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Tunnelling molecular motion in glassy glycerol at very low temperatures as studied by ^1H SQUID nuclear magnetic resonance

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Abstract. The ^1H nuclear spin–lattice relaxation process in glycerol has been studied at temperatures from 3.5 K to 300 K over a very wide range of Larmor frequency between 236 kHz (0.00554 T) and 21.0 MHz (0.4932 T). A superconducting quantum interference device (SQUID) was used to detect the longitudinal component of magnetization of the proton at very low frequencies below 1.62 MHz. At sufficiently low temperatures the nuclear spin–lattice relaxation rate obeys a relation $1/T_1 \propto (T^2/\omega^\beta) \int_0^{6/T} [(x dx)/\sinh x]$, (with β around 0.9 below 25 K), implying that the relaxation rate is governed by an excitation of low-frequency disordered modes inherent to the glassy state of glycerol and becomes asymptotically $1/T_1 \propto T^2$ below $T = 3$ K and $1/T_1 \propto T$ above $T = 3$ K. The relaxation phenomena can be interpreted as the nuclear spin flipping associated with a Raman process which is induced by a coupling of thermally activated low-frequency disordered modes or low-frequency excitation (LFE) with a phonon bath. The LFE originates from a quantum-mechanical two-level system (TLS) reflecting an asymmetric-double-well (ASDW) potential which is formed by the hydrogen bonding configuration in the glassy state of glycerol. The maximum characteristic asymmetry of the double-well potential was found to be (3 ± 1) K. This quantum-mechanical molecular motion dominates the other relaxation mechanisms at low temperatures, such as the dipolar relaxation due to molecular classical reorientation with distributed correlation times.

1. Introduction

It has been well known for some time that the heat capacity of normal crystalline material varies as T^3 at low temperatures as is expected by Debye's phenomenological theory. Zeller and Pohl revealed in 1971 that the heat capacities of some inorganic glasses vary linearly with temperature below 1 K, in contrast to normal crystalline solids [1]. It was also recognized that the thermal conductivities of inorganic glasses vary as T^2 , being different from crystalline solid.

The anomalous behaviour of the heat capacity, the thermal conductivity and also the ultrasonic absorption at low temperatures in glassy material has been pointed out to be universal [2]: several kinds of inorganic amorphous material [1], organic polymers [3, 4], as well as hydrogen bonded organic glass formers [5–7] show distinct anomalies. These anomalous

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physical properties common to amorphous materials suggested the existence of very low-energy or low-frequency excitation (LFE) intrinsic to amorphous substances.

A number of theoretical approaches to such interesting phenomena in amorphous materials at low temperatures has been proposed so far: these are localized electronic states, dispersion of damped phonons, tunnelling in two-level states, cavity models, cellular and microcrystalline effects, scattering by structural inhomogeneities, dislocations and propagating bosons and/or solitons. However, only the tunnelling mechanism in a two-level system (TLS) [8, 9] can satisfactorily account for the anomalous heat capacity, thermal conductivity and ultrasonic attenuation, as well as other experimental results concerning dielectric absorption, low-frequency Raman spectra and so on, in glasses at low temperatures.

Although the phenomenological TLS model is very successful in interpreting a variety of experimental works on the low-temperature glasses, the nature of the tunnelling entities remains still unknown. It is thus desired to identify the tunnelling entity in glasses, by performing experiments which can provide microscopic and localized information on the structure and dynamics of glassy materials.

Magnetic resonance can be one of the most suitable experimental techniques to investigate the existence of the tunnelling entity and its dynamical nature. Several kinds of inorganic glass have been studied at low temperatures by nuclear magnetic resonance (NMR): temperature dependence of the nuclear spin–lattice relaxation rate was measured for each nucleus in glassy As_2S_3 [10], glassy B_2O_3 and $(\text{Na}_2)_{0.3}(\text{SiO}_2)_{0.7}$ [11], glassy $\text{Na}_2\text{B}_4\text{F}_7$ and selenium [12]. Pulsed electron spin resonance was also applied to examine local amorphous structure in glassy V_2O_5 by probing V^{4+} [13] and the nature of paramagnetic centres produced by irradiation of amorphous K, Li and Na β -alumina [14]. Low-temperature properties of sodium β -alumina and fluorozirconate glasses were extensively studied by NMR [15–21], and the nuclear spin–lattice relaxation rate was found to show a simple power-law dependence on temperature, suggesting the presence of LFE [15, 18–21].

