

Spin Concentration in a Possible ESR Dosimeter: An Electron Spin Echo Study on X-Irradiated Ammonium Tartrate

Marina Brustolon,* Alfonso Zoleo,* and Anders Lund†

*Department of Physical Chemistry, Via Loredan 2, I-35131, Padova, Italy; and †Department of Physics and Measurement Techniques, Linköping University, S-58183 Linköping, Sweden

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Several single crystals and powder samples of ammonium tartrate, recently proposed as a possible ESR dosimeter, have been X-irradiated with different doses. The total radical concentration has been determined by quantitative cw ESR, by comparison with a standard. The samples have been studied by electron spin echo spectroscopy. The two-pulse echo decay has been obtained and simulated by a single exponential function for different values of the microwave power of the pulses and for different pulse lengths. The dependence of the phase memory time T_M on the microwave power has been exploited to get information on the contribution of the instantaneous diffusion to spin dephasing. At room temperature in the range of radical concentrations of 10^{18} – 10^{19} spins/cm³ the instantaneous diffusion is the dominant spin dephasing mechanism. The linear dependence of the instantaneous diffusion on the total concentration of the radicals is in agreement with the theory. From the latter result we conclude that the average radical-radical distance corresponds to a random distribution of the radicals in the matrix. A simple method of measuring the radical concentration by the ESE decays in powder samples of irradiated ammonium tartrate is described. © 1999 Academic Press

Key Words: electron spin resonance; electron spin echo; ESR dosimetry; ammonium tartrate; electron spin relaxation.

INTRODUCTION

ESR dosimetry is a well-established method of measuring doses of ionizing radiation. It consists of the measure of the ESR spectrum intensity of radicals formed by the radiation in a substance used as a dosimeter. The amino acid L-alanine is today the most popular dosimeter for high-dose radiation (1). The radical produced by the irradiation is mainly the radical $\text{CH}_3\text{-CH-COOH}$, but recently it has been shown that other radicals are formed (2).

L-alanine is only one of the possible dosimeters, and other substances could prove to be more convenient for the scope. Ammonium tartrate (AT) has been recently proposed as a possible dosimeter (3). One of the advantages of the latter substance with respect to L-alanine is its much narrower ESR spectrum when irradiated and the formation of a unique radical.

The radical formed in AT γ - or X-irradiated at room temperature is $\text{H}_4\text{NOOC-}\dot{\text{C}}\text{OH-CHOH-COONH}_4$. This stable radical shows an ESR spectrum with a width of ~ 10 G, which is therefore narrower than that of many other irradiated organic crystals. Its hyperfine coupling tensors have been determined by an ENDOR and ESEEM study (4). Because of the conformation of the radical in the crystal matrix, the hyperfine coupling tensors of the unpaired electron with the two OH protons and with the CH proton in β position are quite small in comparison with those of α and β protons of the large majority of radicals with a localized unpaired electron (as, for example, those formed in L-alanine).

ESR dosimetry is possible for radiation doses in a limited range, whose lower limit, determined by the radical formation efficiency, is given by the minimum spin concentration that allows a reliable quantitative ESR measurement, and whose higher limit, by the condition that the interactions between the radicals are low enough to give rise to a pure doublet ESR spectrum. The latter interactions, i.e., the exchange and electron-electron dipolar ones, should therefore be smaller than the hyperfine interactions (5). They depend on the average distance between the radicals and therefore on the total concentration and also on the radicals distribution in the matrix.

The microscopic average concentration of radicals in a solid sample has been obtained in a small number of cases by measuring the phase memory time T_M characterizing the two-pulse electron spin echo (ESE) decays (6, 7). In fact it has been shown that one of the processes affecting the rate of the echo decays is the perturbation created on the electron spin system by the microwave pulses themselves, the so-called instantaneous diffusion (8, 9). The latter perturbation depends on the average distance between the radicals and therefore on their average local concentration.

In many cases it is difficult to extract the instantaneous diffusion rate from the simple two-pulse echo decay, since other relaxation mechanisms dominate in causing the loss of phase memory time. In these cases the so-called 2 + 1 ESE experiment has been shown to be able to measure selectively the instantaneous diffusion (10). However, for the radicals in the matrix described in this paper the latter relaxation process

