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Influence of paramagnetic impurities on molecular self-diffusion as seen by nuclear spin-lattice relaxation and dynamic polarization*

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Measurements, near the melting point, of nuclear spin-lattice relaxation and dynamic polarization in plastic cyclohexane doped with a nitroxide free radical show deviations from the expected spin-diffusion theory. These deviations are explained by the quenching of the molecular self-diffusion around the radical and interpreted semiquantitatively in terms of a two zone model. It is shown that the quenching extends up to more than four intermolecular distances and the spin-diffusion coefficient in this region is shown to be around $0.3 \times 10^{-12} \text{ cm}^2 \text{ sec}^{-1}$. It seems that similar measurements would be of interest in any crystal which exhibits NMR motional narrowing due to fast molecular self-diffusion.

I. INTRODUCTION

Self-diffusion in the rotationally disordered crystal-line phase of some molecular crystals (usually called plastic crystals) is a well-known phenomenon and has been extensively studied by various techniques, for a large number of substances.¹⁻⁷ High resolution NMR^{1,2} and spin-lattice relaxation in the rotating frame³ allow measurements of activation energies and jump frequencies of the diffusion process. Recent improvements in the spin-echo method allows a direct measurement of the self-diffusion coefficients.⁵ Comparison of the results obtained by these various NMR methods are in general consistent with a simple diffusion process where the molecules jump to a neighboring site, at the jump frequency. On the other hand, plastic flow (creep)⁶ and radioactive tracers⁷ are alternative ways to determine activation energies and self-diffusion coefficients. However, these values are often in great disagreement with those obtained by a NMR technique. For example, the diffusion coefficient found by spin-echo for cyclohexane in its plastic phase,⁵ near the melting point is more than two orders of magnitude smaller than the extrapolated value deduced from radioactive tracers data.⁷ Similar disagreement holds for the activation energies, those measured by NMR being in general smaller. These discrepancies may be related to the presence, near the melting point, of liquidlike zones, whose presence has already been noticed in pivalic acid,¹ cyclohexane,^{5,8} and is probably due to the presence of impurities or temperature inhomogeneities. Following Tanner⁵ this may explain that the radioactive tracer method gives a much higher value for the diffusion coefficient, since the long experimental diffusion time permits complete exchange and averaging of values between the two phases. Thus, the presence of impurities may modify the diffusion process in the crystal lattice.

A study of this effect has already been done in camphene doped by tricyclene.⁶ Up to relatively high concentration of impurities (15%), it was found that the NMR linewidth variation with temperature was independent of the concentration, whereas creep measurements indicate a slight increase of the activation energy, at small concentrations (1.8%) followed by a drop at high concentration (15%). It is thus of interest to study the molecular diffusion near an impurity, but, at sufficiently low concentration to avoid any type of interaction between the impurities. This can be achieved using a paramagnetic impurity and studying spin-lattice relaxation and dynamic polarization because these phenomena are very sensitive to all kinds of motions existing near the paramagnetic center. In this paper, we present such a study in cyclohexane near the melting point, doped by a nitroxide free radical. The main conclusion is that the molecular self-diffusion is considerably reduced around the impurity. In Sec. II, we recall the main results of previous work with this sample and justify a two zone model used here to interpret our experimental data. In Sec. III, calculations on this model are worked out. The experimental results are presented in Sec. IV and analyzed in terms of the model parameters. A value for the diffusion coefficient near the impurity is then deduced, as well as the radius of influence of the impurity in the lattice.