The purpose of the present work is to measure the proton spin–lattice relaxation time T_1 in glassy glycerol over a very wide range of Larmor frequency at very low temperatures in order to examine the existence of any LFE mode or other specific modes in the material. Bulk glycerol consists of simple molecules and forms an extremely stable glassy state [22]. There is a possibility of quantum-mechanical tunnelling of protons *via* the hydrogen bonding network of an $\text{O}-\text{H}\cdots\text{O}$ type which is formed over the whole size of the specimen. Thus we would be able to identify the tunnelling entity of question in the TLS model. In order to collect the relaxation data on ^1H over an extremely wide frequency range, we designed and constructed an NMR apparatus by making use of a SQUID (superconducting quantum interference device) magnetometer in addition to using a conventional NMR apparatus for the 10^7 Hz region. This SQUID NMR spectrometer operates at the low Larmor frequencies between 236 kHz and 1.62 MHz. Experimental results of the temperature and frequency dependence of the ^1H spin–lattice relaxation rate in glassy glycerol at low temperatures are discussed in terms of the spin flipping mechanism associated with a Raman process due to the coupling of the LFE to the phonon bath; the process is based on the quantum-mechanical two-level-system model [23].

2. Experiment

A sample of glycerol (commercial redistilled glycerol which contains less than 0.5% of water) was purified by the following three-step dehydration process under reduced pressure down to 10^{-5} Torr to avoid any accidental contamination: (1) dehydration by keeping the specimen at 100°C for 150 hours, (2) dehydration by adsorption at 100°C by the use of the molecular

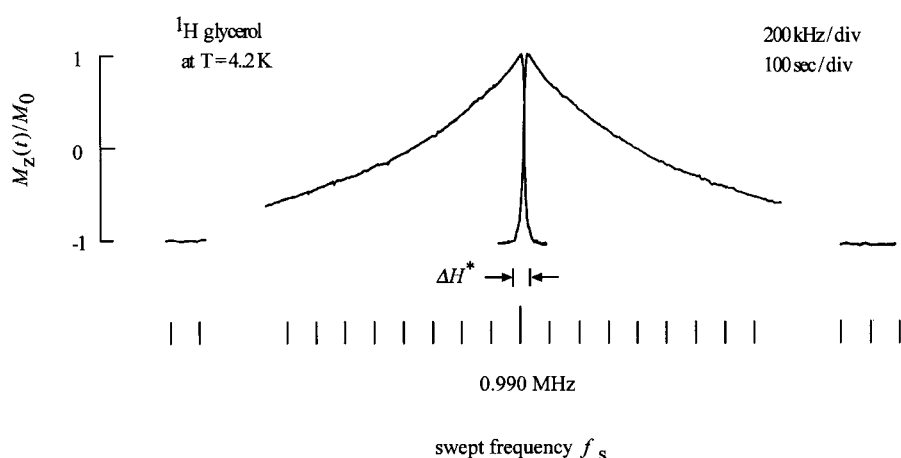


Figure 1. Adiabatic rapid-passage NMR spectrum of protons in glycerol at 4.2 K in a magnetic field of 232 G (0.0232 T) recorded by the use of a SQUID. This trace is the superposition of passages in both directions of the frequency sweep. The ordinate is labelled in units of the equilibrium magnetization of the protons in glycerol in the applied field. The abscissa indicates the lapse of time. In this figure ΔH^* shows an apparent line-width which is defined as the distance between rising points of both directions of the frequency sweep.

sieve 3A for 24 hours and (3) successive fractional distillation. No trace of heavy metals was observed by both ICP (inductively coupled plasma) and AA (atomic absorption) analyses to within their detection limits below 10 p.p.b. or less. No trace of free radicals was detected by an electron spin resonance experiment (X-band) to within its detection limit of 10^9 spins/ ΔH_{pp} at 77 K.

A SQUID magnetometer was used to detect the change in the magnetic flux due to ^1H nuclear magnetic resonance at low magnetic fields below 0.038 T making use of flux-locked-loop operation. The SQUID NMR spectrometer was constructed by referring to a design by Webb [24]. It consists of a SQUID magnetometer system (SHE model 330), a radio-frequency system and a stable external solenoid magnet made of a superconducting field trapping tube.