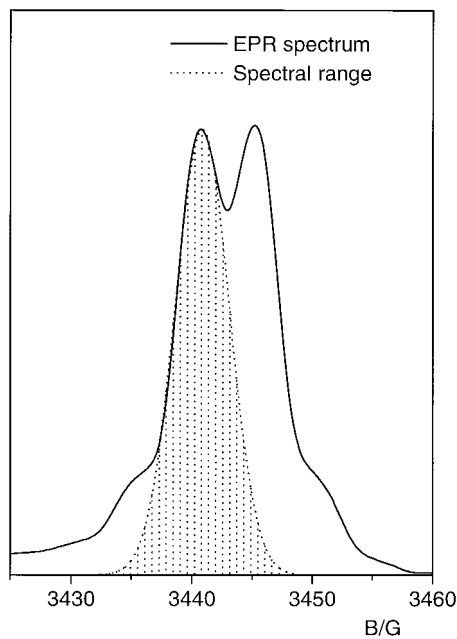


FIG. 1. The continuous line is the integrated cw ESR spectrum of a single crystal of ammonium tartrate X-irradiated for 10 min. The magnetic field is along the *c* crystallographic axis. The dotted signal corresponds to the spectral range affected by the 16–32 ns pulse sequence.

is the dominant one, and therefore we used the two-pulse echo decay to determine the instantaneous diffusion rate for a series of single crystals and crystalline powders of AT X-irradiated with different doses. The concentrations obtained by the pulsed ESR experiments have been compared with the concentrations obtained by quantitative cw ESR.

EXPERIMENTAL

Sample Preparation

Single crystals of AT were grown by slow evaporation at room temperature in an aqueous solution of the salt. AT crystallizes in the monoclinic space group $P2_1$ with $a = 7.083$, $b = 6.128$, $c = 8.808$ Å, $\beta = 92.42$, and $Z = 2$ (11).

Five single crystals of approximately the same dimensions ($4 \times 2 \times 2$ mm), and five samples of crystalline powder obtained from crushed single crystals, were irradiated with different doses at room temperature by X rays at 70 kV and 20 mA using a tube with a W anode. The dose rate emitted by the tube was measured with L-alanine dosimetry to be ca. 250 Gy/min.

The irradiation was done for 5, 10, 15, 20, and 25 min, respectively. The total dose is only approximately proportional to the time of irradiation since it depends on the position and on the type of container of the samples.

The irradiated single crystals were all oriented with the magnetic field along the *c* crystallographic axis. The ESR

spectra of an oriented single crystal and of an X-irradiated powder sample are reported, respectively, in Figs. 1 and 2.

Determination of the Total Concentration by cw ESR

For the spin concentration measurements, a standard was used, produced by including a known amount of Tempone (tetramethyl-4-piperidone-1-oxyl) in PMMA (poly(methyl methacrylate)), as follows: 10 mg of Tempone and ca. 0.5 g of PMMA were dissolved into 1 cm³ of toluene and 12 ml of CHCl₃, respectively. The solutions were mixed together under weak nitrogen flow into a crystallizing dish. A PMMA disk was formed after solvent evaporation and a narrow strip was cut out.

The spin concentration in the standard was determined by comparing the intensity of its doubly integrated ESR spectrum with those of a series of solutions of known concentrations of Tempone in toluene.

The comparison of the intensities of the doubly integrated ESR spectra of two different samples was done by recording the two spectra with the same setting of all the parameters of the ESR spectrometer. The *Q* value of the cavity was set at the same value by varying the iris coupling. The volumes of the samples were approximately the same, and the samples were set in the same position in the cavity. A relative error of about 20% can be estimated in the absolute ESR intensities.

The spin concentrations determined by the quantitative ESR measurements corresponding to the different irradiation times are reported in Table 1.

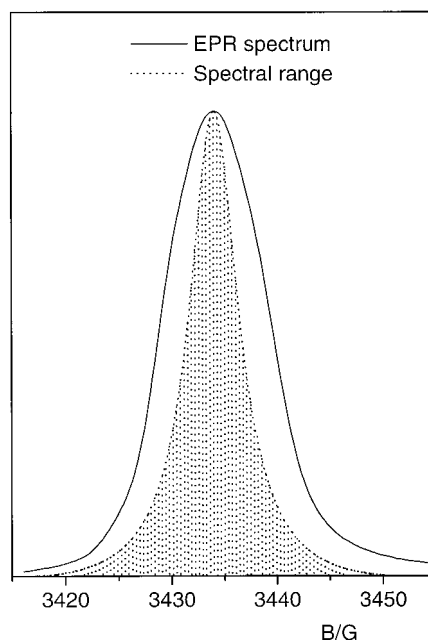


FIG. 2. The continuous line is the integrated cw ESR spectrum of a powdered sample of ammonium tartrate X-irradiated for 10 min. The dotted signal corresponds to the spectral range affected by the 16–32 ns pulse sequence.