II. PLASTIC CYCLOHEXANE DOPED WITH A NITROXIDE FREE RADICAL. QUALITATIVE ASPECTS

Previous work⁸ on proton spin-lattice relaxation and dynamic polarization on cyclohexane in its plastic phase, doped in small concentration with a nitroxide free radical (Tanol and Tanane) showed that near the melting point the radical was concentrated in two

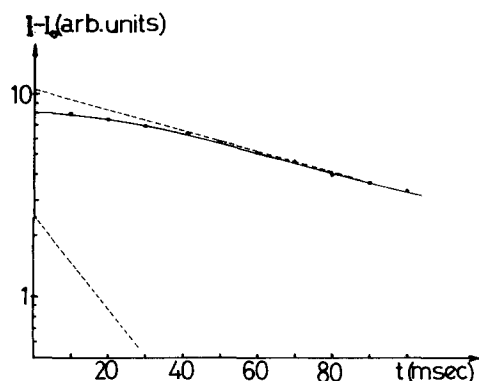


FIG. 1. Behavior of the return to thermal equilibrium of the maximum point of the NMR derivative signal. The microwave pumping power is cut at $t=0$. The points are experimental, the curve represents the best fit of these points with a theoretical expression like Eq. (8) of the text. The dashed straight lines are the decomposition of this curve into two exponential curves from which τ_1 and τ_2 are deduced. Magnetic field $H_0=3300$ G. Temperature -10°C . Concentration $10^{-2}M$ ($6.7 \times 10^{18} \text{ cm}^{-3}$).

different phases, a liquidlike phase (called α) on which negative Overhauser effect occurs and which appears as a "spike" on the NMR line, and the "true" plastic phase (called β) where a molecule of radical substitutes a cyclohexane molecule in the crystal lattice, on which a typical "solid effect" occurs during dynamic polarization. More recently, this sample was used as a test of the spin-diffusion theory⁹ and it was shown that the experimental data were consistent with a rapid diffusion regime, between -10 and -60°C , at intermediate radical concentration ($\approx 10^{-3}M$). However, between -10°C and the melting point $+5.6^\circ\text{C}$, deviations from the expected laws appeared at extreme values of the concentration. Increasing the concentration up to $10^{-2}M$, the observed return of the bulk magnetization to thermal equilibrium was no more exponential, as shown on Fig. 1. Conversely, a decrease of the concentration down to a few $10^{-5}M$ showed that the extrapolated maximum enhancement of the NMR signal during dynamic polarization was smaller than the expected theoretical one (≈ 660), as shown on Fig. 2. These two deviations can be explained both qualitatively and semiquantitatively if one assumes that the molecular self-diffusion is much smaller around the radical than in the bulk. In some way, the molecule of impurity quenches the molecular self-diffusion around it. The qualitative explanation is rather simple if one considers the variation of the NMR linewidth of¹⁰ cyclohexane between -87 and $+5.6^\circ\text{C}$. At -87°C , the molecular reorientation is already sufficiently rapid so that the intramolecular dipolar interaction is completely averaged out to zero and the measured residual linewidth (≈ 3.5 G) can be roughly explained assuming that all the nuclear spins of the molecules are concentrated at the center of mass, located at the lattice

points. Upon increasing the temperature a further reduction of the linewidth appears which can be explained by assuming that at such temperatures, the molecular self-diffusion is sufficiently fast to produce an extra motional narrowing. At -10°C , the linewidth is only 0.1 G, thus, at least 35 times smaller than at -87°C . If we suppose that around the radical, the self-diffusion, but not the rotation of the cyclohexane molecules is quenched, the high temperature NMR signal of the whole sample may be divided into two components: (i) one component due to the quenched molecules which contribute with a line whose width is greater or equal to 3.5 G and whose amplitude is relatively small (in the wideline technique the amplitude is inversely proportional to the square of the linewidth), and (ii) another component due to the cyclohexane molecules away from the impurities which contributes with a much narrower line because the self-diffusion exists as in the pure sample. Consequently its amplitude is much greater because of its relatively small linewidth. It is thus not surprising that this effect is not seen on the NMR spectrum and, indeed, we observed no changes in the NMR signal versus temperature up to concentrations of $10^{-2}M$. This is to be compared to the similar result of Ref. 6.

