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Abstract. A Monte Carlo computing procedure is presented for evaluating the set of parameters which characterize the superhyperfine interaction in electron–nuclear spin coupled systems. The method is illustrated in the determination of the components $T_\parallel$ and $T_\perp$ of the interaction tensor $\overset{\leftrightarrow}{\mathbf{T}}$ together with the linewidth $\Delta H_{\mathrm{p-p}}$ of each of the superhyperfine transitions present in the electron paramagnetic resonance spectrum given by a cubic Gd^{3+} centre in CaF_2 recorded at room temperature. The different steps followed to simulate the 'annealing' of the system are described in detail together with the shortcuts proposed in order to minimize the computing time taken for the procedure to converge to the best set of parameters. This method is applicable even if no good estimates are available for the initial set of parameters as these are usually taken as zero. This modern approach to the complicated problem of fitting the superhyperfine structure to the theoretical expressions is shown to be the best alternative and even if it is time consuming it can be easily run on a microcomputer.

1. Introduction

The advantages of the Monte Carlo method using the Metropolis [1] algorithm for solving optimization problems which involve several inter-related and non-linear parameters have been shown in many fields. In the case of the determination of the effective spin Hamiltonian parameters which best fit the electron paramagnetic resonance (EPR) fine-structure spectrum, there exist several computing procedures [2, 3] which have attempted to systematize the search of these parameters. These procedures give good results but are rather demanding regarding the goodness of the initial parameters and the knowledge of the quantum levels that originate the transitions. The Monte Carlo method applied to this problem [4] avoided these requirements and led to very precise results. This procedure has been successfully applied to fit the spectrum given by Gd^{3+} in sites with different symmetry, e.g. cubic and tetragonal in CaF_2 [4], and cubic and trigonal in BaF_2 [5].

In the more complicated electron–nuclear spin coupled system the existence of significant contributions from allowed and forbidden transitions gives a complex EPR spectrum formed by a very large number (typically a few hundreds) of closely spaced lines. For example, for a Gd^{3+} ion in the centre of a cube formed by eight F^-, 4^8 superhyperfine lines are possible in theory for each fine-structure line. However, these superhyperfine transitions can be grouped in a reduced number of combinations

by considering the number of equivalent Gd^{3+}–F^- pairs for a given orientation of the external magnetic field. Several attempts have been made at finding the tensor components of the superhyperfine interaction by using the expressions deduced by Ranon and Hyde [6] for the resonant fields and the transition probabilities of the superhyperfine lines. Naehring [7] used this formalism to calculate the superhyperfine spectrum originated by a Gd^{3+} in a cubic site in CdF_2 using the values deduced from ENDOR experiments; he obtained a good visual agreement between the recorded lines and the calculated bar spectrum. Later on, attempts were made in order to find precisely the components of the superhyperfine interaction tensor $\overleftrightarrow{T}$, by varying its components and minimizing the intensity difference between the theoretical and experimental spectra [8, 9]. Misra [10] extended the least-squares fitting method to the solution of the hyperfine interaction. The success of this method is based on the goodness of the initial parameters from which the program will start and on the correct identification of the unique pairs of eigenvalues that originate a transition for the various resonant magnetic field values. The hyperfine and superhyperfine splitting was also studied by Madrid *et al* [11] for substitutional Mn^{2+} in PbF_2. The theoretical intensities were calculated in the case where the nuclear Zeeman term in the Hamiltonian could be neglected. In this case the initial parameters that characterize these interactions could be estimated from the experimental splitting, and a computer fitting was then performed which gave a good visual agreement with the experimental EPR lines recorded at room temperature and at 60 K. Recently, the Monte Carlo method has been successfully applied to the hyperfine interaction when $S = 1/2$ and $I = 1/2$ by Heynderickx *et al* [12].

The rigorous fitting of the EPR data when superhyperfine interactions are present has not yet been solved. In this work we propose a Monte Carlo procedure to perform the fitting of the EPR fine and superhyperfine line splittings and apply it to Gd^{3+} in cubic sites in CaF_2 ($S = 7/2$, $I^F = 1/2$). It will be shown how the proposed method permits simultaneous fittings of the EPR lines obtained from different field orientations without the necessity of previous knowledge of the parameters we want to fit or the labels of the quantum levels involved in any of the superhyperfine transitions. Another merit of this method which simulates a 'thermal annealing' of the system, is that when the initial 'temperature' is sufficiently high, all the minima of the function are explored and as the 'temperature' decreases adiabatically it will choose the absolute one, whereas the usual least-square fittings might converge to a local minimum if the starting parameters are far from the real ones. The formalism introduced previously [6, 7] will be followed and only the relations used in the program will be given here for the sake of brevity.