Among several methods of SQUID NMR developed so far, we employed the adiabatic rapid-passage (ARP) experiment [25] throughout the present work because it is suitable to measure the long spin-lattice relaxation time T_1 of protons at very low temperatures. The adiabatic rapid-passage (ARP) method is one of the continuous NMR techniques used to invert the magnetization vector adiabatically by applying a strong rf field and sweeping the frequency quickly through the resonance in a time shorter than the time scale of a spin-lattice relaxation time T_1 . Rf field with a constant amplitude was applied to a specimen by the use of a frequency synthesizer (Hewlett-Packard model 3325A) with its accuracy of frequency to within 10^{-6} .

As shown in figure 1, the magnitude of the equilibrium magnetization, the spin-lattice relaxation time T_1 , the exact resonance frequency (Larmor frequency) and the absorption line-width can simultaneously be determined over a wide range of the Larmor frequency with neither rigorous tuning nor any tedious matching procedure, on sweeping the frequency ω across the resonance under the inequality condition that

$$\gamma H_1^2 \gg d\omega/dt \gg \max(\gamma H_1/T_1, \gamma H_L/T_1, \gamma \Delta H/T_1). \quad (1)$$

In equation (1), γ is the gyromagnetic ratio of ^1H , H_1 the amplitude of the rf field (fixed to

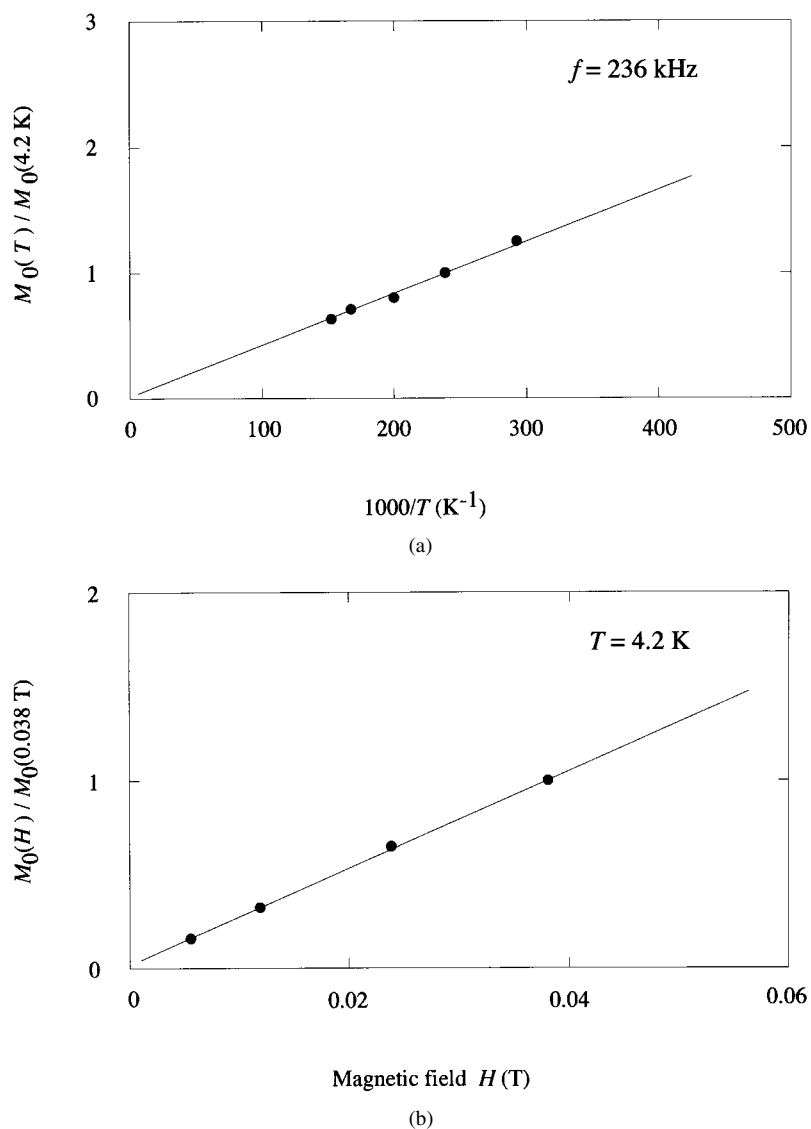


Figure 2. The magnitude of the equilibrium nuclear magnetization, $M_0(H, T)$, of ^1H in glycerol measured under the adiabatic rapid-passage condition by the use of SQUID NMR. (a) Temperature dependence at the fixed external magnetic field of 0.0554 T. The plot gives a straight line, indicating that the Curie law holds. (b) Dependence on the strength of the external magnetic fields at 4.2 K.