Let us analyze now the way in which spin-lattice relaxation measurements are made in our experiment.⁹

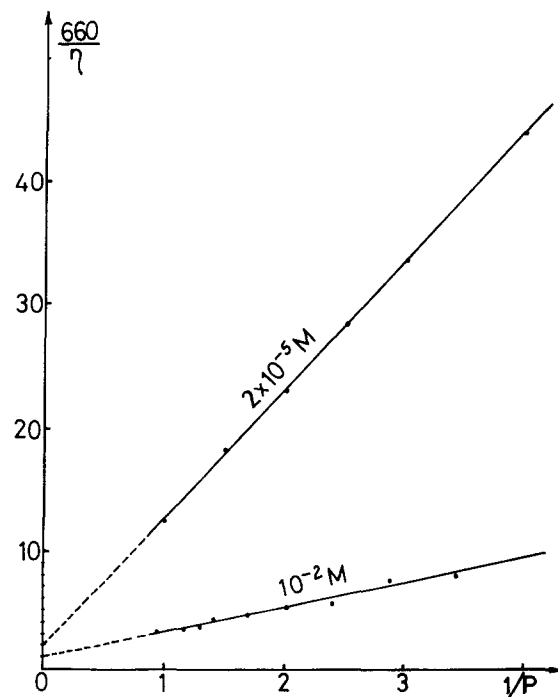


FIG. 2. Behavior of $660/\eta$ vs $1/P$. The amplitude used here is the height peak to peak of the observed derivative NMR curve. The horizontal scale is in arbitrary units, the vertical scale must be multiplied by 10 for the concentration $2 \times 10^{-5}M$. Magnetic field: 3300 G for $2 \times 10^{-5}M$ and 12 500 G for $10^{-2}M$. Temperature -10°C . Details on the apparatus used at 12 500 G is given in Ref. 8.

The NMR signal was detected with a wideline technique. The nuclear frequency was fixed at a maximum of the derivative curve during dynamic polarization and we observed the variation with time of this maximum when the microwave pumping field was removed. As stated above, only the molecules away from the radical correspond to this maximum, which occurs at 0.05 G from the center of the line (-10°C) whereas the quenched molecules signal maximum is shifted to 1.75 G or more. The nuclear spins of the diffusing molecules, being away from the radical, begin to relax with a long relaxation time, as if there were no paramagnetic impurities in the sample, until the magnetization diffuses from the quenched region to the diffusive one. When the corresponding nuclear spins "feel" the influence of the paramagnetic impurity, they relax more rapidly. This explains qualitatively the shape of Fig. 1. The time needed for the magnetization to cross the quenched region is roughly given by the time at which the relaxation becomes purely exponential. Clearly, this effect should be important only if the number of "quenched" molecules is sufficiently high and the motion of diffusive molecules sufficiently rapid so that the two NMR components are well separated. In our case, it is well seen experimentally at concentrations higher than $10^{-3}M$ and temperatures higher than -20°C .

Why the maximum theoretical enhancement is no more obtained at very low concentration is less easy to see, but one can roughly say that the number of pumping centers no more compensates the leakage due to the mechanisms of nuclear spin-lattice relaxation other than those due to the paramagnetic impurity.

III. TWO ZONE MODEL THEORY

The theory of spin-lattice relaxation and dynamic polarization in solids, via paramagnetic impurities in low concentration is extensively covered in the literature.¹¹⁻¹⁴ If the concentration n_e is sufficiently small so that the magnetic interaction between two paramagnetic impurities is negligible compared with their interaction with the lattice, the whole sample may be considered as the juxtaposition of a great number of almost independent spheres, centered on the paramagnetic spin and whose radius R is given by

$$(4/3)\pi n_e R^3 = 1. \quad (1)$$

The evolution of the magnetization of one of these spheres is representative of that of the whole sample and is described by the spin-diffusion theory.¹⁴ A test on this theory with the sample used here, but at lower temperatures, has been the aim of the work described in Ref. 9. The data were consistent with a rapid diffusion regime and the critical radius δ was found to be ≈ 1.7 Å. Clearly, it was implicitly assumed that the NMR signal was proportional to the magnetization of the nuclear