2. Theory

A substitutional trivalent gadolinium ion non-locally compensated in CaF_2 will be considered here. This centre has a cubic symmetry as the impurity is located in the centre of a cube of fluorine ions. The Gd^{3+}–$8F^-$ system is described by the following spin Hamiltonian

$$\mathcal{H} = g\mu_B \boldsymbol{H} \cdot \boldsymbol{S}_e + \mathcal{H}_{cf} + \mathcal{H}_I \tag{1}$$

where the first term is the electronic isotropic Zeeman term. The fine-structure term,

$\mathcal{H}_{\mathrm{cf}}$, describes the crystal field interaction, which can be written as

$$\mathcal{H}_{\mathrm{cf}} = \sum_{l,m} B_l^m O_l^m \tag{2}$$

where the O_l^m are the Steven's operators with $m \le l$. The last term, $\mathcal{H}_{\mathrm{I}}$, describes the superhyperfine interaction of the Gd^{3+} electron spin, S_e, with each of the nuclear spins I_k^{F}, of the eight nearest fluorine ions, together with the nuclear Zeeman interaction. In our case $S_e = 7/2$, $I_k^{\mathrm{F}} = 1/2$ and k varies from 1 to 8 if only the first shell of neighbours is considered. $\mathcal{H}_{\mathrm{I}}$ can then be written as

$$\mathcal{H}_{\mathrm{I}} = \sum_{k=1}^{8} \{ S_e \cdot \overset{\leftrightarrow}{\mathbf{T}}_k \cdot I_k^{\mathrm{F}} - \gamma_N^{\mathrm{F}} H \cdot I_k^{\mathrm{F}} \} \tag{3}$$

where γ_N^{F} is the nuclear gyromagnetic ratio and $\overset{\leftrightarrow}{\mathbf{T}}_k$ is the superhyperfine interaction tensor which can be taken as diagonal when the reference system is chosen in such a way that the z axis is parallel to the direction joining the Gd^{3+} with the kth nearest fluorine, that is a $\langle 111 \rangle$ direction. For this particular pair $\overset{\leftrightarrow}{\mathbf{T}}_k$ is diagonal with components $T_{\parallel}$, parallel and $T_{\perp}$, perpendicular to the z axis. For all the other directions of the bonding axis $Gd^{3+}-F_k^{-}$ the tensor $\overset{\leftrightarrow}{\mathbf{T}}_k$ will not be diagonal and its components can be expressed as functions of $T_{\parallel}$, $T_{\perp}$ and θ_k which is the angle formed by the z axis and the cube diagonal that joins the kth interacting pair. The number of different values of θ_k which characterize the eight fluorine anions can generally be reduced by symmetry considerations. For any orientation of the z axis (always taken in the direction of H), four different values of θ_k are required. Three, two and one different values of θ_k are necessary for H in the [111], [110] and [100] directions, respectively [8].

In order to diagonalize $\mathcal{H}_{\mathrm{I}}$ the eigenfunctions of the predominant electronic Zeeman term are chosen as the electronic basis set. Each term in the sum indicated in (3) can be treated independently since there are no matrix elements relating the different fluorine nuclear spins. The diagonalization of this Hamiltonian leads to the resonance condition for a microwave frequency ν, expressed as

$$h\nu = \Delta E_{\mathrm{FS}}(H, M, M+1) + \sum_j [\mu_j' K_j(M+1) - \mu_j K_j(M)] \tag{4}$$

where ΔE_{FS} is the difference in energies between the M and $M+1$ levels of the fine structure obtained by the diagonalization of the first two terms of the Hamiltonian given by (1). The second term in (4) is the perturbation caused by $\mathcal{H}_{\mathrm{I}}$ to the fine-structure levels. The sum in (4) extends over j which is the number of different θ_k that are necessary to describe the 8 fluorines, and is ≤ 4. μ_j is the sum of the nuclear spin quantum numbers, m_i^{F}, taken over x_j which is the number of equivalent fluorines which have the same θ_k and is

$$\mu_j = \sum_{i=1}^{x_j} m_i^{\mathrm{F}} \tag{5}$$

$K_j(M)$ is defined by

$$K_j(M) = \sqrt{P^2(M) \cos^2 \theta_j + Q^2(M) \sin^2 \theta_j} \tag{6a}$$

$$P(M) = MT_{\parallel} - \gamma_N^{\mathrm{F}} H \tag{6b}$$

$$Q(M) = MT_{\perp} - \gamma_N^{\mathrm{F}} H. \tag{6c}$$

The relative intensity of each superhyperfine resonance line is a function of the probability, $r_j = \cos^2(\epsilon_j/2)$, for allowed nuclear transitions ($\Delta m_j^{\mathrm{F}} = 0$) and of the probability $q_j = \sin^2(\epsilon_j/2)$, for the forbidden nuclear transitions ($\Delta m_j^{\mathrm{F}} = \pm 1$), where ϵ_j is given by

$$\cos \epsilon_j = \frac{P(M+1)P(M)\cos^2\theta_j + Q(M+1)Q(M)\sin^2\theta_j}{K_j(M+1)K_j(M)}. \qquad (7)$$

