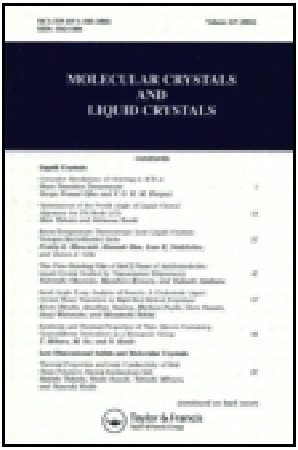

Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

NMR Relaxation in Adamantane and Hexamethylenetetramine: Diffusion and Rotation

H. A. Resing [a]

[a] Naval Research Laboratory, Washington, D. C., 20390

Version of record first published: 21 Mar 2007.

To cite this article: H. A. Resing (1969): NMR Relaxation in Adamantane and Hexamethylenetetramine: Diffusion and Rotation, Molecular Crystals, 9:1, 101-132

To link to this article: http://dx.doi.org/10.1080/15421406908082735

7

NMR Relaxation in Adamantane and Hexamethylenetetramine: Diffusion and Rotation

H. A. RESING

Naval Research Laboratory,
Washington, D. C. 20390

Abstract—The ultraslow-motion NMR technique has been used to measure translational diffusion coefficients in the *plastic* crystal adamantane;

$$D = (4.5 \pm 1.2) \times 10^{5} \exp(- 36.7 \pm .3/RT)\mathrm{cm}^{2}\mathrm{sec}^{-1}.$$

The diffusion coefficients in the *brittle* crystal hexamethylenetetramine (HMT) were too low to be measured by this technique; they are smaller than those for adamantane by a factor of 10^{-4}. It is claimed on the basis of Weertman's theory that this difference in diffusion coefficients accounts for the difference in plastic flow properties between the two materials. For rotation in β-adamantane, α-adamantane, and HMT the respective jump times are:

$$\tau_{\alpha} = (9.4 \pm .9) \times 10^{-14} \exp(3.08 \pm .05/RT)\,\mathrm{sec}$$
$$\tau_{\beta} = (1.13 \pm .22) \times 10^{-15} \exp(6.50 \pm .05/RT)\,\mathrm{sec}$$
$$\tau_{HMT} = (1.2 \pm .2) \times 10^{-16} \exp(19.3 \pm .2/RT)\,\mathrm{sec}.$$

1. Introduction

The purpose of this paper is to compare diffusion in typical *plastic* and *brittle* molecular crystals in order to explain their respective mechanical or plastic deformation properties. The mechanical properties of nonpolymeric molecular crystals represent an enigma of rather long standing.[1] All that the literature has to offer as a qualitative division of molecular crystals into *plastic* and *non-plastic* (or *brittle*) crystals. The *plastic* crystals are those which relatively easily undergo plastic deformation; empirically it has been found that in these materials (a) the molecules are globular, i.e. possess nearly spherical envelopes, (b) the symmetry of the lattice is high, and (c) the barrier to molecular reorientation at a site is relatively low. As a result of these three factors the allowable orientations of molecular axes in *plastic* crystals are distributed over a large number of distinguishable orientations of roughly the same potential energy; and this condition expresses itself through an entropy of melting which is low, less than five e.u. *Brittle* crystals are those which do not easily undergo plastic deformation; these usually fail one or more of the empirical criteria which accompany *plastic* crystalline behavior. The *plastic* crystals themselves invariably undergo a solid-solid phase transition at lower temperatures to a *brittle* phase of lower symmetry in which the rotational reorientational barrier is higher and in which the reorientational disorder is removed.

Plastic deformation is a complex process which depends on the concentration and properties of dislocations in the particular structure, the slip systems which the structure allows, the vacancy concentration, and other factors.[2,3] Nevertheless, at temperatures greater than half the melting temperature T_m it is known for many metals that the rate of plastic deformation at constant stress (which can be taken as the measure of plasticity) is proportional to the diffusion coefficient, as shown, for instance, by Weertman for low stresses.[3]

$$\dot{\epsilon} = A\sigma^{4.5}D/(kT), \tag{1}$$

where $\dot{\epsilon}$ is the strain rate, σ the stress, D the diffusion coefficient, k Boltzmann's constant, and T the absolute temperature. At the start of the present work, the only *plastic* crystal for which this theory had been checked was white phosphorous,[4] therefore this work was undertaken for the purpose of making a comparative study of diffusion in a *plastic* and in a *brittle* crystal. The idea is to test whether the differences in plasticity between *plastic* and *brittle* crystals is summarized in (1) with diffusion being the controlling factor.

Adamantane, $C_{10}H_{16}$, is a plastic crystal, while hexamethylenetetramine (HMT), $C_6N_4H_{12}$, is not. These two substances have the same molecular symmetry (tetrahedral), roughly the same molecular weight, roughly the same melting temperatures (~265 °C), and both possess highly symmetric lattices (adamantane fcc and HMT bcc). But the rotational barrier in adamantane is only 3 kcal/mol while in HMT it is 19 kcal/mol. In a certain sense the study of diffusion in these two systems is a controlled experiment; one keeps as many parameters as possible " constant " and varies only the parameter of interest, i.e. the plasticity.

This paper is not the first to use adamantane and HMT in a comparative study; others have compared heat capacities,[5] coefficients of thermal expansion,[6] *PVT* relations,[7] and lattice vibrations (theory).[8] Because of their high molecular and lattice symmetry these two compounds have become test cases for the understanding of the molecular solid state, especially as regards lattice dynamics.[9,10,11,12,13] The activated state parameters for diffusion and rotation should assist in the understanding of lattice dynamics in as much as all three phenomena are governed by the intermolecular potential energy function.

Both adamantane[14,15,16] and HMT[17,18] have been the subjects of previous NMR relaxation studies, but those have not yielded any information about diffusion. The NMR relaxation technique apparently most suitable for diffusion measurements is that developed by Ailion and Slichter,[19,20] i.e. spin lattice relaxation in the local field. This technique allows the measurement of extremely long diffusional jump times, the only limit being that imposed by spin-lattice relaxation due to other mechanisms such as molecular rotation or electron–nuclear coupling. It was expected on the basis of (1) that diffusion in HMT would be slow, but the jump times proved to be too long for even the Ailion-Slichter technique to be of use; still a lower limit for the jump times in HMT could be set. Another reason for the use of the Ailion-Slichter techniques was the validation of this technique as far as molecular crystals are concerned. The diffusion data for adamantane do indeed furnish such a validation. All relaxation times were measured at a frequency of 12 MHz.

2. Results of Relaxation Theory

A. Definitions

The NMR relaxation times are experimentally measurable inverse rate constants for the exponential return of the nuclear spin system into thermodynamic equilibrium. The equilibria are fundamentally two: the internal equilibrium of the spin system, characterized by the spin-spin relaxation time T_2; and the equilibrium of the spin system with the external heat bath, characterized by the spin-lattice relaxation time T_1. Depending on the magnetic field which *dominates* the situation one may have relaxation in the constant external field H_0 (the ordinary T_1);[21] in the radio frequency field H_1 (The relaxation time in the rotating frame, $T_{1\rho}$);[20] or in the local nuclear dipolar field H_l (the relaxation time in the local field, T_1^*).[22] In this paper measurements of T_2, T_1, and T_1^* are reported.

B. THE SECOND MOMENT

According to accepted theories, the nuclear–spin–energy–level transitions which lead to relaxation are induced by the time dependent nuclear magnetic dipolar fields. The time dependence of this local field arises through the relative motion of nuclei as they are transported through space by the rotational or translational motion of molecules containing them. The second moment M^2 of the NMR absorbtion line is a measure of the strength of this nuclear dipolar field. For the case in which all nuclei are equivalent the powder average second moment can be written:[23]

$$M^2 = \frac{3}{5}\gamma^4\hbar^2 I(I+1)\left[\sum_{i,\,\text{intra}} r_{ij}^{-6} + \sum_{i,\,\text{extra}} r_{ij}^{-6}\right] \tag{1a}$$

$$= M_i^2 + M_e^2 \tag{1b}$$

where γ is the nuclear gyromagnetic ratio, $\hbar$ is Planck's constant over 2π, I is the nuclear spin, r_{ij} is the distance from the j th, or reference nucleus to the ith nucleus. The first summation in (1a) is over nuclei in the same molecule as nucleus j, i.e., it gives rise to the intramolecular second moment M_i^2. The second summation is over nuclei in all neighboring molecules and gives rise to the extramolecular second moment M_e^2. Let τ_r^{-1} and τ_d^{-1} be, respectively, the jumping rates for activated rotational and translational jumps. Equation (1) holds at relatively lower temperatures such that both $M^2\tau_d^2$ and $M^2\tau_r^2$ are greater than unity.

For adamantane and HMT as well as for many other solids composed of spherical molecules $\tau_d \gg \tau_r$, as can be seen for example from the summary in Fig. 5. At temperatures such that $M^2\tau_r \ll 1$ motional narrowing of the NMR line occurs and the second moment decreases to a new constant value, M_d^2. If the rotational motion is isotropic in three dimensions,[24]

$$M_d^2 = \frac{3}{5}\gamma^4\hbar^2 I(I+1) N \sum_{i,\,\text{extra}} R_{ij}^{-6} \tag{2}$$

where R_{ij} is the distance between respective molecular centers, N is the number of nuclei per molecule, and the sum is over all other molecules. Clearly this second moment is extramolecular in origin; all intramolecular contributions have been averaged to zero by the rotational motion.