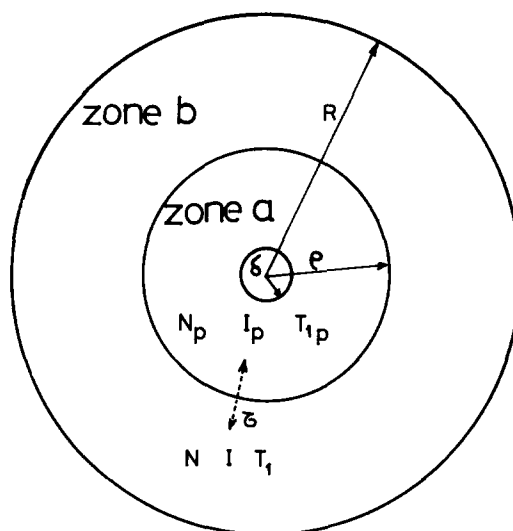


FIG. 3. Scheme of the two zone model.

spins contained between the spheres of radius δ and R . As explained above, if we consider now that only the nuclear spins away from the paramagnetic center are seen in the experiment, we may introduce a new radius ρ defined as follows: The nuclear spins between δ and ρ (called zone a) are not "seen" because the self-diffusion of the corresponding molecules is quenched, and the nuclear spins between ρ and R (called zone b), corresponding to diffusing molecules, are seen (Fig. 3). The spins in the two zones are coupled through spin-diffusion (which can be either the spin-diffusion or the molecular diffusion). The equations we propose to describe the evolution of the magnetizations of these two zones are similar to those proposed earlier by Torrey *et al.*^{15,16} in the study of dynamic polarization in liquids in contact with solid surfaces containing paramagnetic species.¹⁷ A similar model was proposed to explain spin-lattice relaxation measurements of liquids adsorbed at the surface of solids.¹⁸ They are the following:

$$dI/dt = -(I - I_0)/T_1 + (N_p/N)[(I_p - I)/\tau], \quad (2)$$

$$dI_p/dt = -(I_p - I_0)/T_{1p} + (I - I_p)/\tau + \bar{W}_{\pm}(S \pm I_p), \quad (3)$$

$$dS/dt = -(S - S_0)/T_{1e} + \bar{W}_{\pm}(S \pm I_p). \quad (4)$$

I_p , N_p , T_{1p} and I , N , T_1 are the nuclear magnetization per unit volume, the number of cyclohexane molecules and the proton spin-lattice relaxation times of zones a and b , respectively. S is the electronic magnetization per radical molecule and T_{1e} the electronic spin-lattice relaxation time. The index 0 indicates the value of the corresponding quantities at thermal equilibrium. The quantity τ is a time which characterizes the rate of exchange of magnetization between zones a and b . It

represents roughly the time needed for the magnetization to cross the region a . Finally, \bar{W}_{\pm} is the average probability per unit time of induced "forbidden" transitions in zone a , during dynamic polarization by "solid effect." The signs $+$ and $-$ indicate that the microwave pumping field is $\omega_e \pm \omega_n$, ω_e , and ω_n being the electronic and nuclear Zeeman frequencies. Equations (2), (3), and (4) can be resolved and details are given in the Appendix. The most important results for our purpose are the following:

(i) In the stationary state we have $dI/dt = dI_p/dt = dS/dt = 0$. If $T_{1e} \ll \tau$, T_{1p} , T_1 , $1/\bar{W}_{\pm}$, so that we always have $S(t) \simeq S_0$, the nuclear enhancement factor η of zone b , defined by

$$\eta = (I - I_0)/I_0 \quad (5)$$

satisfies the relation

$$\frac{660}{\eta} = \left(1 + \frac{N}{N_p} \frac{\tau}{T_1}\right) + \left\{T_{1p}^{-1} \left[\left(1 + \frac{N}{N_p} \frac{\tau}{T_1}\right) + \frac{N}{N_p} (T_1^{-1})\right] + \bar{W}_{\pm}^{-1}\right\} \quad (6)$$

the factor 660 represents the ratio S_0/I_0 for electrons and protons.