If δ_j is the number of fluorine nuclear spins that change their states from $m_i^{\mathrm{F}} = -1/2$ to $m_i'^{\mathrm{F}} = +1/2$, the relative intensities of the superhyperfine transition can be expressed following the argumentation given by Naehring [7] as

$$I(\mu_1, \mu_2...; \mu_1', \mu_2'...) = \prod_j \left\{ \sum_{\delta_j=0}^{x_j} F(x_j, \delta_j, \mu_j', \mu_j) \, q_j^{(2\delta_j - \mu_j' + \mu_j)} \, r_j^{(x_j - 2\delta_j + \mu_j' - \mu_j)} \right\} \qquad (8)$$

with

$$F(x_j, \delta_j, \mu_j', \mu_j) = \frac{x_j!}{\delta_j!(\frac{1}{2}x_j - \mu_j - \delta_j)!(\delta_j - \mu_j' + \mu_j)!(\frac{1}{2}x_j + \mu_j' - \delta_j)!}. \qquad (9)$$

3. Monte Carlo procedure

The simulated annealing method [1,4] will be used in order to find the values of the parameters P_j that best reproduce the experimental spectra arising from the superhyperfine interaction. This procedure will be illustrated in the case of a cubic Gd^{3+} centre in a CaF_2 crystal at room temperature. The parameters P_j which we fit are the components $T_{\parallel}$ and $T_{\perp}$ of $\overleftrightarrow{T}$, the peak to peak width, $\Delta H_{\mathrm{p-p}}$, of the first derivative of the lineshape that we assume is described by a Lorentzian distribution and that is common to all the superhyperfine lines, and the normalization constants C_λ for each of the fine-structure lines included. The number of these fine-structure lines, $\lambda_{\max}$, considered for the fitting can vary from one up to the maximum number available.

One of the merits of the Monte Carlo method is its ability to explore all the different choices available to the system subject to a set of pre-defined conditions. For instance, for a given set of the parameters $T_{\parallel}$ and $T_{\perp}$, the resonant fields of the superhyperfine transitions between any two fine levels are calculated by using (4). The procedure then evaluates the resulting intensity for each fine line by summing up the relative weights of all the superhyperfine transitions which contribute effectively to it. The superhyperfine quantum levels of the transitions to be considered can change when the program explores different values of the parameters. In the present case, the program calculates the intensities of all the possible transitions between every combination of initial and final quantum states formed by the superhyperfine splitting of the fine levels considered. As this task can be very time consuming, much care has been taken in order to perform the calculations with maximum efficiency. For example, the lines whose intensity is lower than a threshold value I_c are excluded from the calculations of the resonant fields. These weak lines were later taken into account in a final check in order to assure that the addition of such transitions did not modify the results.

The Monte Carlo procedure minimizes the 'energy' Φ defined by

$$\Phi = \frac{1}{N} \sum_{\lambda=1}^{\lambda_{\max}} \sum_{i=1}^{n_\lambda} \left(I_{\exp,i}^{\lambda}(H_i) - I_{\mathrm{cal},i}^{\lambda}(H_i) \right)^2 \tag{10}$$

where λ identifies which one of the fine-structure resonant lines is considered and n_λ is the number of experimental points in that line. Moreover, the different resonant lines might be chosen from the spectra obtained with different field orientations. $I_{\exp,i}^{\lambda}(H_i)$ are the recorded intensities for the chosen lines while $I_{\mathrm{cal},i}^{\lambda}(H_i)$ are the corresponding calculated values of the intensity, both as a function of the external magnetic field.

The calculation of $I_{\mathrm{cal},i}(H_i)$ is performed in two stages. First, the fine-structure problem is solved by using a similar Monte Carlo procedure [4]; the crystal field parameters found there ($b_4^0 = -46.63 \times 10^{-4}$ cm^{-1}, $b_6^0 = -0.0904 \times 10^{-4}$ cm^{-1}, $g = 1.9920$) are used to calculate the variation of the energy eigenvalues as a function of the applied field. This variation of the energy with magnetic field is calculated for all the initial, M, and final, M', states involved in each of the fine-structure lines for which the superhyperfine structure is later desired. Secondly, the superhyperfine interaction described by the Hamiltonian given by expression (3) is included to generate the superhyperfine structure and the Monte Carlo procedure proposed here will determine the values of the set of parameters P_j defined above which best fit the experimental data. The outline of the general procedure is given in the flow diagram shown in figure 1. The simulated annealing described in detail in a previous work [4], needs an initial 'temperature' T, such that the ratio Φ/T reaches a value close to unity after a few Monte Carlo steps (MCS). The main considerations for implementing this procedure are, according to the flow diagram, as follows.