At a still higher temperature such that $M_d^2\tau_d^2 < 1$ the resonance line narrows further and its second moment tends to zero as a limit.[21] Thus one associates with diffusional motion only a fraction of the extramolecular second moment. The remainder of this extramolecular moment $(M_e^2 - M_d^2)$ and the intramolecular moment M_i^2, are associated with the rotational motion. The molecular geometry and dimensions, known for both adamantane and HMT by X-ray methods, serve to define M_i^2, while M_d^2 is completely determined by the density or lattice parameter of the solid. On the other hand M_e^2 depends on the mutual orientation and packing of molecules. For adamantane, second moment studies have been made by Douglass and McCall,[14] and by Smith;[15] for HMT by Smith[17] and Yagi.[18]

C. Relaxation Times

Using obvious extensions of the theory of Bloembergen, Purcell, and Pound[21] the following equations for the relaxation times can be written in terms of the jump times and second moments. The spin-lattice relaxation time T_1 is given as

$$T_1^{-1} = T_{1r}^{-1} + T_{1d}^{-1} \tag{3}$$

where the term T_{1d}^{-1} results from diffusion and T_{1r}^{-1} from molecular rotation:

$$T_{1d}^{-1} = \tfrac{3}{4}\gamma^4\hbar^2 I(I+1)[2S_1(\omega_0) + 8S_1(2\omega_0)]$$

where S_1 is the spectral density at the resonant frequency $\omega_0 = \gamma H_0$ as derived by Torrey for lattice diffusion;[25] and

$$T_{1r}^{-1} = \tfrac{2}{3}M_i^2\left(\frac{\tau_r}{1+\omega^2\tau_r^2} + \frac{4\tau_r}{1+4\omega^2\tau_r^2}\right) \tag{4}$$

$$+ \tfrac{2}{3}(M_e^2 - M_d^2)\left(\frac{\tau_r/2}{1+\omega^2\tau_r^2/4} + \frac{2\tau_r}{(1+\omega^2\tau_r^2)}\right)$$

in which the first and second terms are the intramolecular and extramolecular terms respectively.

For the spin-spin relaxation time T_2 we are concerned only with the region $M_d^2\tau_d^2 < 1$, for which

$$T_{2d}^{-1} = 0.9218\, M_d^2\tau_d \tag{5}$$

where the numberical factor is calculable from the theory of Torrey.[25]

For the spin-lattice relaxation in the local field T_1^* there are also rotational and diffusional contributions as

$$(T_1^*)^{-1} = (T_{1d}^*)^{-1} + (T_{1r}^*)^{-1} \tag{6}$$

For $M_d^2\tau^2 < 1$, Ailion and Slichter[20] have shown that

$$T_{1d}^* = T_{2d} \tag{7}$$

where T_{2d} is given by (5).

For $M_d^2\tau_d^2 > 1$,

$$T_{1d}^* = \frac{\tau_d}{2(1-p)} \cdot \frac{H_1^2 + H_l^2}{H_l^2}\,\frac{G}{G-1} \tag{8}$$

where p is a geometric parameter, H_l is the strength of the local nuclear dipolar field, and G is the number of nearest neighbor molecules.

For T_{1r}^* we take the following equation from Solomon and Ezratty[26]

$$\frac{1}{T_{1r}^*} = \frac{1}{T_{1r}}\left[\frac{h_0^2 + (T_{1r}/T_{2r})H_1^2 + \alpha H_l^2}{h_0^2 + H_1^2 + H_l^2}\right], \tag{9}$$

where T_{1r} is given by (4), the quantity T_{2r} is a transverse relaxation time (due to molecular rotational hopping) in the rotating reference frame, which is supposed to be much nearer in magnitude to T_{1r} than the usual T_2 (i.e. the inverse absorption line width). The magnetic field h_0 is the departure from resonance ($H_0 - \omega/\gamma$), where ω is the frequency of H_1. The parameter α is necessary to describe the return of the dipolar energy to equilibrium; α is supposed to equal 3 if neighboring nuclei experience the same fluctuating Hamiltonian. This α equals $\frac{2}{3}(2 + T_{1r}/T_{2r})$ if the fluctuating Hamiltonians at neighboring nuclei are uncorrelated;[26] and this is the condition we expect to be valid in the present situation. We have been unable to find a suitable theoretical expression for T_{2r} in the literature and have essentially assumed that it is equal to $T_{1\rho}$ as defined by Look and Lowe:[22]

$$\begin{aligned} T_{2r}{}^{-1} = {} & M_i{}^2\tau + \frac{5/3\tau}{1+\omega^2\tau^2} + \frac{2/3\tau}{1+4\omega^2\tau^2} \\ & + \tfrac{1}{2}(M_e{}^2 - M_d)^2\tau + \frac{5/3\tau}{1+\frac{1}{4}\omega^2\tau^2} + \frac{2/3\tau}{1+\omega^2\tau^2}\,. \end{aligned} \tag{10}$$

3. Experimental

A. APPARATUS AND PROCEDURES

The AS procedure for measuring the spin-lattice relaxation time in the local magnetic field T_1^* is as follows.[20] The kilogaus field H_0 is first pulsed off resonance by an amount h_0. A resonant (at H_0) r.f. field of intensity H_1 at right angles to H_0 is switched on, whereupon h_0 is allowed to decay adiabatically to zero in a time much shorter than T_1^*. After a time t, H_1 is decreased sharply to zero, and the amplitude M of the ensuing nuclear signal is determined. The experiment is repeated at several values of t and from the (constant) slope of $\ln M$ vs t the value of T_1^* is deduced. The spin-lattice relaxation time T_1 was determined by the 180°–90° method; and the spin-spin relaxation time T_2 either from the free induction decay or from spin echo experiments. For the latter two relaxation times apparatus described previously was used.[27]

The apparatus specific to the AS-experiment consists of (a) a source of radio frequency pulses, (b) a pulser to modulate the external field, and (c) a device to measure the r.f. field strength; these are described below. The 12 MHz radio frequency field H_1 was generated by a Blume type crystal oscillator and pulsed by modified Tektronix units. The H_1 pulse amplitude was constant within 4 per cent from 1 μsec to 10 sec. Its amplitude was measured by diode detecting the r.f. pulse at the probe head and feeding this envelope to a box car integrator; this reading was calibrated in terms of 180° pulse lengths for the proton resonance of glycerol. The H_1 intensity is thereby known within 5 per cent. It was kept at about 0.7 G and usually measured for each determination of T_1^*. The h_0 pulser is based on the design of Lurie.[29] The h_0 coils were mounted on the probe about 1 cm distant from the pole faces. This pulsed field interacted with the

Fieldial Hall probe sensor so that the sensor had to be fitted with a coil through which a fraction of the h_0 current, sufficient to counteract the pulsed field, was passed. The pulsed field also induced image fields in the pole faces which needed about one msec to die out after the end of an h_0 pulse; this made it difficult to measure T_1^* less than a msec.

The adjustment of H_0 to resonance could be done at temperatures where the molecular rotational mechanism controlled T_1 and T_1^*. In this region, where T_1^*, is given by Eq. (9) above, the free induction decay amplitude is zero after an r.f. pulse much longer than T_1 (i.e. see (14) below).

The r.f. pulse lengths were measured by means of a frequency counter. Nuclear signal amplitudes were measured with a box car integrator. Relaxation times could easily be determined to within ± 3 per cent. The proper temperatures were produced by means of a gas flow system. Temperature was controlled by a simple on-off potentiometric controller, which was fed from a thermocouple in the gas stream. Temperatures could be controlled within ± 0.1K. The accuracy of the temperature is estimated at ± 0.3K.

B. SAMPLE PREPARATION

Samples of adamantane from various sources were used: (a) obtained from the calorimetric sample of Westrum;[5] (b) obtained from P. Von R. Schleyer; (c) obtained from Aldrich Chemical Company. Samples (c) were recrystallized from methanol several times. All samples were sublimed in vacuum several times. The NMR samples were prepared by subliming the adamantane into a cylindrical pyrex ampoule one cm. in diameter at the end of an evacuated tube. This ampoule was then sealed off at a constriction. The purpose of this operation was to minimize the dead space in the sample chamber so that at higher temperatures, where the vapor pressure is several atmospheres, most of the adamantane would remain solid and be present in the NMR coil. The sample that resulted was massive and polycrystalline. Several of the tubes exploded at high temperatures due to this high pressure. No significant difference in the relaxation behavior between samples was noted.

The HMT was obtained from Eastman Organic Chemicals.

Samples were sublimed into the ampoules as for adamantane, again giving rise to massive polycrystalline samples. The pyrex tubes failed at high temperatures for HMT also, but for a different reason. Because of the difference in thermal expansion between HMT and pyrex, and because HMT did not flow, the pyrex cracked at temperatures much lower than necessary to produce super-atmospheric pressures. Samples of HMT powder (~ 1 mm diameter particles) were then used at higher temperatures rather than massive specimens. This did not noticeably affect the relaxation properties. At very high temperatures the HMT would char rapidly so that a new sample would be needed for each T_1 or T_1^* measurement. Strangely, the pyrolysis did not affect the relaxation. It has been postulated that HMT pyrolizes only at its surface.[30] If any high concentration of free radicals were generated uniformly throughout the lattice by the charring one would expect relaxation to be markedly affected. Lack of any effect of charring argues in favor of the surface charring hypothesis.