As \bar{W}_{\pm} is proportional to the microwave pumping power P , the quantity $660/\eta$ vs $1/P$ must be a straight line cutting the ordinate axis at the point U given by

$$U = 1 + (N/N_p)(\tau/T_1). \quad (7)$$

(ii) When $I(t=0)$ and $I_p(t=0)$ are different from I_0 , and $\bar{W}_{\pm} = 0$ (the pumping field is removed at $t=0$), the solution for I is given by

$$I(t) - I_0 = B[-r_2/r_1 \exp(-r_1 t) + \exp(-r_2 t)] \quad (8)$$

with

$$r_1 + r_2 = T_1^{-1} + T_{1p}^{-1} + (1 + N_p/N)(\tau^{-1}) \quad (9)$$

$$r_1 r_2 = (T_{1p}^{-1} + \tau^{-1})(T_1^{-1}) + (N_p/N)(T_{1p}^{-1})(\tau^{-1}). \quad (10)$$

The constant B is a function of the initial values for the magnetization of the two zones. The evolution of $I(t) - I_0$ is thus represented by the difference of two decreasing exponential functions. In the limiting case where the quenched zone a is very small, these equations lead to the standard laws for the relaxation of the bulk magnetization of a solid doped with a paramagnetic impurity (Appendix). In particular, the relaxation is purely exponential and the maximum enhancement factor is the theoretical one (S_0/I_0).

IV. EXPERIMENTAL RESULTS AND DISCUSSION

The apparatus and experimental procedure are already described in Ref. 9. For the discussion we suppose that the theoretical background of the spin diffu-

sion theory is known^{9,14} and we shall use the same symbols as in Ref. 9.

Although the phenomenon studied here can be seen at temperatures between -20°C and the melting point, for convenient radical concentration, we chose to test the model at a fixed temperature in order to make sure that the state of molecular motion (and thus the NMR linewidth) is always the same in the two zones. The interesting parameter to vary is the radical concentration. In fact, the quenching of the molecular diffusion around the radical molecule is clearly a local property due to the very presence of the impurity. Thus, at a given temperature, the quenched zone a has a fixed volume, i.e., ρ is a constant. Consequently, N_p and τ are concentration, independent the only varying parameter being N_p/N through the relation

$$N_p/(N + N_p) \propto n_e. \quad (11)$$

The chosen temperature was -10°C . Figure 1 represents the behavior of the return to thermal equilibrium of the maximum derivative point of the NMR signal, for a radical concentration of $10^{-2}M$ ($n_e \approx 6.7 \times 10^{18} \text{ cm}^{-3}$). The experimental points were fitted by least squares to the expression (8). The values obtained for the parameters are $r_1 \approx 50.1 \pm 16 \text{ sec}^{-1}$ and $r_2 = 11.6 \pm 1 \text{ sec}^{-1}$. Equations (9) and (10) allow the determination of the two unknown parameters N_p/N and τ . T_1 is clearly the spin-relaxation time of pure cyclohexane and we found⁹ $T_1 \approx 4 \text{ sec}$ at -10°C . T_{1p} is the value of the spin-relaxation time of zone a if there were no zone b . As zone a relaxes partially through the paramagnetic center with a rapid diffusion regime we have^{9,11}

$$T_{1p}^{-1} = T_1^{-1} + 4.2n_e' C \delta^{-3}, \quad (12)$$

where n_e' is greater than n_e because the radical is dissolved in a type zones, only. Clearly we have