(i) For each of the $\lambda_{\max}$ fine-structure lines considered, the initial and final electronic spin quantum numbers, M and M', are read. For each of these fine-structure transitions, the variation of the energy of the quantum levels involved with magnetic field is obtained by the exact diagonalization of the Zeeman term and the crystal field Hamiltonian, i.e. the first two terms of the spin Hamiltonian of (1). The span of the field considered, around the centre of each line, is ± 25 G with a field step of 1 G. With the obtained values continuous functions $E_M(H)$ and $E_{M'}(H)$ are constructed by best-fitting those points to quadratic or linear forms. These functions were then used as input to the superhyperfine Monte Carlo procedure to calculate precisely the transition fields due to the superhyperfine perturbation as shown in the input box of figure 1. In this way, the fact that the different superhyperfine transitions lines do not occur at the field corresponding to the centre of each of the fine-structure resonance lines is taken into account. No information is needed regarding either the resonant fields of the superhyperfine structure or the nuclear quantum numbers of the levels involved in those transitions. The initial and final states for each superhyperfine transition that contributes to the intensity is determined as necessary by the procedure. The allowed as well as the forbidden superhyperfine transitions were permitted to occur.

Also, the klystron frequency ν, the initial values of P_j as well as their initial increments are given. The set of parameters to be fitted are the two components $T_\parallel$ and $T_\perp$, $\Delta H_{\mathrm{p-p}}$ and the normalization factors C_λ. The initial increments of the parameters can be set arbitrarily to any non-zero value as they are self adjusting. If these increments are such that the resulting $\Delta\Phi/T$ is far from unity, then several Monte
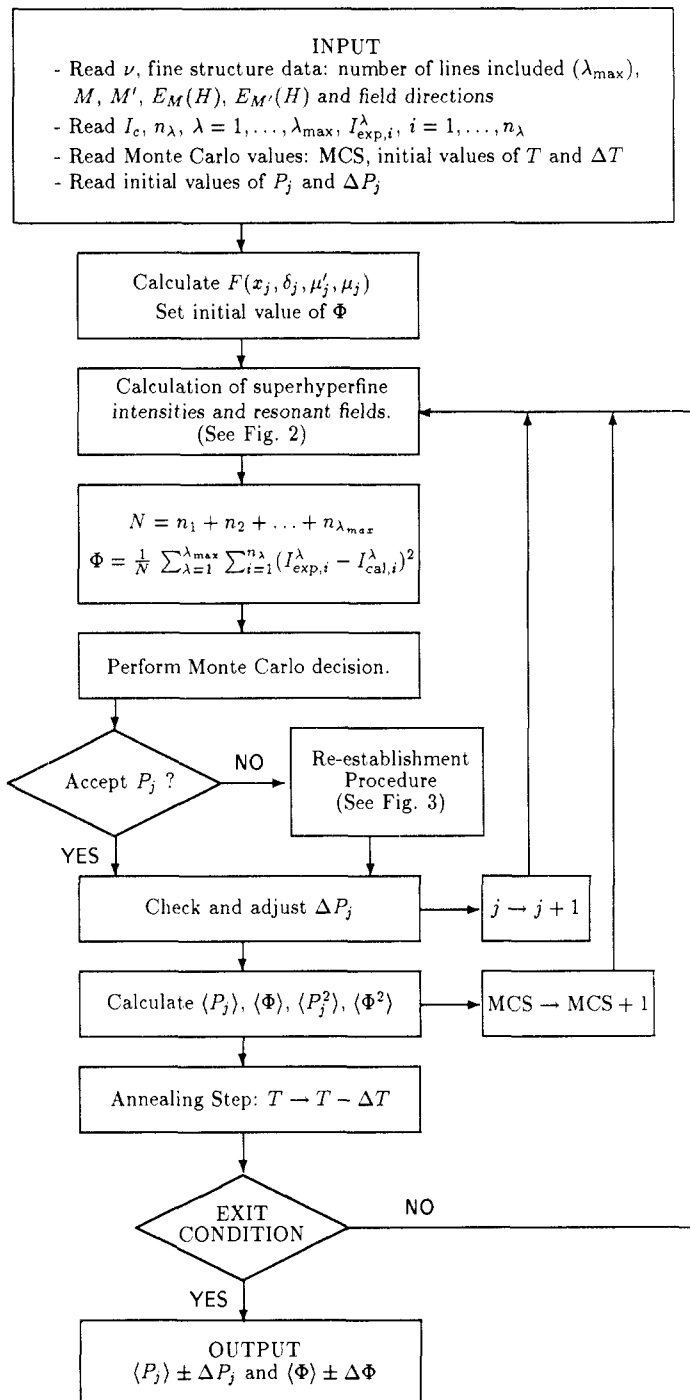
Figure 1. Flow chart representing the Monte Carlo computational procedure for determining the superhyperfine interaction Hamiltonian parameters that best fit the EPR data.

