that the linewidths with both $\boldsymbol{H}$ normal and $\boldsymbol{H}$ lying on the layer increase.

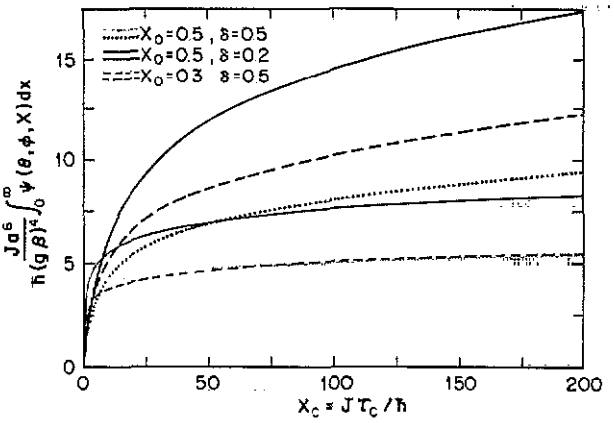

Figure 3. Dimensionless ESR linewidth plotted as a function of the dimensionless cut-off time X_c, and calculated for the extreme values of δ in equation (12) and for two values of the quantum coherence time X_0. In each case, heavy curves (or dots) correspond to $H \| \hat{z}$ and light ones to $H \| \hat{x}$.

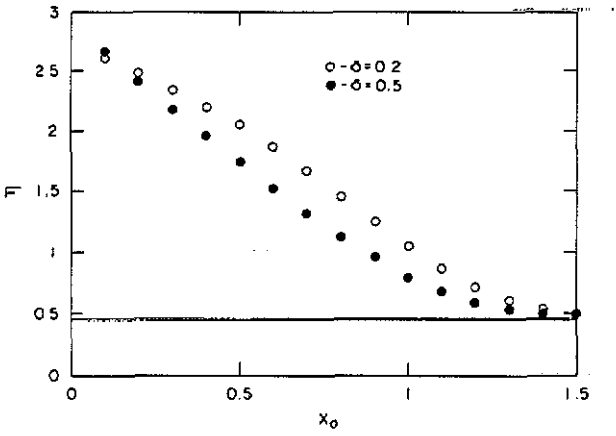

Figure 4. Linewidth anisotropy $\eta = \Delta H(H \| \hat{z})/\Delta H(H \| \hat{x})$ obtained for the dimensionless cut-off time $X_c = 200$, as a function of the dimensionless time $X_0 = J\tau_0/\hbar$ for which it is assumed that quantum coherence is broken. The two extreme values of δ in equation (12) have been considered.

To obtain a clearer insight into the influence on our results of the assumed values of X_0 and the values of δ predicted by the various theories, we have plotted in figure 4 the quotient $\eta = \Delta H(H \| \hat{z})/\Delta H(H \| \hat{x})$, giving the linewidth anisotropy, at $X_c = 200$, as a function of X_0, for the extreme values $\delta = 0.2$ and $\delta = 0.5$. Although the absolute values of the linewidth are strongly dependent on δ, as shown in figure 3, figure 4 shows that the values of the anisotropy η only vary about 20% between the extreme values of δ, for $X_0 \leq 0.5$. On the other hand, figure 4 shows that η depends strongly on X_0. It is interesting to remark that if we had considered $X_0 = 1$, i.e. that the short-time regime was valid until $\tau = \hbar/J$, as done by Gulley *et al* [12], we would have obtained $\eta \simeq 1$, i.e.

the same linewidth for $H \| \hat{x}$ and $H \| \hat{z}$, which does not coincide with the experimental data. The horizontal line in figure 4 corresponds to the value of η that would result if only short-time contributions determine the linewidth, i.e. the anisotropy corresponding to the dipolar second moment.

To compare our calculations with experimental data, we consider the case of Cu(D,L-but)$_2$, a layered Cu–amino acid system for which can be estimated $5 \leqslant J/J' \leqslant 15$ [14, 19]. In this case, equation (3) will give X_c in the range $25 \leqslant X_c \leqslant 225$. We have plotted in figure 5 the experimental data of the linewidth in Cu(D,L-but)$_2$, taken from [20], together with the angular variation predicted by our model. An isotropic linewidth $\Delta H_0 = 30.9$ G was subtracted from experimental data, and the full curves in figure 5 correspond to $\Delta H_c(\theta, \varphi) - \Delta H_0 = 0.34 \Delta H_M(\theta, \varphi)$. Here ΔH_M is given by equation (14), using $J \simeq 0.6$ K [19], $X_c = 200$, $\delta = 0.2$, $X_0 = 0.3$ and the cell parameter taken from [20]. The residual linewidth $\Delta H_0 = 30.9$ G may be attributed to perturbative interactions other than dipolar.