$$n_e' = n_e(N_p + N)/N_p, \quad (13)$$

hence

$$T_{1p}^{-1} = T_1^{-1} + T_s^{-1}(1 + N/N_p), \quad (14)$$

where $T_s^{-1} = 4.2n_e C \delta^{-3}$. In Ref. 9, it was verified experimentally that, at -60°C , T_s^{-1} was proportional to n_e up to $2 \times 10^{-3}M$. At -10°C , it is reasonable to think that the same law is valid, at least up to $10^{-2}M$. With $T_s^{-1} \approx 1.7 \text{ sec}^{-1}$ at -10°C for $10^{-3}M$, relation (14) can be written, for $10^{-2}M$ as

$$T_{1p}^{-1} = 0.25 + 17(1 + N/N_p). \quad (15)$$

Inserting (15) in (9) and (10), N/N_p and τ can be deduced. Taking for r_1 and r_2 the central value, we get $N/N_p = 0.63$ and $\tau = 75 \text{ msec}$. Due to the imprecision on r_1 and r_2 , N/N_p and τ are accurate only to a factor 1.5 to 2.

We show now that these results are consistent with the dynamic polarization data. The extrapolated value

of $660/\eta$ at infinite power is given by U . From relation (7) and (11), and using the above numerical results, we get $U = 1.012, 1.30, 29$, for concentrations of $10^{-2}, 10^{-3}, 2 \times 10^{-5} M$, respectively. These values are in rather good agreement with the experimental data which shows that for the first two concentrations, the corresponding experimental curves cut the ordinate axis practically at the point of ordinate 1, whereas for the last one the extrapolated value falls at around 20.

Figure 2 shows $660/\eta$ vs $1/P$ for 10^{-2} and $2 \times 10^{-5} M$. For the corresponding curve at $10^{-3} M$, see Fig. 4 of Ref. 9. As it can be seen, at very small concentrations, the accuracy of such measurements is worse than with higher concentrations due to the limited quantity of available microwave power.

We now discuss the values found for τ and N/N_p . The meaning of τ is roughly the time needed for the magnetization to cross zone a or in other words, the time needed for zone b to "feel" the influence of the paramagnetic center. Experimentally it should be the time needed for the relaxation of zone b to be almost purely exponential. It is seen in Fig. 1 that the value found theoretically is in very good agreement with this statement. The quantity N/N_p fixes the relative volume of zones a and b . With a concentration of $10^{-2} M$ ($n_e = 6.7 \times 10^{18} \text{ cm}^{-3}$), relation (1) gives $R \approx 32.5 \text{ \AA}$. As $(\rho/R)^3 = N_p/(N+N_p)$ we get $\rho \approx 28 \text{ \AA}$. It is seen that the dimension of the zone a is relatively big and extends over more than four intermolecular distances ($\approx 6.3 \text{ \AA}$) around the radical. From the values of ρ and τ , a value for the spin-diffusion coefficient D can be estimated from the relation $D \approx \rho^2/4\tau$. We get $D \approx 0.3 \times 10^{-12} \text{ cm}^2 \text{ sec}^{-1}$. This value for D supports strongly the hypothesis of the quenching of the molecular diffusion in zone a , because it is much smaller than the value of the molecular self-diffusion coefficient in pure cyclohexane at this temperature.^{5,7} Such a value for D is of a good order of magnitude for spin-diffusion in solids and no translational diffusion mechanism is needed to explain its magnitude. Roughly speaking it seems that, just below the melting point, kinds of clusters are formed around the molecules of radical, which are represented by the a -like zones. These "clusters" are dispersed in the plastic phase of cyclohexane, represented by the b -like zones. They are much heavier than the cyclohexane molecules and do not diffuse. This explains fairly well the observed phenomena, in particular, why, for dynamic polarization, this sample behaves as a "good" solid as soon as the melting point is crossed.