Carlo steps will be needed to adjust them to the proper values. The experimental recorded intensity $I_{\text{exp},i}(H_i)$ is also provided with a density of three points per gauss.

The number of Monte Carlo steps per 'annealing temperature', the initial 'temperature' and how many intervals each 'temperature' decade is divided into are also read.

(ii) For each direction of the magnetic field H the values of $F(x_j, \delta_j, \mu'_j, \mu_j)$ are calculated only once and stored in an array for later use.
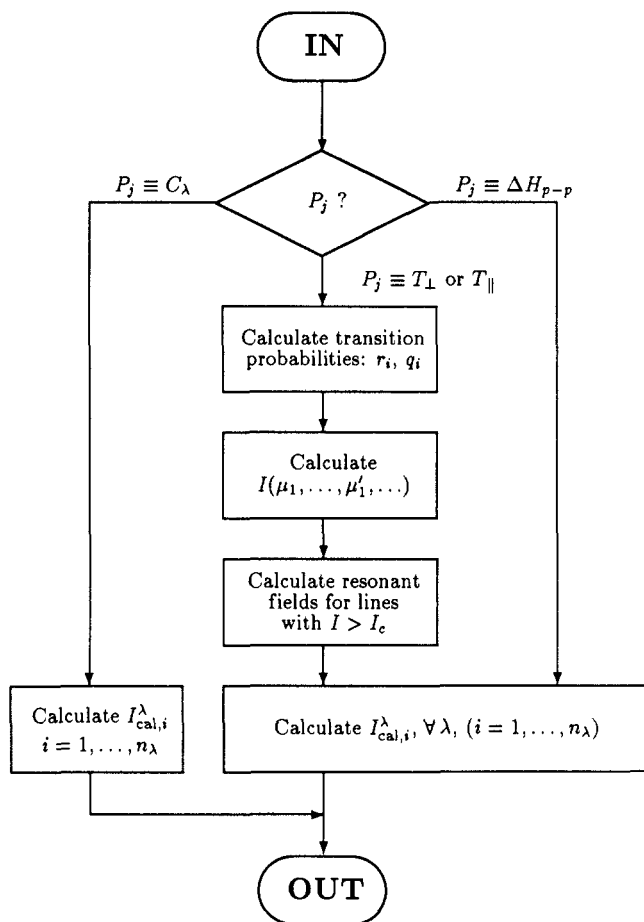

Figure 2. Flow chart used in the calculation of the relative intensities and the resonant fields of the superhyperfine allowed and forbidden EPR transitions. The procedure first adjusts $T_\parallel$ and $T_\perp$, then $\Delta H_{\text{p-p}}$ and finally C_λ.

(iii) Every time the parameters $T_\parallel$ and $T_\perp$ are changed by the program, the transition probabilities q_j, r_j, the relative intensities $I(\mu_1, \mu_2, \ldots; \mu'_1, \mu'_2, \ldots)$ and the resonant fields are recalculated according to the scheme shown in figure 2. The transition probabilities q_j and r_j are calculated at the fields corresponding to the centre of the fine-structure resonant lines to which they are associated. These values are not too sensitive to the fact that all the superhyperfine transitions do not occur at the centre-field value of the fine-structure line. This approximation reduces considerably the computing time involved in the calculation of the lines intensity and the error made

by this assumption was checked to be lower than 0.3%. Additionally, only the transitions whose relative weights are greater than a threshold value I_c, chosen here as 0.2% of the height of the most intense superhyperfine component are included. The omission of these terms results in a total intensity change of less than 1% but also reduces the computing time drastically. The resonant field obtained by means of equation (4) are recalculated only for the superhyperfine transitions whose intensities are above I_c.

Each fine-structure line is made of a large number of superhyperfine transitions. The number, quantum levels and resonant fields of these superhyperfine transitions that contribute to the intensity of the fine line, varied appreciably within the range of values randomly assigned by the Monte Carlo procedure to $T_\parallel$ and $T_\perp$. The discrete variation of the number and positions of the resonant superhyperfine lines taken into account makes the function to fit discontinuous. Some of the peculiarities of this particular Monte Carlo procedure are due to this unusual behaviour. A small change in one of the tensor parameters, near one of these discontinuities may lead to an energy difference $\Delta\Phi$ higher than expected.