TABLE 1
Total Concentrations of Radicals Determined by cw ESR
in Irradiated Samples of Ammonium Tartrate

Min of X-irradiation	Spins/cm ³ (single crystals)	Spins/cm ³ (powder samples)
5	$1.2 \cdot 10^{17}$	$2.0 \cdot 10^{18}$
10	$1.6 \cdot 10^{18}$	$2.6 \cdot 10^{18}$
15	$3.9 \cdot 10^{18}$	$3.9 \cdot 10^{18}$
20	$4.7 \cdot 10^{18}$	$5.5 \cdot 10^{18}$
25	$5.6 \cdot 10^{18}$	$7.2 \cdot 10^{18}$

Electron Spin Echo Experiments

The spectra were in part recorded by using a Bruker ESP 380 spectrometer (Padua) and a Bruker Elexsys E580 FT/CW X-band spectrometer (Linköping). The cavity was in both systems the Bruker ER 4118 dielectric resonator.

The experiments have been performed at room temperature, if not differently specified. Variable temperature experiments have been performed with the latter instrument equipped with a Bruker BVT 3000 digital temperature controller and an Oxford CF 935 cryostat.

Two-pulse echo decays were collected by using a pulse sequence $p_1\text{--}\tau\text{--}p_2$. Experiments with different pulse lengths p_1 and p_2 were performed, but in any case $p_2 = 2p_1$. Typical values of the pulses lengths were $p_1 = 16$ ns, $p_2 = 32$ ns.

The decays were collected by varying τ from an initial value of 200 ns up to 3300 ns. The echo was integrated by using a window of 160 ns.

Series of echo decays were obtained for any crystal and powder sample by varying the microwave power. Each decay was fitted with a monoexponential function,

$$I(\tau) = I_0 \exp(-2\tau/T_M), \quad [1]$$

with I_0 (initial echo amplitude) and T_M (phase memory time) as fitting parameters.

It should be noted that both in the powdered samples and in the single crystals at the chosen orientation in the magnetic field the ESEEM modulation depth was small enough to allow us to neglect it in the fitting procedure.

KINETICS OF THE DECAY OF THE ELECTRON SPIN ECHO SIGNAL

Theory

Two-pulse electron spin echo dephasing in solids is determined by contributions from different processes, as pointed out in a series of theoretical and experimental works (12–15). We can distinguish between the spin relaxation processes intrinsic to the sample and those due to the experiment itself, i.e., due to

the perturbing effect of the microwave pulses (instantaneous diffusion).

Among the intrinsic relaxation mechanisms we can envisage those due to the electron–electron interactions and those due to the nuclear–electron interactions. Both interactions can produce dephasing of the electron spin packets by a relaxation of the first kind (time fluctuation of the magnetic interaction parameter) or of the second kind (time fluctuation of the coupled spin) (12, 16, 17).

The relative importance of the different intrinsic relaxation mechanisms at a given temperature depends on the concentration of the radicals, on their residual mobility in the solid matrix, on the presence of intramolecular motions such as methyl group rotation, and on the nuclear spins present in the diamagnetic matrix.

Moreover, the spin packets not affected by the pulses (usually called spins B) contribute to the spin dephasing because of their fluctuations giving rise to a time-dependent dipolar interaction with the resonant spin packets (spins A) (18). Therefore the dephasing rate depends also upon the concentration of spins B.

On the other hand the instantaneous diffusion depends on the concentration of spins A and on the extent of the perturbation created by the pulses on them, i.e., on the turning angles θ_i where

$$\theta_i = \gamma B_1 p_i. \quad [2]$$

B_1 is the amplitude of the microwave field, and p_i is the length of the i th pulse.

As long as the random spin flips due to the intrinsic relaxation processes do not overcome the instantaneous diffusion effect, the intrinsic relaxation processes and instantaneous diffusion contribute to the rate of spin dephasing in an additive way (12). Since the effect of the pulses is independent of the temperature, the instantaneous diffusion is expected to be also independent of the temperature.

By assuming that all the spin packets giving rise to the ESR signal were turned to the same angles θ_1 and θ_2 by the two pulses generating the echo, the echo intensity would be given by the expression (14)

$$I(\tau) \propto \sin \theta_1 \sin^2(\theta_2/2) \exp(-2\tau/T_M). \quad [3]$$

By taking into account that in our case $\theta_2 = 2\theta_1$, Eq. [3] becomes

$$I(\tau) \propto \sin^3 \theta_1 \exp(-2\tau/T_M), \quad [3']$$

where, by assuming that the dephasing was due to the instantaneous diffusion and to other relaxation processes in an additive way,