The last point to be discussed is the model itself. Its main virtue is that it allows qualitative and semi-quantitative agreement with the experimental observations. In reality, of course, the situation is not so simple and instead of two well distinct zones, it would be more realistic to consider a multizone model to allow a smooth variation for the translational diffusion co-

efficient from the radical to the limits of its sphere of influence. Under these conditions, a NMR signal would contain a great number of components rather than only two distinct components. However due to the way in which our experiments are done, even in this case, we must observe a nonexponential decay of the longitudinal magnetization because the most quenched molecules are necessarily those which are nearest to impurity. This is why the model describes quite well qualitatively the basic phenomenon, but one should not attach too much importance to the deduced numerical values, in particular to the dimension of zone a . We end this discussion with the following remark: The fact that an impurity quenches the molecular self-diffusion seems *a priori* contradictory with what is usually accepted for plastic cyclohexane, i.e., that the presence of impurities mobilizes the cyclohexane molecules in the crystal lattice as is suggested by the presence of a sharp line (spike) on the NMR spectrum of impure samples. In fact, these mobilized molecules can well be attributed to the phase α which was described in Ref. 8. However, this phase has no influence on our relaxation measurements because we enhanced only the component of the NMR line on which the solid effect appears, the microwave frequency having a wrong value to produce an Overhauser effect on the liquidlike zones. In other words, we did the experiments at a pumping frequency corresponding to point B of Figs. 3 and 4 of Ref. 8. In a sense, the dynamic polarization has acted as a selector for the solid-(plastic)-like component of the NMR line and thus we are sure that the observed phenomena are related to this very component.

Our conclusion may thus be expressed as follows: In plastic cyclohexane, around the molecules of radical which are trapped in the crystalline lattice, the molecular self-diffusion is quenched. This is another and complementary aspect of the influence of (organic and paramagnetic) impurities in plastic cyclohexane and perhaps more generally in plastic crystals.

V. CONCLUSION

The deviations from the spin-diffusion theory for nuclear spin-lattice relaxation and dynamic polarization in plastic cyclohexane are consistent with the hypothesis of the quenching of the molecular self-diffusion around the paramagnetic impurity molecule. The two zone model developed can explain semi-quantitatively the experimental results. The dimension of the quenched zone is representative of the range of influence of the impurity on the molecular self-diffusion in the lattice. The relatively long range found here indicate that the impurity increases notably the interactions between the neighboring cyclohexane molecules, probably because these interactions are weak in the pure sample. This stronger interaction is consistent with

the measured correlation times of the rotational motions. The reorientation correlation time of the radical near the melting point, and measured by EPR⁸ is found to be about 0.5×10^{-10} sec, whereas that of the cyclohexane molecules, in the pure sample, and measured by quasi-elastic neutron scattering¹⁹ is about 10^{-12} sec. As a consequence, the cooperative rotational motions, which already exist in the pure sample,²⁰ are probably more important between the radical and the cyclohexane molecules of the quenched zone. As the influence of impurities on the self-diffusion in plastic crystals seems to be an important phenomenon, the use of paramagnetic impurities is of great interest because techniques such as EPR and dynamic polarization can be used for its study, in addition to techniques like NMR, tracers or plastic flow. The main advantage of the former techniques is that they are very sensitive to the motions which exist at the impurity, or very near it, whereas the latter ones measure a variation of a property of the bulk due to the presence of these impurities. These variations can be very small and not easy to detect. Finally, we think that these new methods may be useful to resolve apparent discrepancies. For example, suppose that in a given sample the presence of impurities quenches the molecular self-diffusion around it and that the number of quenched and diffusing molecules are of the same order of magnitude. The plasticity of the impure sample is clearly smaller than that of the pure one. Consequently, a creep measurement would indicate an increase of the activation energy of the molecular diffusion. On the other hand, a NMR measurement using a wideline technique would indicate a slight variation in the line shape (because the quenched molecules are shifted to the wings of the NMR line), but no variation in the motional narrowing process (because only the diffusing molecules, away from the impurities are seen around the center of the NMR line). Consequently, no variation in the activation energy of the molecular diffusion would be deduced. This may be compared to the results of Ref. 6.