Another consideration related to the fact described above is illustrated by the following example. If a new value of a parameter is explored in the vicinity of a discontinuity, which leads to a much higher value of the energy Φ, the probability of accepting this new value is very low. However, upon rejection of the involved parameter, the function remains with the internal structure resulting from the last calculation and the old value of Φ is not re-established by setting the increment of the parameter to zero. For this reason, some extra time is needed to re-establish some of the essential features of the function to ensure that $\Delta\Phi = 0$ as the parameter recovers its previous value. The way the re-establishment is done is described in the diagram of figure 3 and also carried out in the most efficient possible way. Only the part of the function affected by the most recent changes is re-established. The order in which the parameters P_j are changed in figures 2 and 3 is first $T_\parallel$ and $T_\perp$, then ΔH_{p-p} and last the normalization constant C_λ.

(iv) For each possible superhyperfine transition calculated, a first derivative of a Lorentzian lineshape is associated to it. The relative intensity of each superhyperfine transition is given by $I(\mu_1, \mu_2, \ldots; \mu'_1, \mu'_2, \ldots)$. The width of each line, ΔH_{p-p} is the same for all the transitions considered and is a global parameter of the fitting. The total resonant spectra was then obtained by adding all the contributions from all the superhyperfine transitions associated with each fine-structure line. The calculated total intensity of the superhyperfine structure is then compared with the experimental data to obtain the value Φ defined in equation (10).

Is to be noted that the experimental intensities of each line introduced as data to the Monte Carlo procedure for the minimization of Φ were normalized to the same maximum intensity. This was done in order to ensure that all the lines included were weighted equally in the fitting procedure as they all are of the same good quality.

4. Experiments and results

The experiments were carried out at room temperature in a Varian spectrometer in the X-band frequency range ($\nu = 9.51$ GHz). The samples used in this work were CaF_2 bought from Optovac Inc. as 'pure' single crystals. The accidental impurity content was estimated to be of 3×10^{-7} in molar fraction for Gd^{3+} and traces of Mn^{2+}. The sample was cleaved to a size of approximately 1 mm × 1 mm × 6 mm and was aligned

IN

$P_j \equiv C_\lambda$ P_j ? $P_j \equiv \Delta H_{p-p}$

$P_j \equiv T_\perp$ or $T_\parallel$

Re-establish old values of
$I_{\text{cal},i}^\lambda$
$(i = 1, \ldots, n_\lambda)$

Re-establish old values of
r_i, q_i, $I(\mu_1, \ldots, \mu'_1, \ldots)$
and resonant fields

Re-establish old values of
$I_{\text{cal},i}^\lambda$
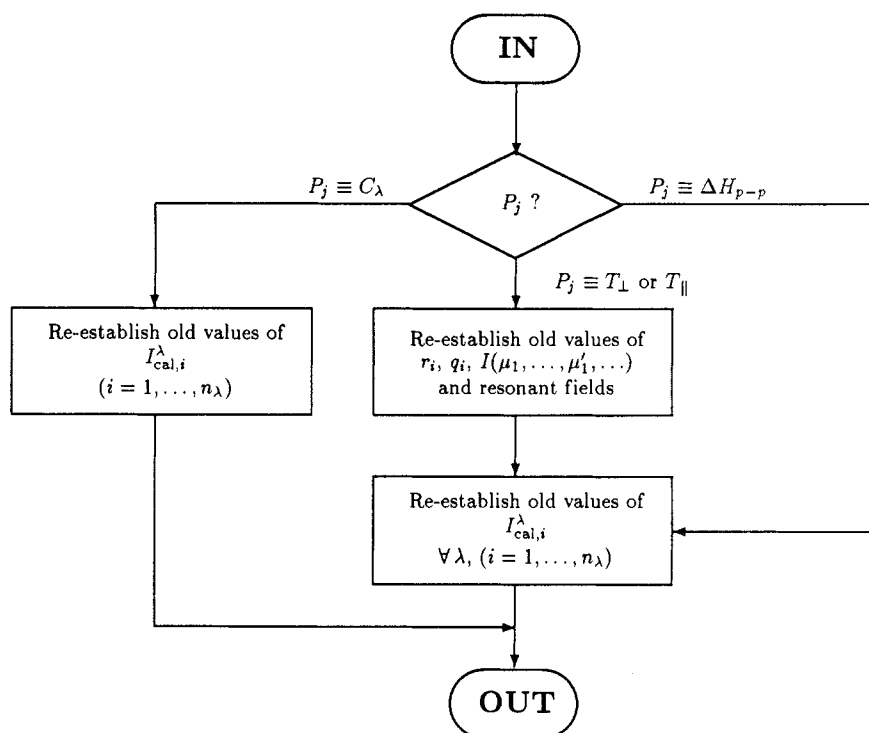$\forall \lambda$, $(i = 1, \ldots, n_\lambda)$

OUT

Figure 3. Procedure for the re-establishment of the relative intensities and resonant fields for the superhyperfine transitions to their previous values when the current parameters are rejected.