15 mG), $d\omega/dt$ the sweeping rate of the angular frequency of the rf field, H_L the local field strength in the rigid lattice which is estimated from the observed second moment of 2.9 G^2 , and ΔH the apparent line-width of the resonance absorption of 5 G.

The present experimental condition was chosen to satisfy equation (1) as follows:

$$\gamma H_1^2 = 12.3 d\omega/dt = 183\text{--}840 \gamma \Delta H/T_1. \quad (2)$$

Because superconducting materials such as Nb-Ti alloy and lead were used in the present experiments, the highest temperature of the measurement was limited by their critical temperatures ($T_c = 7 \text{ K}$ for Nb-Ti alloy). The temperature dependent critical field also limited

the maximum magnetic field to 0.038 T at elevated temperatures above 6 K. Temperature stability was severely controlled to within 10^{-2} K. The control of the vapour pressure of liquid helium was also essential to the stable detection of a weak signal at the lowest field of 5.54 mT (55.4 G).

At high Larmor frequencies above 4.01 MHz a home-built pulsed NMR apparatus was employed to measure T_1 using the pulse sequence of [saturation comb pulses]– τ – $\pi/2$ reading pulse. The recovery of the magnetization signal after the probe pulse as well as the decay of the ARP signal were found to be single exponential throughout the whole measurements, implying that the ^1H relaxation may always be described by a single relaxation process. The lower detection limit of proton nuclear spins in our system at 0.0232 T was deduced to be 3×10^{18} from charged amounts of specimen, the S/N ratio of observed ARP signal as shown in figure 1, and the effective size of radio-frequency coils of 2 mm in diameter.

Figure 2 shows that the magnitude of the equilibrium magnetization M_0 of ^1H in glycerol depends linearly on the reciprocal temperature at the lowest resonance frequency of 236 kHz. A similar linear dependence of the magnitude of M_0 of ^1H in glycerol on the resonance frequency was also confirmed at 4.2 K between 236 kHz and 1.62 MHz, implying that the Curie law holds and the rapid-passage condition is satisfied in each measurement throughout the present experiments, ensuring one obtains a reliable spin–lattice relaxation rate even at ultra-low Larmor frequencies.

3. Results and discussion

Figure 3 shows the observed temperature dependence of the spin–lattice relaxation rate, $1/T_1$, of protons in glycerol at the Larmor frequencies of 4.1 MHz and 21.0 MHz between 4.2 K and 300 K. Also shown in figure 4 is the temperature dependence of the spin–spin relaxation time, T_2 , which was measured by the spin-echo technique above $T_g = 194$ K and by a free-induction-decay time T_2^* below T_g . The characteristic decay time T_2^* was defined by the elapsed time for a free-induction-decay signal to become $1/e$ of an initial value in magnitude using pulsed NMR at 21.0 MHz under the inequality condition that the field inhomogeneity $<$ the resonance line-width $<$ the strength of pulsed H_1 . The spin–spin relaxation time, T_2 , a measure of the inverse of the resonance line-width, shows remarkable change only at T_g . In order to further clarify the relaxation mechanism below T_g , we indicate in figure 5 the frequency dependence of T_1 at two NMR frequencies in the temperature range from 4.2 K to 300 K by assuming that $T_1 \sim \omega_0^\delta$ [26] and extracting $\delta(T)$ at $\omega_0 = 2\pi \times 4.1$ MHz and at $\omega_0 = 2\pi \times 21.0$ MHz. We can see from figure 5 that with increasing temperatures up to those above T_1^{-1} maxima the value of δ approaches zero and the relaxation becomes frequency independent because of extreme motional narrowing. With decreasing the temperatures from those above corresponding to T_1^{-1} maxima down to T_g the relaxation process becomes strongly frequency dependent with δ around 1.3. This exponent stays around 1.3 even at 100 K, which is far below $T_g = 194$ K. At sufficiently low temperatures below 25 K, the exponent δ drops from around 1.3 to lower values around 0.9.