4. Results and Data Analysis

A. OVERVIEW

The general purpose of Section 4 is to present the data and to analyse it in terms of molecular jump times for rotation and diffusion. Throughout it has been assumed that these jump (correlation) times follow the simple activated state law:

$$\tau = \tau_0 \exp(H_{\text{act}}/RT) \tag{11}$$

where the pre-exponential factor τ_0 and the enthalpy of activation H_{act} are assumed to be independent of temperature. Discussion of τ_0 and H_{act} for the various motions is given in a later section. Examination of the relaxation Eqs. (4), (8), (9), and (10) shows the relaxation times to vary either directly or inversely in proportion to τ over much of the range of τ. Since the logarithm of τ is a linear function of inverse temperature, so also should the logarithms of the various relaxation times show a linear dependence on inverse temperature. Therefore in Figs. 1 and 2 the logarithms of the measured relaxation times are plotted vs reciprocal temperature for adamantane and HMT respectively. Any resulting linear portion of these plots shows the validity of (11) for some molecular process; any

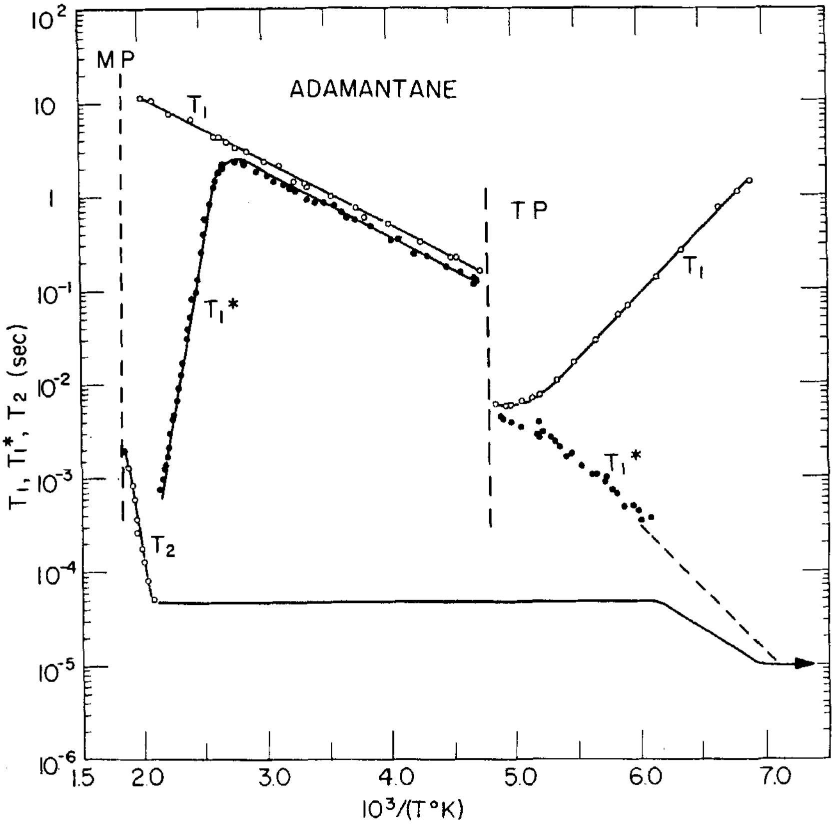

Figure 1. The relaxation times T_1, T_1*, and T_2 for adamantane plotted versus reciprocal temperature. The melting temperature (MP) and transition temperature (TP) are indicated. The lower solid line represents the linewidth study of Douglass and McCall. T_2 and T_1* on the left arise from diffusion. T_1 is everywhere dominated by molecular rotation. The solid lines are merely smooth curves through the data points.

change of slope must be explainable in terms of the relaxation equations themselves or in terms of a change in dominance of the nuclear dipolar relaxation mechanism from one kind of molecular motion to another. For adamantane and HMT it has not been necessary to invoke any other relaxation mechanism than nuclear dipolar motion to explain the data.

The relaxation data for adamantane are shown in Fig. 1. The results of the line-width and second moment study of Douglass and

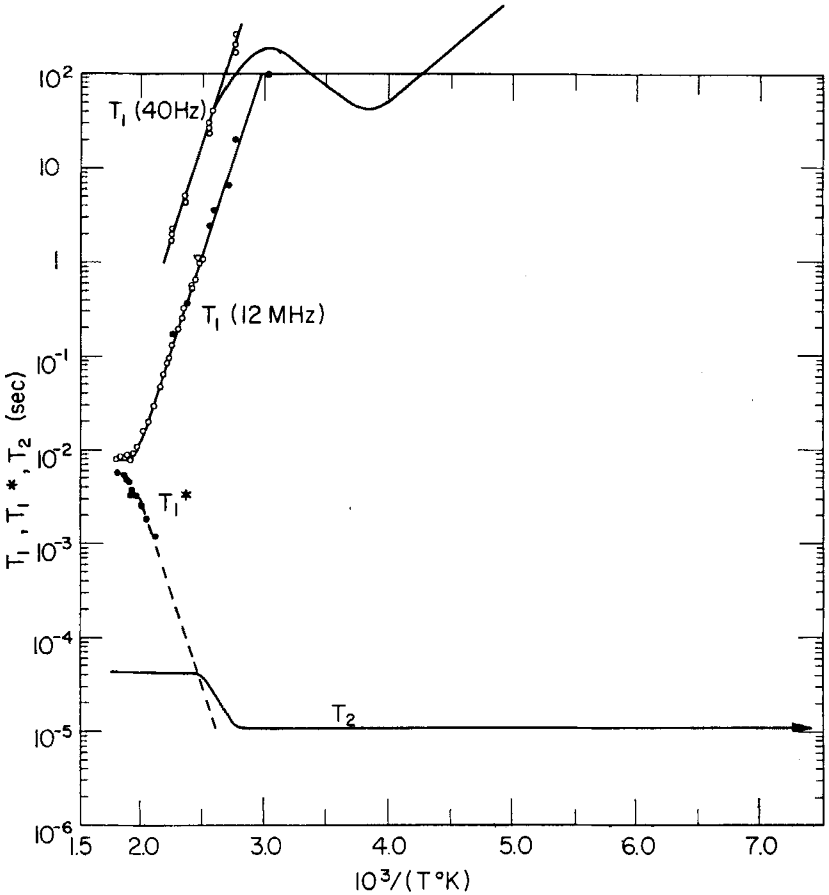

Figure 2. The relaxation times T_1, T_1* and T_2 for HMT plotted versus reciprocal temperature. The scale is exactly the same as for Fig. 1 in order to emphasize the difference between the two systems. The lower solid line represents the linewidth study of Smith (as extended here to slightly higher temperatures). The upper T_1 data (should be 40 MHz) are also those of Smith; the extra minimum due to water diffusion that he found is shown schematically. Smith's T_1's corrected to 12 MHz are shown as the upper filled circles.

McCall[14] are also shown there, somewhat schematically, as T_2's or inverse line-widths. Their measurements clearly show a line-width transition (at $10^3/T = 6.5$) due to molecular rotation; at lower temperatures the second moment of the line is given by (1) and at higher temperatures by (2), as they show.[31] At the phase transition (indicated in Fig. 1) there is no noticeable change in line width. In the low temperature or β phase, the spin-lattice relaxation time T_1 shows a minimum value; both the value at the minimum and the rotational correlation time deduced therefrom are theoretically consistent with rotational relaxation. The relaxation time in the local field T_1^* is consistent with a rotational mechanism in the β phase also, and represents that part of the local field (line width) which is being averaged by rotational motion; the interpolated line between T_1^* and T_2 in Fig. 1 has a slope reflecting the rotational activation energy (as deduced from T_1) and reveals their consistency quite graphically. The discontinuities in the values of T_1 and T_1^* at the β to α phase transition demonstrate a discontinuity in the rotational jump time; the jumping rate changes by more than a factor of ten at the transition. In the α phase all of the observed T_1 values are controlled by a rotational mechanism. That part of the T_1^* plot parallel to the T_1 plot also reflects rotational motion. The T_1^* and T_2 at the highest temperatures are governed by the translational diffusion.

For HMT certain line width and relaxation time data of Smith[17] are included along with the present results. His line-width data show a transition similar to that for adamantane due to molecular rotation, but at a temperature more than twice as great as for adamantane. His T_1 measurements show a minimum due to water impurity diffusion, but at the highest temperatures they reflect the rotational motion, as he showed. The T_1, T_1^* and T_2 results presented here show only the expected rotational effects. The failure of T_1^* to show any diffusion effects allows an upper limit for the diffusion rate in HMT to be established.

B. Data Analysis

The data were fitted to the appropriate relaxation equations by means of a least squares computer routine. This program, written in Fortran, was devised to fit several kinds of data simultaneously to specified analytic functions (not necessarily linear) involving the desired parameters. The program could also estimate the standard deviations σ of the deduced parameters. Thus all resulting parameters P are quoted herein as $P \pm \sigma$.

Throughout the data analysis it was assumed that the independent variables, temperature, and r.f. field strength, were completely free from error, which is not exactly true. The quoted standard deviations do not reflect this uncertainty in temperature and H_1 intensity. The relaxation times were always introduced in the form of logarithms; this procedure automatically weighted each measurement properly, i.e. while the relaxation time varied over five powers of ten, the per cent error remained roughly constant. Occasionally a certain datum or set of data was assigned weight less than unity; for example this was done intuitively to reflect the uncertainty of measurement of T_1^* less than one msec.