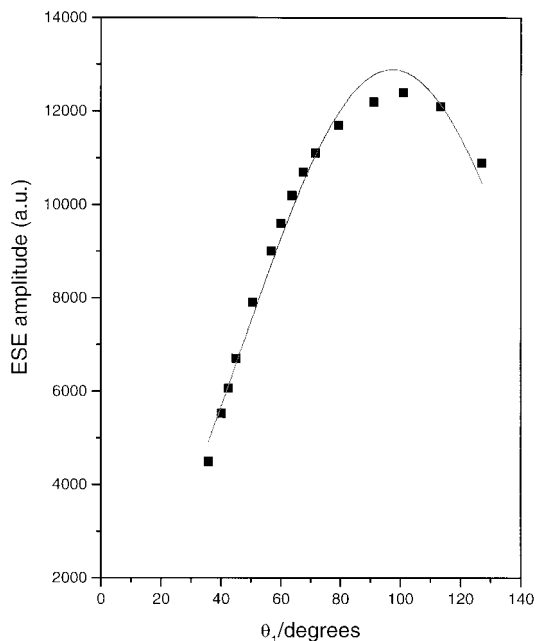


FIG. 3. Squares, initial intensity of the echo as obtained by the best fitting of the exponential echo decays for a single crystal irradiated 10 min and oriented as in Fig. 1. The θ_i values are obtained for the different microwave power settings as explained in the text; see Eq. [10]. Continuous line, $\sin^3\theta_i$; see Eq. [8].

$$1/T_M = A + B \cdot \sin^2(\theta_2/2) \quad [4]$$

and

$$B = (4\pi^2\gamma^2\hbar C/9\sqrt{3}) = b \cdot C, \quad [5]$$

where $b = 8.2 \cdot 10^{-13} \text{ cm}^3 \text{ s}^{-1}$, and C is the concentration of the spins affected by the pulses in spins/cm³ (14). If all the spin packets are turned by the pulses, C is the total spin concentration in the sample.

In general the spectral range affected by the pulses is smaller than the width of the ESR spectrum, and not all the spin packets will be turned in the same way by the pulses. Therefore the turning angle θ_i produced by the pulse p_i of frequency ω_0 on the spin packet resonating at the Larmor frequency ω will be given by the relation

$$\theta_i(\omega) = \gamma B_{\text{eff}} p_i, \quad [6]$$

where

$$\gamma B_{\text{eff}} = \sqrt{(\gamma B_1)^2 + (\omega - \omega_0)^2}. \quad [7]$$

Therefore, in Eqs. [3'] and [4] the trigonometric functions must be averaged over the frequency distribution of the spin

packets. From Eqs. [3], [4], and [5] we obtain the expression for the echo decay

$$I(\tau) \propto \langle \sin^3\theta_1 \rangle \cdot \exp(-2\tau \cdot (A + B\langle \sin^2\theta_1 \rangle)), \quad [8]$$

where the averages are made on the frequency distribution of the ESR spectrum.

Method

The echo decays are collected at different values of microwave power P by varying its attenuation.

The relationship between microwave power and microwave field amplitude is given by

$$B_1 = \text{const} \cdot \sqrt{P}. \quad [9]$$

In order to calculate the average quantities in Eq. [8] for any attenuator setting we need to obtain B_{eff} from Eq. [7] and, therefore, to know B_1 .

This is a simple problem when the microwave pulses turn all the spin packets the same angle. In fact in this case the microwave power P_{max} corresponding to the maximum of the initial value of the echo signal $I_{0\text{max}}$ would correspond to $\theta_1 = \pi/2$, and B_1 can then be obtained from Eq. [2].

It has been shown (14) that in absence of complete excitation the absolute value of B_1 cannot be obtained by the latter simple method, and the dependence of the shape of the echo signal on

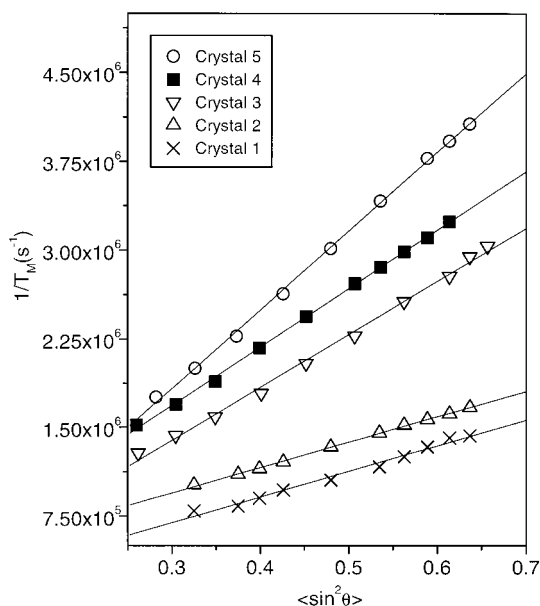


FIG. 4. Dependence of the phase memory loss rates on $\langle \sin^2\theta_i \rangle$ for five crystals of ammonium tartrate X-irradiated with different doses (respectively 5, 10, 15, 20, and 25 min of irradiation for crystals 1 to 5). θ_i is the turning angle of the first pulse. The intercepts and the slopes of the fitting lines correspond to the parameters A and B in Eq. [4].