in the spectrometer cavity with a [110] axis vertical. With this set-up the external field can be parallel to either the [001], the [111] or the [110] crystalline direction. The data acquisition system consists of a Hewlett Packard scanner–voltmeter controlled by an IBM PC-AT to record in digital form the EPR signal against the applied field. This digital signal was then used by the Monte Carlo procedure which fitted these data to the theoretical predictions. Each fine-structure line was stored in a file for latter use with a density of three points per gauss and a total field span of 50 G. The conversion of the field scale from volts to gauss was done during a very slow sweep of each line by constantly monitoring the magnetic field value with a Sentec nuclear magnetic resonance probe. The six experimental lines corresponding to Gd^{3+} in cubic sites recorded at room temperature shown in figure 4 (dotted curve) for H in the [111] direction were used for the fitting. This choice was motivated by the fact that the [111] direction presents the best resolution of the superhyperfine splitting and that the inclusion of more lines would result in an unnecessary longer computing time for an already time consuming problem. The central line, not shown here, was not used for the fitting due to its overlapping with a weaker signal due to Mn^{2+} ions which distorted the profile of the Gd^{3+} line.

The Monte Carlo minimization procedure was started with the following initial values, $T_\parallel = 0$, $T_\perp = 0$ and $\Delta H_{p-p} = 2$ G. The initial 'temperature' used was high enough so that the value of Φ/T was of the order of unity after a few iterations. The
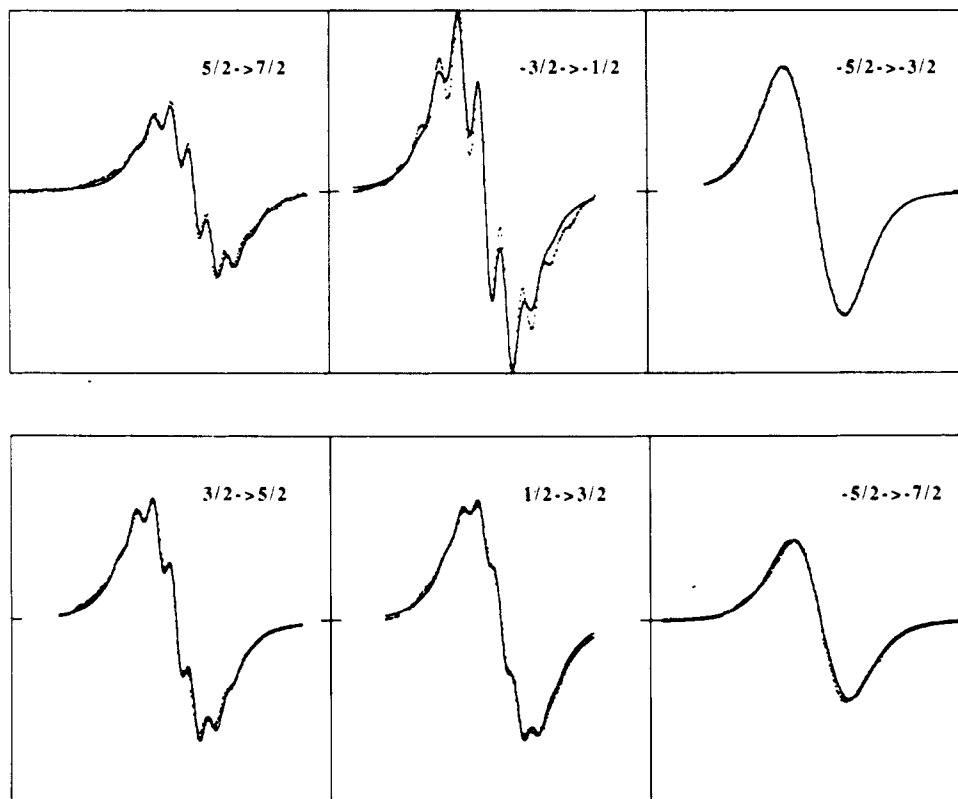
Figure 4. Comparison of the experimental EPR signal (dotted curve) with $H \parallel$ [111] recorded at room temperature with the theoretical spectrum (full curve) generated with the parameters that gave the best fit with the Monte Carlo procedure (see table 1).

initial values of the increments for $T_\parallel$ and $T_\perp$ were set equal to 10^{-4} cm^{-1} and for ΔH_{p-p}, 0.1 G. The number of MCS was set equal to 50. The rest of the parameters were the six normalization constants all set equal to unity and their initial increments were all equal to 0.1. The maximum intensity for each of the fine-structure lines included was normalized to the value corresponding to the most intense line included. This normalization was done automatically in the Monte Carlo minimization procedure. Each 'temperature' decade was divided into five equal steps. For each 'temperature', the mean values and the standard deviations for all the parameters and for the 'energy' Φ were calculated.