C. The Local Field

An important parameter for the proper interpretation of the relaxation times is the quantity H_l^2, the square of the local dipolar magnetic field as in (8) and (9). It has not yet been established theoretically whether H_l^2 is one third of the entire second moment as in (1) or of the rotationally decreased second moment (2). It has proven possible, however, to determine H_l^2 by several experimental methods as described below: the result is that

$$H_l^2 = \tfrac{1}{3} M_d^2/\gamma^2 \tag{12}$$

within experimental error, where M_d^2 is given by (2). The results of the various methods are summarized in Table 1 for the high temperature phase of adamantane.

Table 1 The Square of the Local Field for α-Adamantane‡

Method	$H_l^2 = \frac{1}{3}M_d^2/\gamma^2$
H_1 comparison	.32 ± .02
M_{eq} vs h_0	.28
T_1/T_1^*	.25 ±.06
Theory	$.31_0$
Broad Line	.32
Free Ind. Decay	~.4

‡All at 298 K; in units of G².

(1) H_1 comparison. If one performs an adiabatic demagnetization from a large field H_0 into the field of magnitude $(H_1^2 + H_l^2)^{\frac{1}{2}}$ one observes only the component of magnetization which lies along H_1, which is given (in the absence of relaxation, and at resonance) as

$$M_x = M_0 H_1/(H_1^2 + H_l^2)^{\frac{1}{2}} \tag{13}$$

where M_0 is the equilibrium magnetization. The free-induction-decay amplitude is proportional to M_x, and H_l^2 was extracted by a least squares fit of the observed amplitudes as a function of H_1 to Eq. (13).

(2) $(M_{\mathrm{eq}})_x$ vs h_0. If the H_1 pulse is allowed to last several times T_1, the magnetization comes to equilibrium with the resultant field of magnitude $(h_0^2 + H_1^2 + H_l^2)^{\frac{1}{2}}$. The free-induction-decay amplitude on switching off H_1 is a measure of the x component of the equilibrium magnetization $(M_{\mathrm{eq}})_x$, which Solomon and Ezratty[26] show to be

$$(M_{\mathrm{eq}})_x = \frac{M_0 h_0 H_1}{h_0^2 + H_1^2 + \alpha H^2}\,. \tag{14}$$

The derivative of $(M_{\mathrm{eq}})_x$ with respect to h_0 has extrema at

$$h_{\max} = \pm (H_1^2 + \alpha H_l^2)^{\frac{1}{2}}$$

and in terms of $h_{\max}$, H_l^2 is given as

$$H_l^2 = \alpha^{-1}(h^2_{\max} - H_1^2).$$

In these equations α was taken to be $\frac{2}{3}(2 + T_{1r}/T_{2r})$, and the method was applied at room temperature where $T_{1r}/T_{2r} = 1$ (assumed); therefore $\alpha = 2$.

(3) The ratio T_1/T_1^*. This ratio is given by (9). Only the rotation-controlled relaxation data for the high temperature phase of adamantane were used in a least squares analysis to give H_l^2, as will be described in more detail later. Thermal expansion was allowed for. Again it was assumed that $\alpha = 2$.

As can be seen from Table 1 the results obtained by these three methods agree with each other within experimental error. The value of $\frac{1}{3}M_d^2$ was also determined by several methods: (a) calculation by means of (2) using a room temperature lattice constant of 9.45° Å, (b) from broad line data; and (c) from the free induction decay. These results are also gathered in Table 1 and adequately confirm (12). Therefore for HMT and for the β phase of adamantane (12) was accepted as the proper definition of H_l^2. This assumption must of course break down at temperatures slightly above the rotational line width transition. Below the transition the whole second moment (1) must be used to define H_l^2.

D. ROTATION IN THE β-PHASE OF ADAMANTANE

In Fig. 1 there are three sets of data on the low temperature or β-phase side of the phase transition line; the line-width or T_2 data, the T_1^* data, and the T_1 data. As asserted in the overview these three sets of data fit together rather well when interpreted in terms of activated molecular rotation in three dimensions. The line-width data have already been conclusively discussed in terms of molecular rotation.[14,15] A summary of the arguments follows. At low temperatures, effectively no molecular motion occurs $(\tau_r < (M_2^2 + M_e^2)^{-\frac{1}{2}})$ and the full second moment (1) is observed. As the temperature is raised a T_2 or 'line-width' transition occurs, ending at about 170°K. Above this temperature, to about 475°K, the spin-spin relaxation time T_2 remains constant; even the phase transition has no effect upon it. For this " middle temperature " plateau, the second moment is what one expects for rapidly rotating molecules at fixed sites. That is to say, on this plateau a fraction of the internuclear dipolar field is averaged away by molecular rotation; the remainder can only be averaged by relative translational motion of molecules (diffusion), which does occur in the α-phase *above* 475°K. For the β-phase, the T_1^* curve can be viewed as an extension of the T_2 curve in the transition region. The T_1 curve shows a minimum in the proper place and of the proper value at the minimum to be interpreted in terms of rotation; i.e. from the value of T_1 at its minimum the strength of the field modulated by the motion has been calculated, and it agrees with expectation for molecular rotation.

The T_1 and T_1^* data were fitted by the method of least squares to Eqs. (4), (9) and (10). It was assumed that $\alpha = \frac{2}{3}(2 + T_{1r}/T_{2r})$. The quantity H_l^2 was calculated from the density of the β-phase and Eqs. (2) and (12) to be .36 G^2; H_l^2 was assumed independent of temperature. The original goal was to deduce independently the values of τ_0, H_{act}, M_2^2, and $(M_e^2 - M_d^2)$ from the data. The slopes of the linear portions of the T_1 and T_1^* curves should fix H_{act}; the location of the T_1 minimum should fix τ_0; the value of T_1 at the minimum should give essentially the sum of $M_i^2 + M_e^2 - M_d^2$; the independent T_1^* data should furnish another mathematically independent relation involving M_i^2 and $(M_e^2 - M_d^2)$. This plan failed essentially because there was not enough data on the high temperature side of the T_1 minimum to fix the location of the minimum and hence to fix the value of τ_0; hence convergence to meaningful second moment values did not occur. It was therefore decided to reduce the number of parameters by fixing the ratio of M_i^2 to $(M_e^2 - M_d^2)$ at the value deduced from theory (Table 2). The remaining three parameters were then deduced by least squares fits to (a) the T_1 data alone and (b) simultaneously to the T_1 and T_1^* data. The second moments which resulted are given in Table 2 and the activated state parameters in Table 3. The " best fit " curves for T_1 and T_1^* are reproduced along with the data in Fig. 3.

TABLE 2 Second Moment Summary[i]

	Theory	Broad line	T_1	T$_1$ and T_1*
Adamantane—β				
M_i^2/γ^2	15.8[a]		15.1 ± 0.4[f]	12.8 ± 0.3[f]
M_e^2/γ^2	6.63[a]			
$(M_i^2 + M_e^2)/\gamma^2$	22.4[a]	~22.[a]	21.4[h]	18.3[h]
M_d^2/γ^2	.93[b]	0.9[c]		
$(M_e^2 - M_d^2)\gamma^2$	5.73		5.4[f]	4.6[f]
HMT				
M_i^2/γ^2	16.5_d, 14.2[e]		10.9 ± 0.2[g]	10.6 ± 0.2[g]
M_e^2/γ^2	5.85[e]			
$(M_i^2 + M_e^2)/\gamma^2$	20.0[e]	20.2[e]	15.5[h]	15.1[h]
M_d^2/γ^2	1.04[e]	0.85[e]		
$(M_e^2 - M_d^2)/\gamma^2$	4.80		3.6[g]	3.5[g]

a. Reference 15.
b. Eq. (2) with lattice parameter = 9.45°A.
c. Reference 14.
d. Calculation using molecular dimensions of Reference 11.
e. Reference 17.
f. Ratio $M_i^2/(M_d^2 - M_e^2)$ fixed at 15.8/5.73 in data reduction.
g. Ratio $M_i^2/(M_d^2 - M_e^2)$ fixed at 14.2/4.80 in data reduction.
h. $M_i^2 + (M_e^2 - M_d^2) + M_d^2$ (theory).
i. All in units of Gauss squared.

In Table 2 it can be seen that the total second moment calculated from the T_1 data agrees fairly well with theoretical calculations based on molecular and lattice dimensions. This result along with the line-width data conclusively verifies that molecular rotation is the motion which modulates the nuclear dipolar field and leads to relaxation in β-adamantane. For the fit to the T_1^* and T_1 data the resulting second moment (Table 3) is about 15 per cent low, but yet in substantial agreement with theory.