Figure 6(a) shows the observed temperature dependence of the spin–lattice relaxation rate, $1/T_1$, of protons at various Larmor frequencies from 236 kHz to 1.62 MHz using SQUID NMR between 3.5 K and 6 K in addition to the results obtained by the pulsed NMR between 4.2 K and 25 K, where δ stays around 0.9 as appeared in figure 5. Figure 6(b) also indicates the temperature dependence of the relaxation rate, $1/T_1$, at 4.01 MHz and 21.0 MHz by the pulsed NMR between 4.2 K and 100 K, where δ varies from around 1.3 to around 0.9.

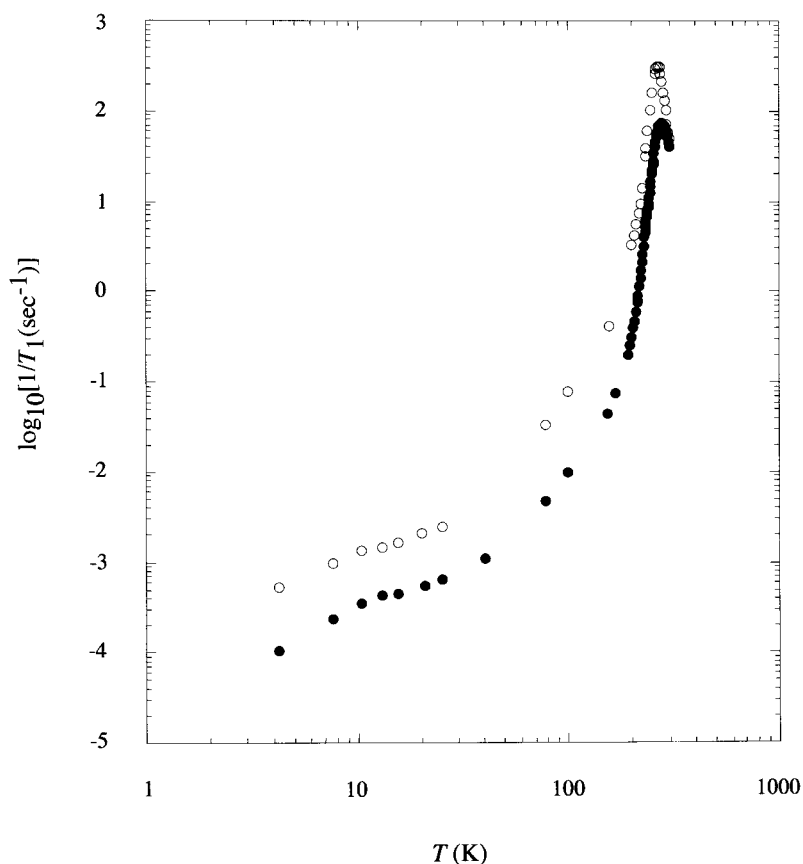


Figure 3. Temperature dependence of the spin–lattice relaxation rate, $1/T_1$, of protons in glycerol at the Larmor frequency of 4.1 MHz (○) and 21.0 MHz (●) between 4.2 K and 300 K obtained by pulsed NMR with $T_g = 194$ K.

In figure 7 we indicate the dependence of T_1 on the Larmor frequency over the frequency range between 236 kHz and 21.0 MHz at 4.2 K.

The T_1 data above about 240 K obtained from the conventional pulsed NMR at 4.10 MHz and 21.0 MHz are consistent with those reported earlier [27–29]. However, the absolute value of T_1 at 77 K (see in figure 3) in the glassy state is almost twice as long as that reported in an earlier study [27]. The value of T_1 observed at the Larmor frequency of 21.0 MHz at around 4.2 K might be larger by a factor of 1.6 than the one measured at 35 MHz [29], if we assume the linear frequency dependence of T_1 as being confirmed in our experiments at 4.2 K at higher Larmor frequencies above 4.1 MHz. The reason for the discrepancy is unknown at the present stage.

We can summarize our experimental results on the glassy state of glycerol at low temperatures far below T_g as follows.