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APPENDIX

In the stationary state, we have $dI/dt = dI_p/dt = dS/dt = 0$. Replacing the first members of Eqs. (2), (3), (4) by zero, one gets [from Eq. (2)]

$$I_p - I_0 = U(I - I_0). \quad (A1)$$

Eliminating S and I_p between these three equations,

one gets

$$\begin{aligned} \eta &= \frac{I - I_0}{I_0} \\ &= U^{-1} \\ &\times \frac{[\mp (S_0/I_0) + 1] \bar{W}_{\pm}}{(1 + T_{1e} \bar{W}_{\pm}) [(U\tau)^{-1} - (T_{1p}^{-1} + \tau^{-1} + W_{\pm}) + T_{1e} \bar{W}_{\pm}^2]}. \end{aligned} \quad (A2)$$

If we assume that $T_{1e} \ll \tau$, T_1 , T_{1p} , \bar{W}_{\pm}^{-1} , which is generally the case at high temperature (in no extreme saturation experiments), and recalling that for electrons and protons $S_0/I_0 \approx 660$, one gets Eq. (6) of the text.

When the nuclear populations have been changed from thermal equilibrium by dynamic polarization and the pumping field removed at $t=0$, the evolution of the magnetizations is given by Eqs. (2) and (3) with $\bar{W}_{\pm}=0$ and the initial condition:

$$I_p(0) - I_0 = U[I(0) - I_0]. \quad (A3)$$

These two equations may be written as

$$\begin{aligned} d(I - I_0)/dt &= -[T_1^{-1} + (N_p/N)(\tau^{-1})][I - I_0] \\ &\quad + (N_p/N)(\tau^{-1})[I_p - I_0], \end{aligned} \quad (A4)$$

$$d(I_p - I_0)/dt = (\tau^{-1})[I - I_0] - (T_{1p}^{-1} + \tau^{-1})[I_p - I_0]. \quad (A5)$$

Putting

$$\begin{aligned} a &= 1/T_{1p} + 1/\tau; \\ b &= -1/\tau; \\ c &= -(N_p/N)(1/\tau); \\ d &= 1/T_1 + (N_p/N)(1/\tau), \end{aligned} \quad (A6)$$

the solution may be written as

$$I(t) - I_0 = A \exp(-r_1 t) + B \exp(-r_2 t), \quad (A7)$$

$$\begin{aligned} I_p(t) - I_0 &= [(r_1 - d)/c]A \exp(-r_1 t) \\ &\quad + [(r_2 - d)/c]B \exp(-r_2 t), \end{aligned} \quad (A8)$$

where r_1 and r_2 are solutions of the equation

$$r^2 - (a + d)r + ad + bc = 0. \quad (A9)$$

Equation (A9) is equivalent to relations (9) and (10) of the text.

Writing Eq. (A7) and (A8) for $t=0$ and using Eqs. (A3) and (A6), one gets

$$A/B = -(r_2/r_1). \quad (A10)$$

Plugging this relation into Eq. (A7), one gets Eq. (8) of the text.

In the limiting case where the quenched zone a is very small ($N_p \ll N$), we clearly have $T_{1p} \ll T_1$ and τ very small. Consequently, one of the roots of Eq. (A9)

is very large. In these conditions, rather simple expressions for r_1 and r_2 can be derived. We get

$$r_1 = 1/T_{1p} + 1/\tau, \quad (\text{A11})$$

$$r_2 = 1/T_1 + (N_p/N)/T_{1p}. \quad (\text{A12})$$

As $r_2/r_1 \ll 1$, Eq. (8) shows that the relaxation of the magnetization of zone b is practically exponential with a time constant r_2^{-1} . Using Eqs. (12), (13), (14), (A12)

may be written as

$$r_2 = 1/T_1 + 1/T_s. \quad (\text{A13})$$

Equation (A13) shows that, in the limiting case, r_2^{-1} is the standard relaxation time for the bulk magnetization of a solid doped with a paramagnetic impurity.^{9,14} For dynamic polarization, as τ goes to zero, but N_p is never really zero (at least the first neighbors of the radical relax with the time T_{1p}) it is seen from Eqs. (7) that U goes to the value 1, as expected.

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