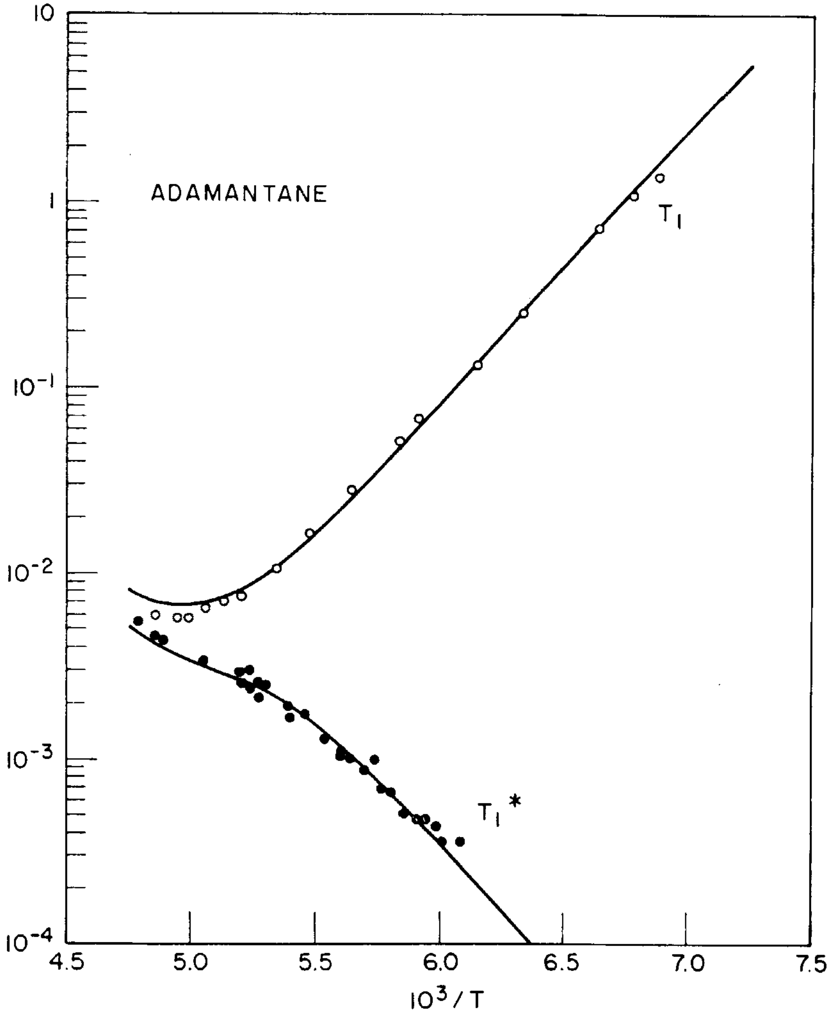

Figure 3. Relaxation times T_1 and T_1* for β-phase adamantane plotted versus reciprocal temperature. The solid lines represent the best fit of the theoretical equations to the data.

A rather curious fact is that the β-phase distortion (from f.c.c. cubic symmetry), which leads to more efficient molecular packing than in the α-phase, does not affect the three dimensional or isotropic character of the rotation in any obvious way as far as NMR relaxation is concerned; one might have expected the description in terms of a single jump time to break down.

TABLE 3 Molecular Jump Parameters

	τ_0 (sec)	H_{act} (kcal/mole)	ν_D Sec^{-1}	S_{act} eu
Adamantane				
β-phase				
rotation				
T_1	$1.13 \pm 0.22 \times 10^{-15}$	6.50 ± 0.05	9.90×10^{11}	$13.5\,(5.2)^c$
T_1 and T_1^*	$0.57 \pm 0.18 \times 10^{-15}$	6.66 ± 0.10		
α-phase				
rotation				
T_1	$9.4 \pm 0.9 \times 10^{-14}$	3.08 ± 0.05	7.4×10^{11}	$9.9\,(5.4)^c$
αphase				
diffusion	$1.6 \pm 0.6 \times 10^{-21}$	36.7 ± 0.3	1.6×10^{12}	$39.3\,(65)^c$
HMT				
rotation				
T_1 and T_1^*	$1.2 \pm 0.2 \times 10^{-16}$ 2.1×10^{-16a}	19.3 ± 0.2 18.7^a 17.9^b	1.7×10^{12}	$16.9\,(13.9)^c$

a. Smith, reference, line-width data.
b. Smith, reference, T_1 data.
c. Calculated from $S_{act} - 4\alpha H_{act}$.

E. ROTATION IN THE α-PHASE OF ADAMANTANE

Intuitively one expects that a phase transition to a less dense phase should lower the rotational potential barrier and lead to a discontinuous change in both the rotational jump rate and the associated relaxation time. We assert that this situation does indeed occur at the β-α phase transition in adamantane, and we analyze the data accordingly. There is no T_1 minimum to give second moment information which would substantiate this assertion; the second moments must be chosen on the basis of the motional model. The only way to completely verify the model is a comparison of the resulting jump rates with similar information from another source; for adamantane slow neutron scattering[10] furnishes that information and verifies the model, as is discussed later.

In Fig. 1 it can be seen that the T_1 plot is linear in reciprocal temperature and that the lower temperature portion of the T_1^* plot parallels the T_1 plot. There are three parameters which can be taken from the data: τ_0, H_{act}, and the ratio (T_1/T_1^*). The last parameter is dependent on H_l^2, α, and through α on the ratio (T_{1r}/T_{2r}) as (9) shows. The data presented here are sufficient to provide a quantitative verification of the Solomon and Ezratty[26] theory, which verification (for lack of a suitable system) has heretofore been lacking.

In fitting this data the theoretical values of M_1^2 and $(M_e^2 - M_d^2)$ listed for adamantane in Table 2 were used with (4) and (9) to deduce τ_0, H_{act}, and one other parameter. The τ_0 and H_{act} values are listed in Table 3. For the other parameters the results are as follows: (a) It was assumed that $\alpha = \frac{2}{3}(2 + T_{1r}/T_{2r})$ and that $(T_{1r}/T_{2r}) = 1$: hence $\alpha = 2$. The square of the local field H_l^2 was found to be 0.26 ± 0.6 G^2 which agrees with the theoretical 0.31 G^2 (see Table 1) within experimental error; (b) H_l^2 was taken as 0.31 G^2. The parameter α was assumed to be $\frac{2}{3}(2 + T_{1r}/T_{2r})$. The least squares fit to the data gave the ratio (T_{1r}/T_{2r}) as 0.97 ± 0.05 which agrees with the expected value of unity within experimental error.

F. Diffusion in α-Adamantane

That molecular translational self-diffusion does indeed occur in α-adamantane is shown most directly by consideration of the T_2 increase above 475 °K (Fig. 1). As discussed previously, the averaging of nuclear dipolar fields which this increase of T_2 represents can only be the result of such diffusion. The T_1^* data above 360 °K (Fig. 1) have the proper temperature dependence and numerical values to be theoretically compatible with the T_2 data and with diffusion.

The T_2 and T_1^* data have been analyzed simultaneously according to (5), (7) and (8) to obtain τ_0 and H_{act} for diffusion (Table 3). Because the values of τ deduced from T_2 at a given temperature are somewhat smaller than expected from extrapolation of T_1^* the ratio $\tau_0(T_2)/\tau_0(T_1^*)$ was also deduced from the data and found to 0.68 ± 0.05. All that is necessary to calculate the local field parameters H_l^2 and M_d^2 which occur in (5) and (8) is the density at any temperature and the knowledge that the structure is face centered cubic. The corrections for the effect of temperature on density were made using the coefficient of thermal expansion found by Mirskaya.[6] The raw values of T_1^* were first corrected for the effects of α-phase rotation to obtain T_{1d}^* according to (7) and the results of the previous section.

In the Eq. (8) which relates τ to T_{1d}^* there is a geometrical factor p which arises in considering the magnetic energy change per jump.[20] This factor p has been shown recently to be by nature anisotropic.[32] However for vacancy diffusion in an fcc lattice the anisotropy is small;[32] and vacancy diffusion is the most likely process in molecular crystals.[33,34] The value of p was calculated using the formula for the average over all orientations as given by Ailion and Slichter.[20] The lattice sum was evaluated by computer out to fifteenth nearest neighbors. The value of p was found to be 0.2234, in agreement with the recent results of Ailion and Ho.[32]

G. MOLECULAR ROTATION IN HEXAMETHYLENETETRAMINE

The results of the present study for HMT are shown in Fig. 2 along with the previous data of Smith.[17] His data at 40 MHz are shown, as are certain of his T_1 values corrected via (4) to 12 MHz, which was used in the present study. The analysis is the same in all respects as for the β-phase of adamantane. The value of H_l^2 which appears in (9) was calculated from the room temperature lattice parameter (using the fact that HMT has a body centered cubic structure) in (12) and (2); $H_l^2\,(\text{HMT}) = 0.36\ \text{G}^2$. The second moment and activated state parameters deduced from the present results are shown in Tables 2 and 3 respectively. It can be seen in Table 2 that the second moment data deduced from the relaxation measurements are not in as good agreement with theoretical expectations as for adamantane. The activation enthalpy H_{act} for HMT rotation (19.3 k cal/mol) is somewhat greater than that obtained by Smith (17.9 k cal/mol). However, the T_1 data for the two studies agree rather well in the region of overlap, and the best fit curve for the present results fits Smith's data (converted to 12 MHz) quite well; see Fig. 4. The fact that a T_1 minimum was observed in the present study fixes the absolute value of the jump time quite firmly.