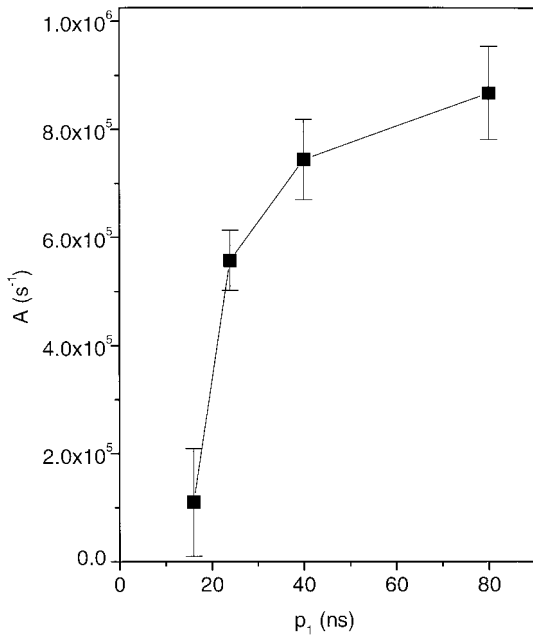


FIG. 5. A parameters (see Eq. [4]) obtained for the same crystal in the same orientation from the power dependence of $1/T_M$ on varying the pulse lengths p_1 (length of the first pulse) and $p_2 = 2p_1$. The line is only a guide for the eye.

the microwave power must be analyzed in order to obtain θ_i at the different power settings.

However in the present case the width of the microwave spectral range for $p_1 = 16$, $p_2 = 32$ ns (19), is such that a large part of the spin packets in the single crystal spectra are affected by the pulses, as can be observed in Fig. 1, and therefore we assume that the value of B_1 can be obtained from Eq. [2] for $\theta_i = \pi/2$, corresponding to P_{\max} .

The turning angles at different attenuations (dB) can then be obtained by using the relation

$$\theta_i = (\pi/2) \cdot 10^{(dB_{\max} - dB)/20}, \quad [10]$$

where dB_{\max} is the power attenuation corresponding to the maximum of the echo intensity, and the definition of decibels units of power level is used.

RESULTS AND DISCUSSION

Single Crystal Measurements

The cw ESR spectrum of the single crystal irradiated for 5 min, at the orientation used for the measurements, is reported in Fig. 1.

The echo decays have been obtained by setting the magnetic field on the top of the low field component. The dotted line is the shape of the hole burned by the pulses $p_1 = 16$ ns and $p_2 = 32$ ns corresponding to turning angles $\pi/2$ and π , assumed to be Gaussian (20).

We have analyzed the echo decays with a simple exponential. The fitting was always very good, and the parameters I_0 (dB) and $1/T_M$ (dB) were obtained for any microwave power.

In Fig. 3 we report the I_0 values for a single crystal vs the turning angle θ_1 obtained by Eq. [10] for any attenuation.

The averages of the trigonometric functions in Eq. [8] have been calculated on the ESR spectrum in Fig. 1, simulated as the sum of two Gaussian curves.

In Fig. 4 are shown the values of the dephasing rate $1/T_M$ of the two-pulse echo decay measured at room temperature vs $\langle \sin^2 \theta_1 \rangle$ for the five crystals oriented in the same way. The slopes and the intercepts of the fitting lines are, respectively, the parameters A and B in Eqs. [4] and [8]. The parameters A are small with respect to B and they vary in a way independent of the concentration of the radicals for the five crystals. A range of values $A = 0 \div 3 \cdot 10^5 \text{ s}^{-1}$ is obtained, to be compared with the B values, spanning the range $(2 \div 7) \cdot 10^6 \text{ s}^{-1}$.