In figure 4 the resulting spectrum calculated with the best parameters found by the Monte Carlo procedure is shown (full curve) and compared to the corresponding experimental lines plotted as a dotted curve on this same figure. One can conclude that overall excellent agreement between the two signals exists. When the spectra with H parallel to the [100] and the [110] directions were generated with this same set of parameters, the observed agreement was slightly worse but of the same overall quality provided that the Mn^{2+} hyperfine lines did not interfere with the gadolinium spectrum.

In table 1 a summary of our results together with other results found in the literature are reported for this same cubic centre. Sook Lee *et al* [9] results were

Table 1. $CaF_2:Gd^{3+}$, cubic site, superhyperfine interaction parameters.

$T_\parallel$ (10^{-4} cm^{-1})	$T_\perp$ (10^{-4} cm^{-1})	ΔH_{p-p} (G)	Reference
2.75 $\pm$ 0.02	-2.29 $\pm$ 0.01	—	[13][a]
2.70 $\pm$ 0.07	-2.37 $\pm$ 0.07	2.3	[9][b]
2.925 $\pm$ 0.003	$-2.459 \pm$ 0.003	2.616 $\pm$ 0.005	(This work)[c]

[a] ENDOR data taken at 8 K.
[b] EPR data taken at 77 K, Gaussian lineshapes.
[c] EPR data taken at 300 K, Lorentzian lineshapes.

obtained by starting from the ENDOR data of Bill [13], also reported on table 1. With these initial values they were able to correlate each experimental superhyperfine line with one or more specific theoretical superhyperfine transitions. Based on the knowledge of this correlation, the values of $T_\parallel$ and $T_\perp$ as well as the Gaussian linewidth were adjusted until the theoretical spectra gave the best fit to the data which were recorded at 77 K. The advantage of the Monte Carlo procedure proposed here is that the result was reached without any previous knowledge on the parameters values or on the specific superhyperfine transitions which contribute to the spectrum. Also, the errors on the parameters were found to be smaller than any previous determination. They were calculated from the mean values obtained for the corresponding parameter at the lowest 'temperature' reached here and consistent with the minimum value of the function Φ following the procedure previously discussed by us [4].

It is to be noted that our results for $T_\parallel$ and $T_\perp$ were obtained by using a Lorentzian lineshape centred at each superhyperfine-line resonant field. Attempts were also made to fit the same data using a Gaussian distribution rather than a Lorentzian in order to make a straightforward comparison with the results of Sook Lee *et al* [9]. First, we used the same parameters obtained for the superhyperfine tensor in the case of the Lorentzian distribution and fitted the ΔH_{p-p} for the Gaussian linewidth together with the normalization factors for each fine-structure line. This procedure gave a value of the 'energy' Φ, a measure of the goodness of the overall fitting, 4.8 times larger than the one found for the Lorentzian distribution. Then we restarted the Monte Carlo procedure, and the value of the resulting superhyperfine tensor parameters were slightly different (within 15%) from those calculated before but the 'energy' was still a factor of 3.9 times larger than in the Lorentzian case. The inability for the Gaussian lineshape to fit our results adequately is attributed to the impossibility of this distribution describing the long tails which are part of our signal. As the minimization of the 'energy' Φ entails the search for the best global agreement between the envelope of the calculated intensity of the resonant lines and the experimental data, the procedure tends to choose those parameters that reproduce the tails of the curves whose weights are important in the evaluation of Φ. When using Gaussian lineshapes which go to zero too rapidly the automatic minimization of Φ does not lead to the best set of parameters.

A Monte Carlo procedure to find precisely the superhyperfine interaction constants in electron–nuclear spin coupled systems from the structure observed in EPR fine-structure lines has been proposed. The program sums up the contributions of all the forbidden and allowed transitions with intensities higher than a threshold value, for each combination of the parameters that it explores. Thus, no information on the quantum states that are involved in each transition is needed. Also, no previous

knowledge of the parameters is required in order to start with a good set of initial parameters, as the program usually starts with null initial values. The program, which runs on an IBM-AT personal computer with numerical co-processor, included many short cuts in order to reduce the computing time. The whole procedure took around eighty hours if we started from very high 'temperature' and with six fine-structure lines included. This procedure has been shown to work remarkably well in the case of the Gd^{3+} cubic site in CaF_2. We have found good agreement with the previous calculated values of the superhyperfine tensor parameters although the lineshapes we used were not Gaussian but Lorentzian. In our case the Gaussian lineshape was inadequate to properly fit the signals obtained for a cubic Gd^{3+} molar concentration of 3×10^{-7}. However, with the Lorentzian distribution there were some fine details in the tail of the signal that were not exactly reproduced even if there were some transitions occurring at these fields. This fact tells us that a better fit would still be obtained if the lineshape, instead of being purely Lorentzian, fell off a little faster in the wings.

Acknowledgments

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