Alexander and Tzalmona[35] have determined τ for HMT rotation by a nuclear-quadrupole-resonance ultra-slow-motion technique; τ values of 10^{-3} to one sec were measured at correspondingly lower temperatures. This range begins about a factor of ten above the end of Smith's NMR results. Values of τ calculated for the tem-

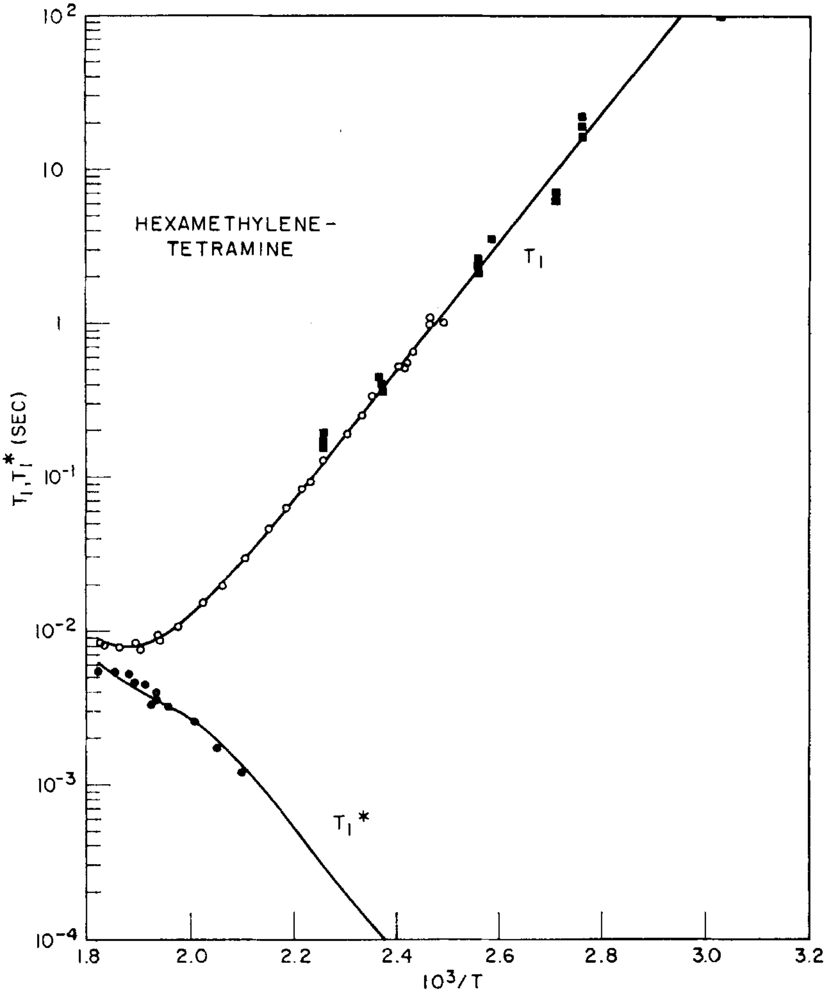

Figure 4. Relaxation times T_1 and T_1^* for HMT plotted versus reciprocal temperature. The solid lines represent the best fit of the theoretical equations to the data. The filled squares are the data of Smith corrected to 12 MHz.

perature range of their study using (11) and the τ_0 and H_{act} found here agree with their results within a factor of two. Because they obtain an activation enthalpy of only 15.6 k cal/mol, however, an extrapolation of their data to 540 °K would give τ values differing from the results of the present study by more than an order of magnitude.

H. DIFFUSION IN HEXAMETHYLENETETRAMINE

For adamantane the translational diffusion manifested itself most sensitively as an added contribution to the spin-lattice relaxation time in the local field T_1^* over and above that due to molecular rotation. Diffusion in HMT was expected to make itself felt in the same way. In Fig. 4 it can be seen that within experimental error there is no contribution of diffusion to T_1^*; the data are described adequately in terms of molecular rotation. This negative result allows only a lower limit to be set on the value of T_1^* and hence on the time τ between diffusional jumps. The lower limit on T_{1d}^* is about 10^{-2} sec; the lower limit on τ is $\sim 2 \times 10^{-2}$ sec, as estimated with the aid of (8). Likewise the free induction decay did not show any change in shape or length to the highest temperatures. This indicates that T_2 has not increased due to diffusional motion. Such an increase could not have occurred however unless there were an observable T_1^* due to diffusion, since T_1^* is a more sensitive indicator (by orders of magnitude) for diffusion. Thus the high temperature T_2 plateau in Fig. 2 has been extended to the melting temperature.

5. Discussion

A. OVERVIEW OF JUMP-RATE RESULTS

In the previous section the NMR measurements were analyzed to give the jump-times for rotation and diffusion as functions of temperature. In Fig. 5 the jump times have been expressed as jump frequencies, $\nu = \tau^{-1}$ and plotted on a semi-log scale versus reciprocal temperature. These linear plots represent the least squares fits to the appropriate data, and the plots extend only over the temperature range in which data was actually obtained. The results of Smith for the diffusion of the water impurity in HMT are also included. A glance at Fig. 5 shows that through NMR techniques we have measured jumping rates from less than one per sec to greater than 10^{11} per sec.

The simple Arrhenius law (11) has been used to fit the data; τ_0 and H_{act} have been deduced. The fact that such a law fits the data is a *sine qua non* for the validity of that law. But the values of τ_0 and H_{act} must also be found reasonable. The enthalpy of activation should agree with a theoretical estimate based on a suitable inter-

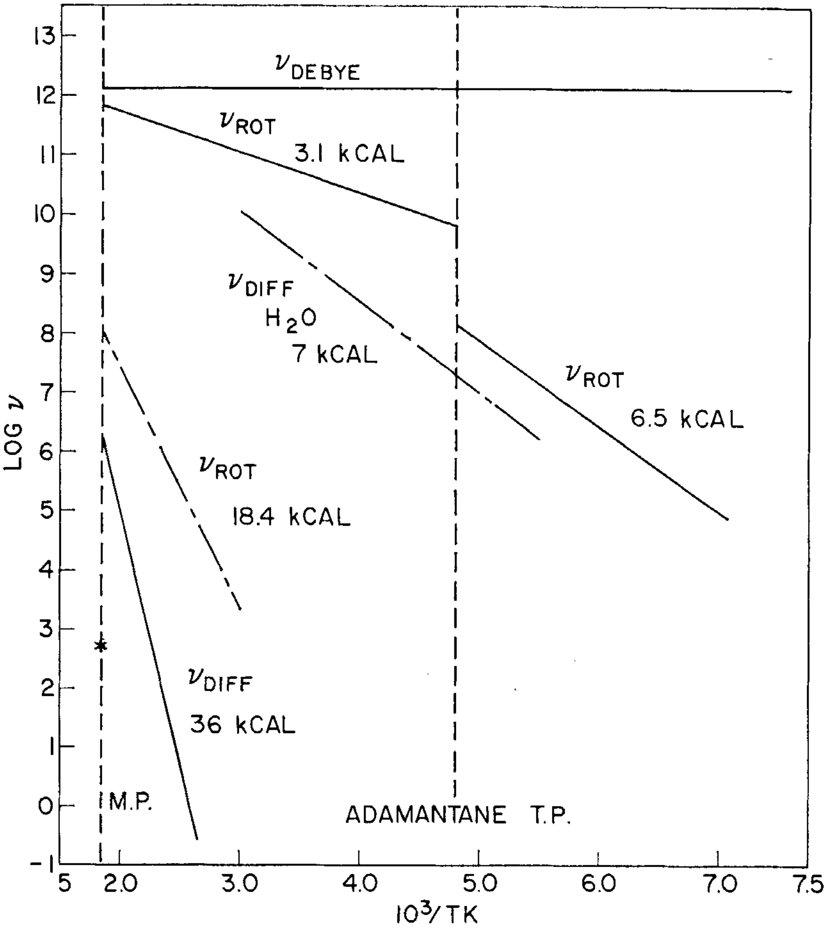

Figure 5. Summary of jump frequencies for the various motional processes: solid lines; adamantane: dashed lines; HMT. The frequency ν_D is the Debye frequency for adamantane. The * indicates the upper limit to the jump frequency for HMT diffusion.

molecular potential function. Unfortunately such calculations for rotation in adamantane and HMT do not exist; nor will they be given here. For diffusion an estimate of H_{act} can be made by scaling the theory for rare gas solids,[33,34] if one wishes to neglect the angular part of the intermolecular potential function; this will be discussed later. The pre-exponential factor is a product of two factors:

$$\tau_0 = \nu_D^{-1} \exp(-S_{\text{act}}/R), \tag{15}$$

Where ν_D is roughly equal to the Debye cutoff frequency, which characterizes the phonon spectrum of the solid, and S_{act} is the entropy of activation. For rotation the frequencies were estimated from the relation[36]

$$\nu_D = (n/2\pi)(H_{\mathrm{act}}/21)^{\frac{1}{2}}$$

where n is 2π divided by the angular separation of nearest neighbor potential minima, and I is the moment of inertia (485×10^{-40} g cm^{-2} for adamantane; assumed the same for HMT). For diffusion ν_D was taken from slow neutron scattering data.[10] These frequencies are listed in Table 3.

From the frequencies and pre-exponential factors the experimental vibrational entropies of activation were calculated (Table 3). These can be compared with the results of an empirical correlation found by Keyes[37] for diffusion in various solids:

$$S_{\mathrm{act}} = 4\alpha H_{\mathrm{act}} \tag{16}$$

where α is the coefficient of thermal expansion. For α the values given by Mirskaya[6] were used except for β-adamantane for which his number seemed much too low and for which the value 2×10^{-4} was taken.[38] It can be seen that agreement is obtained within a factor of about two, so that the measured values of S_{act} seem reasonable with respect to the summary of past experience expressed in (16). It should be observed, however, that every difference of 4.6 e.u. between the experimental and theoretical values of S_{act} corresponds to a factor of ten in the pre-exponential factor.