The small values of the A parameters with respect to the B ones indicate that in these experiments the instantaneous diffusion is the main dephasing source. It should be noted that the amplitude of the intermolecular motions of the radical in the crystal is expected to be very small, since the radical is held tightly in the solid matrix by H bonds. Also the effect of intramolecular motions should be negligible, since no rotating groups are present in the radical itself and in the surrounding matrix. Therefore we expect a relatively slow intrinsic electron spin relaxation, depending mainly on the effect of the fluctu-

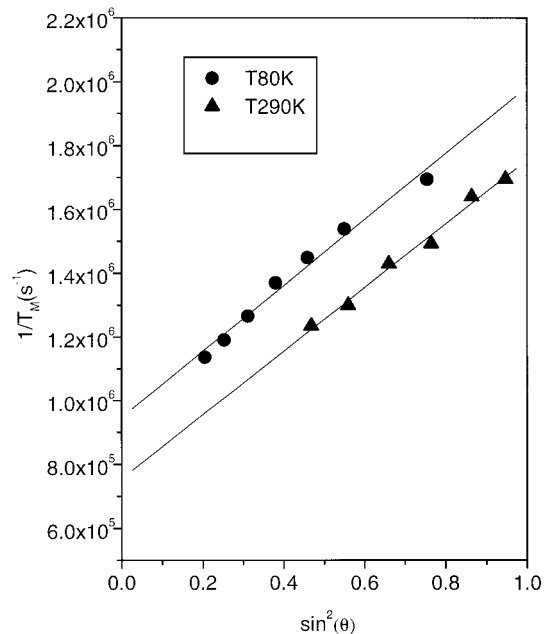


FIG. 6. Dependences of $1/T_M$ on $\sin^2 \theta_1$ for a crystal of ammonium tartrate at two different temperatures. The crystal was irradiated for 5 min, and the orientation was different with respect to the one in Fig. 1. The very similar slopes indicate that the parameter B is independent of the temperature.

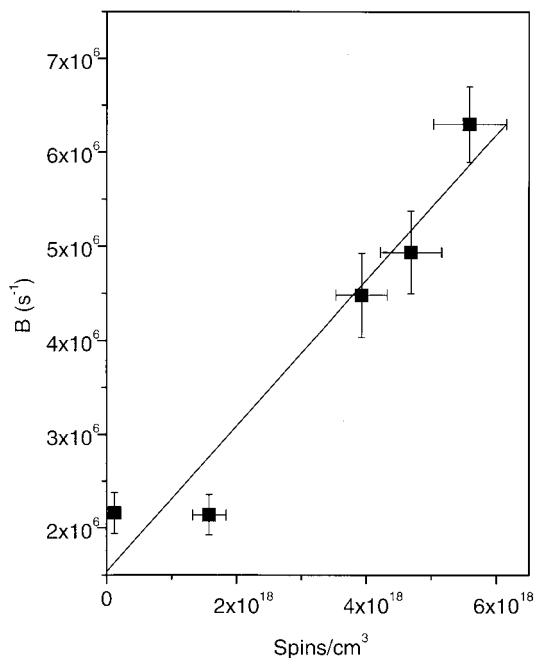


FIG. 7. B values obtained for the single crystals by the best fitting lines in Fig. 4 vs the spin concentrations C in spins/cm³ obtained by quantitative cw ESR measurements. Within experimental error the slope of the fitting line b is as expected by the theory; see Eq. [5].

ating magnetic field due to the presence of the dipolar interactions with nonresonant electron spins.

To check the dependence of the intrinsic electron spin relaxation on the concentration of nonresonant spins we can measure the spin echo decay by varying the latter concentration. This can be done by using different pulse lengths, therefore varying the ratio between the spectral ranges respectively affected and not affected by the pulses (13). We have performed a series of experiments on the same crystal by measuring $1/T_M$ for pulses p_1 and p_2 of different lengths (respectively 16–32, 24–48, 40–80, and 80–160 ns) at different power settings. For each type of pulse a diagram of the same type as in Fig. 4 has been obtained. The A parameters obtained by the linear best fits are reported in Fig. 5. It can be noted that the A values are very small for the shortest pulses and increase on increasing the pulse length, therefore increasing the concentration of the electron spins not affected by the pulses.

It is worth noting that the possibility of obtaining reliable information on the instantaneous diffusion rate in irradiated AT, at least in the radical concentration range used in the present work, is due to the slow intrinsic electron spin relaxation of the radicals in this system, also at room temperature. For other irradiated crystals this is not the case, as, for example, for irradiated L-alanine, which has a faster intrinsic electron spin dephasing ($1/T_M \approx 10^7 \text{ s}^{-1}$ at room temperature), due to the methyl group rotation (21).

We have measured the power dependence of $1/T_M$ for an irradiated AT crystal at two different temperatures, 290 and 80

K. The results are collected in Fig. 6. It can be noted that the intercepts of the two fitting lines (A parameters) depend on the temperature, whereas the two slopes (B parameters) are nearly the same, as expected since the instantaneous diffusion rate depends only on the spin dynamics produced by the pulses.

In Fig. 7 we report the B values obtained by the best fitting lines in Fig. 4 vs the spin concentrations C in spins/cm³; see Table 1.