The factor 0.34 needed for our calculations to fit the absolute values of the linewidth, and the greater anisotropy of the calculated linewidth in the layer, can be explained by considering that our model was developed for a square lattice, while the Cu(D,L-but)$_2$ lattice is nearly triangular. The calculation of the dipolar second moment for this geometry shows a much smaller in-layer anisotropy than for the square lattice. However, it can be seen in figure 5 that our model gives the correct η for this system at $X_c \simeq 200$, i.e. for the cut-off time $\tau_c \simeq 200\hbar/J$. Using equation (3), we may conclude that $J/J' \simeq 14$ in Cu(D,L-but)$_2$. Although it is also possible to adjust the experimental data using $X_0 = 0.5$, a value $X_c \simeq 400$ is needed in this case to obtain the experimental anisotropy, leading to $J/J' \simeq 20$. If $X_0 = 0.6$, then $X_c \simeq 800$ and $J/J' \simeq 30$. Estimations based on previous work [14, 19, 20] put an upper bound $J/J' \leqslant 15$, so that we may establish that it should be $X_0 \leqslant 0.5$, supporting the assumption that the breakdown of quantum coherence in our non-ideal systems must be at times $\tau_0 \leqslant 0.5\hbar/J$.

5. Conclusions

Our calculation of the dipolar field correlation function ψ_d at high temperature allowed us to obtain the way in which its angular dependence evolves with time in a two-dimensional system. Working in reciprocal space provides a natural way to avoid the use of arbitrary functions for intermediate times, by assuming that a diffusive equation provides a good description of the normal modes of spin-pair correlations as soon as quantum coherence is broken.

In this way, we obtained information about ψ_d at every time, illustrating the way in which local field dipolar correlations are strongly damped when the magnetic field is along the layer but have a longer life when H is in the normal direction. We show that the angular dependence obtained by Richards, characteristic of 'long times', is reached at times $\tau \leqslant 23\hbar/J$.

Systems with appreciable interlayer exchange are considered by introducing a cut-off of the 2D correlations. The time integration of ψ_d yields the ESR linewidth, whose angular dependence is analysed as a function of the dimensionless cut-off time X_c and the quantum coherence time X_0. It is shown that, in order to obtain the correct dipolar contribution to the linewidth in the layered Cu–amino acid system Cu(D,L-but)$_2$, $\tau_0 \simeq \hbar/2J$ must be considered an upper limit for the breakdown of quantum coherence. Using

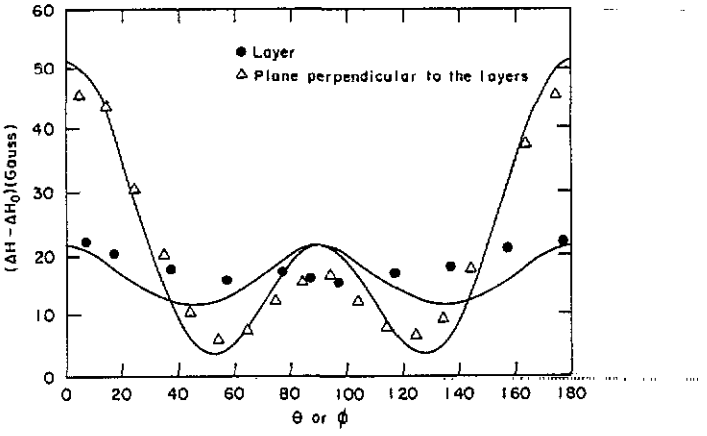

Figure 5. Experimental ESR linewidth data as a function of the orientation of the magnetic field H for the layered Cu–amino acid Cu(D,L-but)$_2$, taken from [20]. An isotropic linewidth $\Delta H_0 \simeq 30.9$ G has been subtracted. The full curves correspond to the expression $\Delta H_c - \Delta H_0 = 0.34\Delta H_M$, where ΔH_M is that predicted by our model using $X_c = 200$, $X_0 = 0.3$, $\delta = 0.2$ and previous measured parameters of Cu(D,L-but)$_2$ [19, 20].

bounding values for cut-off times based on previous estimations [19, 20], we showed that experimental data are consistent with $J/J' \simeq 14$ and $X_0 = 0.3$.

It is interesting to remark that our results support $\alpha \simeq 1$ in equation (3), in agreement with the reasoning of Hennesy *et al* [8]. Smaller values of α would yield much smaller values for the cut-off times, for which the experimental anisotropy could not be reproduced.

Our method may be applied to any square 2D magnetic system with arbitrary values of the interlayer exchange, to obtain the correct dipolar contribution to the high-temperature ESR linewidth.

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