B. MOLECULAR ROTATION

Rotation in β-adamantane and in HMT can be considered theoretically well understood, if it is assumed that the value of H_{act} could be successfully calculated from an intermolecular potential. The jump rate is small with respect to the Debye frequency (Fig. 5), and this corresponds to the assumptions of the activated state theories. With respect to this last point, however, rotation in α-adamantane presents a problem. At high temperatures the jump rate differs by only a factor of two from ν_D; yet the Arrhenius law—linearity of $\ln \tau$ *versus* reciprocal temperature—is well obeyed (Figs. 1 and 5).

In more detail, the problem is as follows. The time spent by molecule in the actual process of jumping is about ν_D^{-1}. The time between jumps is τ. The potential well is defined by the neighboring molecules, which in the usual situation ($\tau \gg \nu_D^{-1}$) are in their equilibrium positions. However, when $\tau \sim \frac{1}{2}\nu_D^{-1}$ half of the neighbors are in a state of jump at any instant and H_{act} should be somewhat modified; $T_1 \propto \tau^{-1}$ shouldr eflect this change, but it does not.

Another way of looking at this high temperature situation for α-adamantane rotation is that when $\tau \sim \nu_D^{-1}$ the rotation is becoming free or unhindered. Stockmeyer and Stiller[10] have deduced from their slow neutron scattering results that rotation in adamantane should be free in this sense above 500°K, in agreement with the results of this paper. This effect might also show up as an increase in the heat capacity at high temperatures.

C. Self Diffusion[39]

The diffusion coefficients for adamantane were calculated from the jump times using the relation

$$D = r^2/(6\tau) \tag{17}$$

where r is the elementary jump distance. For vacancy diffusion (assumed in the T_{1}^{*} calculations) r is just the nearest neighbor distance. The diffusion coefficients are shown in Fig. 6. As mentioned previously those derived from T_2 and those derived from T_{1}^{*} do not form a colinear plot. The solid lines represent the least squares fit for which a single H_{act} (i.e. parallel T_2 and T_{1}^{*} plots) was assumed. The separation of the lines is quite outside the experimental error. Ailion and Slichter observed a similar discrepancy in the same direction. Corke and Sherwood have studied diffusion by a plastic flow technique;[39] they estimate the diffusion coefficient for adamantane to be almost a factor of ten greater than reported here despite the fact that they obtain the same activation enthalpy. This discrepancy is perhaps to be expected from the uncertainties in the values of several parameters in the equations relating plastic flow to diffusion. It remains to be seen how closely the values of D reported here would agree with the results of a direct or tracer

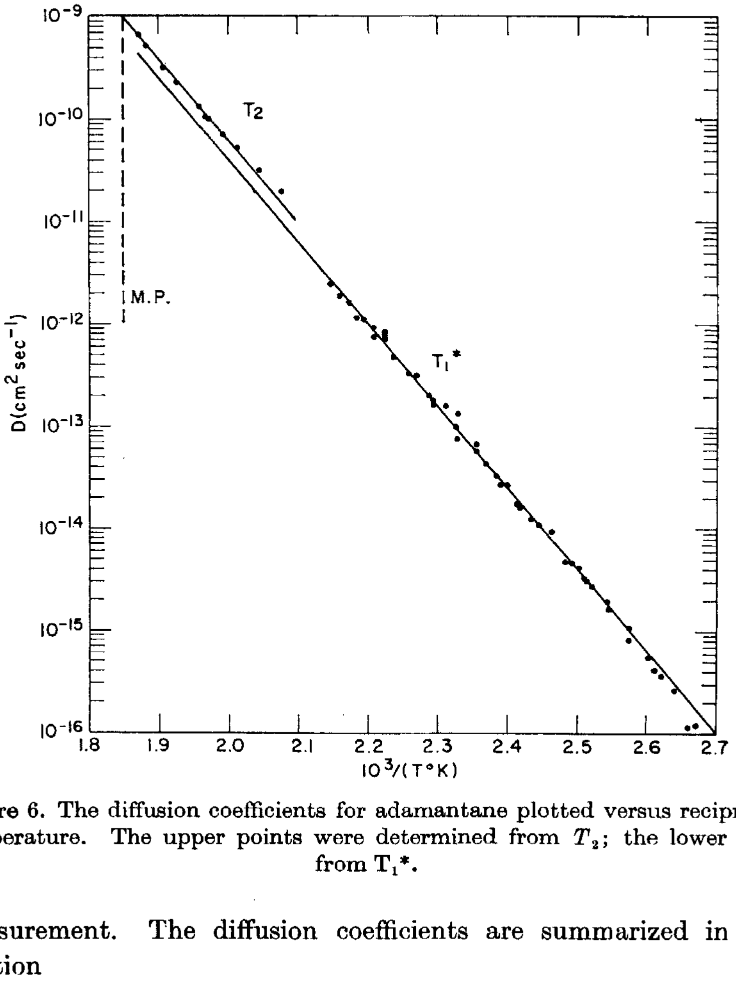

Figure 6. The diffusion coefficients for adamantane plotted versus reciprocal temperature. The upper points were determined from T_2; the lower ones from T_1^*.

measurement. The diffusion coefficients are summarized in the relation

$$D = (4.6 \pm 1.2) \times 10^5 \exp(-36.7 \pm 0.3/RT)\mathrm{cm}^2\,\mathrm{sec}^{-1}$$

This line passes through the points derived from T_1^*.

For HMT the upper limit to the diffusion coefficient at the melting temperature has been estimated to be 10^{-13} cm^2 sec^{-1} (via (7), (8), (9) and (17), i.e. from the lower limit allowable for T_{1d}^*). This is compared with the diffusion coefficients for adamantane and other molecular solids at their respective melting temperatures and with that of liquid water in Table 4. Because of this broad variation the author suspects that the distinction between *plastic* and *brittle*

TABLE 4 Comparison of Diffusion Coefficients at the Melting Temperature

	D(cm^{2}sec^{-1})
Liquid Water	10^{-5}
Cyclohexane[a]	10^{-7}
Adamantane	10^{-9}
Naphthalene[b]	10^{-11}
HMT	$\leqslant 10^{-13}$

a. Hood, G. M. and Sherwood, J. N., *Mol Cryst.* **1**, 97 (1966).
b. Sherwood, J. N. and White, D. J., *Phil. Mag.* **15**, 745 (1967).

crystals is not really as sharp as has been supposed. In order to emphasize the difference between the diffusional mobility of adamantane and HMT however, let the reader note (from Table 4) that at their melting temperature HMT is as different from adamantane as adamantane is from liquid water, i.e. there is a jump of at least four orders of magnitude in each comparison. *This comparison of the diffusion coefficients of adamantane and HMT at the melting temperatures is the main result of this paper. The hypothesis that adamantane, a plastic crystal, and HMT, a brittle crystal, should be vastly different in their self diffusion coefficients is well verified.* Corke and Sherwood[39] have partially substantiated this conclusion in another way; they have shown that self diffusion is the rate limiting step in the plastic deformation of adamantane, according to (1), and they have used the plastic deformation measurements to deduce H_{act}. What remains to be done to complete the picture is a similar study on HMT.

Sherwood in his presentation[40] has compared the diffusion data for molecular crystals. In what follows we compare the activated state parameters for adamantane with those for lead, a typical metal, in order to emphasize the differences between the two classes of materials. For metals one may fairly closely estimate the enthalpy of activation as $32\,T_m$. This product for adamantane is 17, hardly half the observed value of $H_{act} = 36.7$ kcal/mol^{-1}. By this criterion the activation enthalpy for adamantane is a large number indeed. The activated state parameters must of course reflect the strength of the intermolecular forces, and we wish to inquire briefly into a comparison of such forces between lead and adamantane. If diffusion occurs by a vacancy mechanism, H_{act} is the sum of two parts,

H_f the enthalpy of formation of a vacant lattice site, and H_m the enthalpy necessary to move a neighboring atom or molecule to the top of the potential barrier. An upper limit on H_f is the cohesive energy or heat of vaporization H_{vap} of the crystal; if relaxation of near neighbors occurs $H_f < H_{vap}$. For metals such relaxation has been shown to occur; for lead it has been shown that $H_f \sim \frac{1}{3} H_{vap}$ (see Table 5). For molecular crystals theory shows that such extensive relaxation should not occur.[33,34] Thus despite the fact that lead has a cohesive energy ~3 times greater than adamantane, the enthalpy of formation of the respective vacancies is nearly the same (Table 5). If these values of H_f are subtracted from the respective values of H_{act}, one obtains the enthalpy of motion H_m, which is twice as great for adamantane as for lead (Table 5). The lack of relaxation, and the high enthalpy of motion both show that the repulsive part of the intermolecular potential energy function must be quite steep for adamantane. On intuitive grounds this seems quite plausible; one views the metal atom as an easily deformable (polarizable) body, but one sees the molecular framework as a rigid structure. Now Pb and adamantane have roughly the same diffusion coefficient at their respective T_m's, which are rather