The linear best fit gives a line with a slope: $b = (8 \pm 1) \cdot 10^{-13} \text{ cm}^3 \text{ s}^{-1}$, in agreement with Eq. [5]. Therefore we conclude that in AT crystals, in the range of spins concentrations obtained in the present work, the microscopic concentration of the radicals produced by X-irradiation is equal to the macroscopic one, i.e., the radicals are formed at random in the crystals.

Powder Samples Measurements

It could be of some interest to set up a standard procedure in order to routinely measure the microscopic average radical concentration in a dosimeter by pulsed ESR experiments.

For this scope it would be highly preferable to use powder samples, to avoid the orientation of the crystal in the magnetic field, and to directly correlate the phase memory time with the microwave power (avoiding the procedure of getting the effective microwave field at the different microwave frequencies). We have checked this possibility by measuring the echo decay parameters of five AT powder samples X-irradiated with different doses.

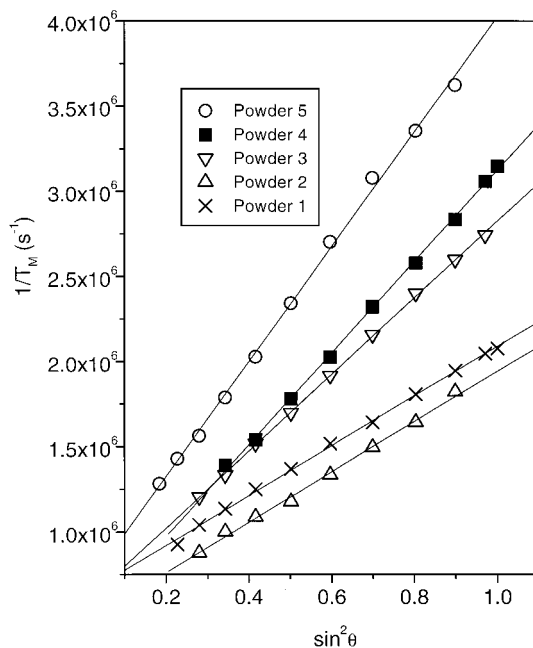


FIG. 8. Linear fits of the $1/T_M$ values vs $\sin^2\theta$, for five powdered samples of ammonium tartrate irradiated with different doses (respectively 5, 10, 15, 20, and 25 min of irradiation for samples 1 to 5).

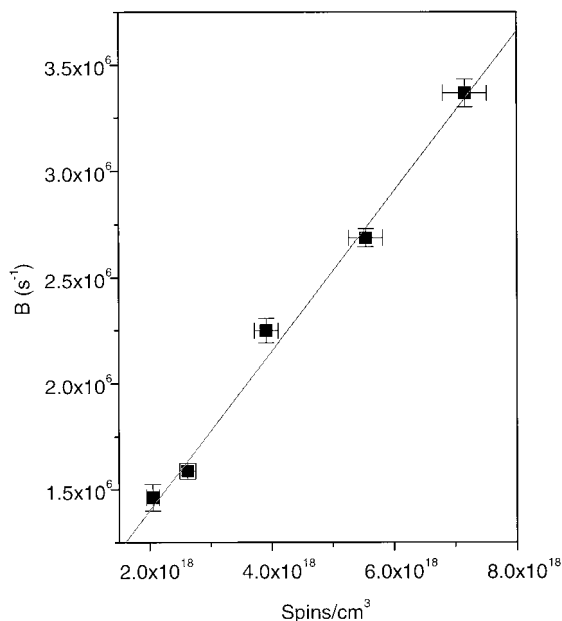


FIG. 9. B values obtained from the slopes of the best fitting lines in Fig. 8 vs the spin concentrations C in spins/cm³ obtained by quantitative cw ESR measurements.

Figure 2 shows the cw ESR spectrum of an AT powder sample irradiated for 5 min. Superimposed to the ESR spectrum is the Gaussian shape of the hole burned by the pulses with p_1 and p_2 equal to 16–32 ns.

The magnetic field has been set on the center of the spectrum, and the echo decays have been collected for different microwave powers and fitted with a simple exponential, as in the single crystal experiments. The initial echo intensity I_0 at the different power attenuations has been used to obtain the turning angles θ_1 ; see Eq. [10]. In Fig. 8 we report the linear fits of the $1/T_M$ values vs $\sin^2\theta_1$ for the five samples.

In Fig. 9 the slopes (B parameters) of the fitting lines are shown vs the spin concentrations C in spins/cm³, determined as explained for the single crystal measurements.