TABLE 5 Activation Parameters for Diffusion: Comparison of Adamantane and Lead

	Adamantane	Lead
T_m (°K)	540	600
H_{vap} (k cal/mol)	14.5[a]	43
H_{form} (k cal/mol)	~ 14.5	~13[c]
H_{motion} (k cal/mol)	2 2[b]	13[b]
H_{act} (k cal/mol)	36.7	26[d]
S_{act} (e.u.)	40	11[e]
F_{act} at T_m (k cal/mol)	15[f]	19[f]

a. Bratton, W. K., Szilard, I. and Cupas, C. A., *J. Org. Chem.* **32**, 2019 (1967).
b. $H_{motion} = H_{act} - H_{form}$
c. Leadbetter, A. J., Newsham, D. M. T. and Picton, N. H., *Phil. Mag.* **13**, 371 (1966).
d. Resing, H. A. and Nachtrieb, N. H., *J. Phys. Chem. Solids* **21**, 40 (1961).
e. Calculated from (d).
f. Calculated as $F_{act} = H_{act} - T_m S_{act}$.

close; but they have vastly different values of $H_{\rm act}$. The real rate governing parameter however is the free energy of activation

$$F_{\rm act} = H_{\rm act} - TS_{\rm act},$$

and these are much closer for the two materials than the $H_{\rm act}$, due of course to the vastly different $S_{\rm act}$. This large entropy of activation for diffusion seems characteristic of molecular solids,[40] while $S_{\rm act}$ for metals is much smaller.[41]

Adamantane is a large molecule, having a molar volume $V_{\rm mol}$ of 128 cm^3. If the volume of activation $V_{\rm act}$ were an appreciable fraction of $V_{\rm mol}$ the effect of pressure on diffusion and hence on relaxation would be quite large, i.e. roughly ten times greater than for lead[42] ($V_{\rm act}({\rm Pb}) = 12$ cm^3 mol^{-1}). No information on the effect of pressure is given here however; these considerations are merely speculations to form the basis for future experiments. To go further, there are several theoretical relations to estimate $V_{\rm act}$. Burton and Jura[33] in their calculations on argon estimate $V_{\rm act} = 1.2\ V_{\rm mol}$. A correlation found by Keyes[37] leads one to expect

$$V_{\rm act} = 4\beta H_{\rm act} = 123\ {\rm cm^3\ mol^{-1}},$$

(using a reasonable estimate for the compressibility β). According to Lawson's thermodynamic analysis[43]

$$V_{\rm act} = (\beta/\alpha)S_{\rm act} = 78\ {\rm cm^1\ mol^{-1}}.$$

If the assumption is made as Nachtrieb[42] has done, that the diffusion coefficient remains constant at the melting temperature as the latter is changed by pressure, then

$$V_{\rm act} = H_{\rm act}\frac{1}{T_{\rm m}}\frac{dT_{\rm m}}{dP}$$

$$= H_{\rm act}\frac{V_{\rm melt}}{H_{\rm melt}} = 23\ {\rm cm^3\ mol^{-1}}$$

if one uses the value of $dT_{\rm m}/dP$ from the work of Pistorius and Snyman.[7] This last result is quite far from the other estimates. Thus the effect of pressure on adamantane diffusion would be a crucial test of Nachtrieb's $T/T_{\rm m}$ law, since its predictions differ so much from the others.

6. Summary

The conclusions of this paper are the following:

1. The hypothesis that adamantane, a *plastic* crystal, and HMT, a *brittle* crystal, should be vastly different in their self diffusion properties has been verified.
2. The diffusion coefficient for adamantane has been measured over nearly seven orders of magnitude.
3. An upper limit for the diffusion coefficient of HMT has been deduced.
4. The ultra-slow motion technique of Ailion and Slichter has been verified for molecular crystals; it has been shown experimentally that the proper local field to be used in their theory when molecules are rotating rapidly must be derived from the motionally reduced second moment.
5. The theory of Solomon and Ezratty as regards the ratio T_1 to T_1^* has been verified.
6. The jump rate for molecular rotation in HMT has been measured. This extension of the work of Smith is in agreement with his earlier results.
7. The jump rate for molecular rotation in both phases of adamantane has been measured. That in the high temperature phase is anomolous as far as the activated state theory is concerned.

Acknowledgements

The author would like to thank Steven L. Knapp for his assistance in setting up the experiment. A letter of advice from Prof. C. P. Slichter was helpful.

REFERENCES

1. The first paragraph epitomizes the conclusions of the 1960 Oxford symposium on " Plastic Crystals and Rotation in the Solid State "; *J. Phys. Chem. Solids* **18** pp 1–92, (1961). See especially the first article by J. Timmermans.
2. Barrett, C. R. and Nix, W. D., *Acta Met.* **13**, 1247 (1965).
3. Weertman, J., *J. Appl. Phys.* **28**, 362 (1957).
4. De Vries, K. L., Gibbs, P., Miles, H. and Staten, H. S., *J. Appl. Phys.* **35**, 536 (1964).
5. Chang, S. and Westrum, E. F., *J. Phys. Chem.* **64**, 1547 (1960).

6. Mirskaya, K. V., *Soviet Phys. Cryst.* **8**, 167 (1963).
7. Pistorius, C. W. F. T. and Snyman, H. C., *Z. Phys. Chem.*, N.F. **43**, 278 (1964).
8. Biem, W., *Phys. Stat. Sol.* **3**, 1927 (1963).
9. Kitiagorodskii, A. J., Koreshkov, B. D. and Kul'kin, A. G., *Soviet Phys., Solid State* **7**, 511 (1965): (adamantane).
10. Stockmeyer, R. and Stiller, H. H., *Phys. Stat. Sol.* **19**, 781 (1967): (adamantane).
11. Becka, L. N., *J. Chem. Phys.* **37**, 431 (1962); Becka, L. N. and Cruickshank, D. W. J., *Proc. Roy. Soc. A*. **273**, 455 (1963): (HMT).
12. Carbonell, A. and Canut, M. L., *Rev. Cien. Apl.* (Madrid), **18**, 126 (1964): (HMT).
13. Dolling, G., talk at symposium " Molecular Dynamics and Structure of Solids "; Gaithersburg, Maryland, Oct 1967.
14. McCall, D. W. and Douglass, D. C., *J. Chem. Phys.* **33**, 777 (1960).
15. Smith, G. W., ibid, **35**, 1134 (1961).
16. Resing, H. A., ibid. **43**, 1828 (1965).
17. Smith, G. W., ibid. **36**, 3081 (1962).
18. Yagi, M., *Sci. Repts. Tokoku Univ.* First Ser. **42**, 182 (1958).
19. Slichter, C. P. and Ailion, D. C., *Phys. Rev.* **135**, A1099 (1964).
20. Ailion, D. C. and Slichter, C. P., *Phys. Rev.* **137**, A235 (1965).
21. Bloembergen, N., Purcell, E. M. and Pound, R. V., *Phys. Rev.* **73**, 679 (1948); as modified by Kubo, R. and Tomita, K., *J. Phys. Soc. Japan* **9**, 888 (1954).
22. Look, D. C. and Lowe, I. J., *J. Chem. Phys.* **44**, 2995 (1966).
23. Van Vleck, J. H., *Phys. Rev.* **74**, 1168 (1948).
24. Kroon, D. J., *Philips Res. Repts.* **15**, 501 (1960).
25. Torrey, H. C., *Phys. Rev.* **92**, 962 (1953); ibid. **96**, 690 (1954); Resing, H. A. and Torrey, H. C., ibid. **131**, 1102 (1963).
26. Solomon, I. and Ezratty, J., *Phys. Rev.* **127**, 78 (1962).
27. Resing, H. A. and Thompson, J. K., *J. Chem. Phys.* **46**, 2876 (1967).
28. Blume, R. J., *Rev. Sci. Instr.* **32**, 554 (1961).
29. Lurie, F. M., Thesis, University of Illinois; University Microfilms (Ann Arbor 1964); No. 64–6103.
30. Stranski, I. N., Klipping, G., Bogenschuetz, A. F., Heinrich, H. J. and Maening, H., *Advances in Catalysis* **9**, 406 (1957).
31. See, however, reference 15.
32. Ailion, D. C. and Ho, P. P., *Phys. Rev.* **168**, 662 (1968).
33. Burton, J. J. and Jura, G., *J. Phys. Chem. Solids* **27**, 961 (1966); ibid. **28**, 705 (1967).
34. Glyde, N. R., *J. Phys. Chem. Solids*, **27**, 1659 (1966); *Rev. Mod. Phys.* **39**, 373 (1967).
35. Alexander, S. and Tzalmona, A., *Phys. Rev.* **138**, A845 (1965).
36. Waugh, J. S. and Fedin, E. I., *Soviet Physics—Solid State* **4**, 1633 (1963).
37. Keyes, R. W., *J. Chem. Phys.* **29**, 467 (1958).
38. Bondi, A., *Physical Properties of Molecular Crystals, Liquids and Glasses* (John Wiley and Sons, Inc., New York, 1968) p. 44.
39. The data of this section have already been presented in the literature: Resing, H. A., Corke, N. T. and Sherwood, J. N., *Phys. Rev. Letters* **20**,

1227 (1968). Due to a numerical error the pre-exponential factor given there for the NMR-determined diffusion coefficients was in error.

40. Sherwood, J. N., previous paper.
41. Zener, C., *J. Appl. Phys.* **22**, 372 (1951).
42. Nachtrieb, N. H., Resing, H. A. and Rice, S. A., *J. Chem. Phys.* **31**, 135 1959).
43. Lawson, A. W., *J. Phys. Chem. Solids* **3**, 250 (1957).