The slope of the fitting line is $b = 3.8 \pm 0.1 \cdot 10^{-13} \text{ cm}^3 \text{ s}^{-1}$. As expected this value is smaller than the b value obtained for the single crystals when we used the correct procedure of calculating $\langle \sin^2\theta_1 \rangle$ for any power setting, and therefore, obtained a b value very similar to the one derived from the theory; see Eq. [5]. In fact, the powder ESR spectrum is appreciably wider than the spectral range explored by the 16–32 ns pulses (see Fig. 2), and therefore the concentration of the spins affected by the pulses is smaller than the total concentration C . However, as one can see the B values are linearly dependent on the total concentration, and therefore they can be used to obtain the spin concentration in irradiated AT by fitting them on the straight line in Fig. 9.

Further work would be necessary to establish the bounds of the range of radical concentrations in this system, allowing one

to measure reliably the instantaneous diffusion contribution to the phase memory loss, and therefore allowing a reliable use of the method described.

CONCLUSIONS

The radicals produced by X-ray irradiation in crystals of ammonium tartrate are formed at random in the crystal, since the average distances between radicals obtained from the spin relaxation properties are found to correspond to those expected on the basis of the total spin concentration.

The electron spin echo dephasing of the radicals in the concentration range $2\text{--}8 \cdot 10^{18}$ spins/cm³ is mainly due to instantaneous diffusion, if pulses of lengths of 16–32 ns are used in the pulse sequence generating the echo. The intrinsic relaxation processes contributing to spin dephasing at room temperature are mainly due to the time fluctuations of the non-resonant electron spins.

The dependence of the dephasing rate on the microwave power can be exploited to obtain information on the total concentration of the spins. The method can be used both for single crystals and for powdered samples.

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REFERENCES

1. F. Kunz, B. Chabanais, D. Karamanoukian, J. P. Delpuch, and E. Marchioni, *J. Chim. Phys. Phys. Chim. Biol.* **95**(4), 796 (1998); E. S. Bergstrand, E. D. Hole, and E. Sagstuen, *Appl. Radiat. Isot.* **49**(7), 845 (1998).
2. E. Sagstuen, E. O. Hole, S. R. Haugedal, and W. H. Nelson, *J. Phys. Chem.* **101**(50), 9763 (1997).
3. S. K. Olsson, S. Bagherian, E. Lund, and A. Lund, *Appl. Radiat. Isot.* in press, (1999).
4. M. Brustolon, A. L. Maniero, S. Jovine, and U. Segre, *Res. Chem. Intermed.* **22**(4), 359 (1996).
5. N. M. Atherton, "Principles of Electron Spin Resonance," Ellis Horwood, London (1993).
6. I. M. Brown, *J. Chem. Phys.* **58**, 4242 (1973).
7. S. S. Eaton and G. R. Eaton, *J. Magn. Reson. A* **102**, 354 (1993).
8. J. R. Klauder and P. W. Anderson, *Phys. Rev.* **125**(3), 912 (1962).
9. R. Boscaino and F. M. Gelardi, *Phys. Rev. B* **46**, 14550 (1992).
10. V. V. Kurshev, A. M. Raitsimring, and T. Ichikawa, *J. Phys. Chem.* **95**, 3564 (1991).

11. V. S. Yadava and V. M. Padmanabhan, *Acta Cryst. B* **29**, 493 (1973).
12. K. M. Salikhov and Yu. D. Tsvetkov, Electron spin-echo studies of spin-spin interactions in solids, in "Time Domain Electron Spin Resonance" (L. Kevan and R. N. Schwartz, Eds.), pp. 231-277, Wiley-Interscience, New York (1979).
13. I. M. Brown, Electron spin-echo studies of relaxation processes in molecular solids, in "Time Domain Electron Spin Resonance" (L. Kevan and R. N. Schwartz, Eds.), pp. 226-229, Wiley-Interscience, New York (1979).
14. A. M. Raitsimiring, K. M. Salikhov, B. A. Umanskii, and Yu. D. Tsvetkov, *Sov. Phys. Solid State* **16**(3), 492 (1974).
15. D. C. Doetschmen and G. D. Thomas, *Chem. Phys. Lett.* **232**(3), 242 (1995).
16. A. Abragam, "Principles of Nuclear Magnetism," pp. 308-309, Clarendon Press, Oxford (1961).
17. Yu. D. Tsetkov and S. A. Dzuba, *Appl. Magn. Reson.* **1**, 179 (1990).
18. B. Herzog and E. L. Hahn, *Phys. Rev.* **103**(1), 148 (1956).
19. M. K. Bowman, in "Modern Pulsed and Continuous Wave Electron Spin Resonance," (L. Kevan and M. K. Bowman, Eds.), pp. 28-29, Wiley, New York (1990).
20. M. Romanelli and L. Kevan, *Concepts Magn. Reson.* **9**, 403 (1997).
21. M. Brustolon and U. Segre, *Appl. Magn. Reson.* **7**, 405 (1994).