- (1) There seem to be two regions in which different types of molecular motion govern the spin–lattice relaxation above and below $T_g = 194$ K. However, as figure 3 shows some low-frequency excitation seems to play an important role for the spin–lattice relaxation rate especially at low temperatures far below T_g although this is not obvious in T_2 results.

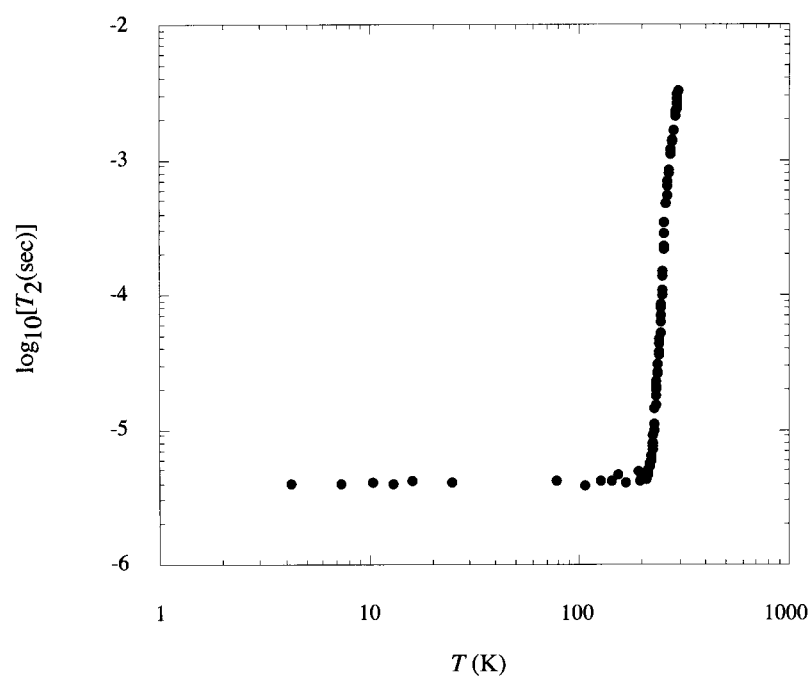


Figure 4. Temperature dependence of the spin–spin relaxation time, T_2 , of protons in glycerol as measured by the spin-echo technique above $T_g = 194$ K and by a free-induction-decay time T_2^* below T_g using pulsed NMR at 21.0 MHz under the detailed conditions described in the text.

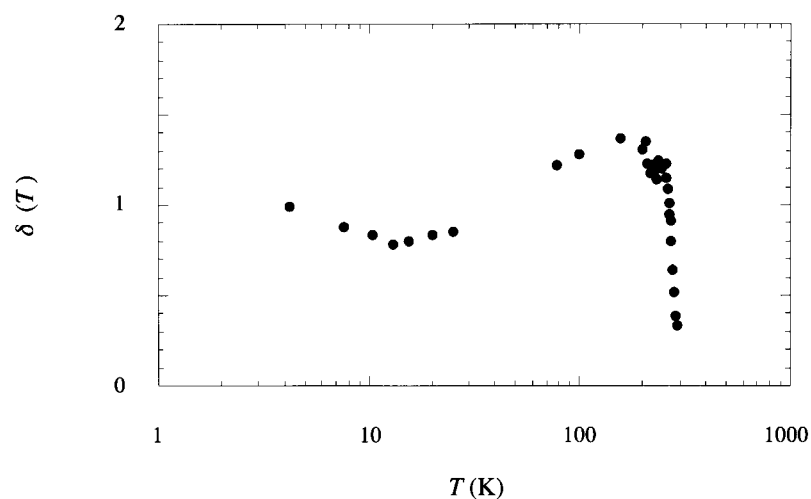


Figure 5. The frequency dependence of T_1 at two NMR frequencies between 4.2 K and 300 K by assuming that $T_1 \sim \omega_0^\delta$ and extracting $\delta(T)$ at the Larmor frequencies of 4.1 MHz and 21.0 MHz.

- (2) The temperature dependence of relaxation time at higher frequency above 4.1 MHz reveals that the exponent δ in $T_1 \sim \omega_0^\delta$ changes from around 1.3 to lower values around 0.9 at sufficiently low temperatures below 25 K as shown in figure 5.

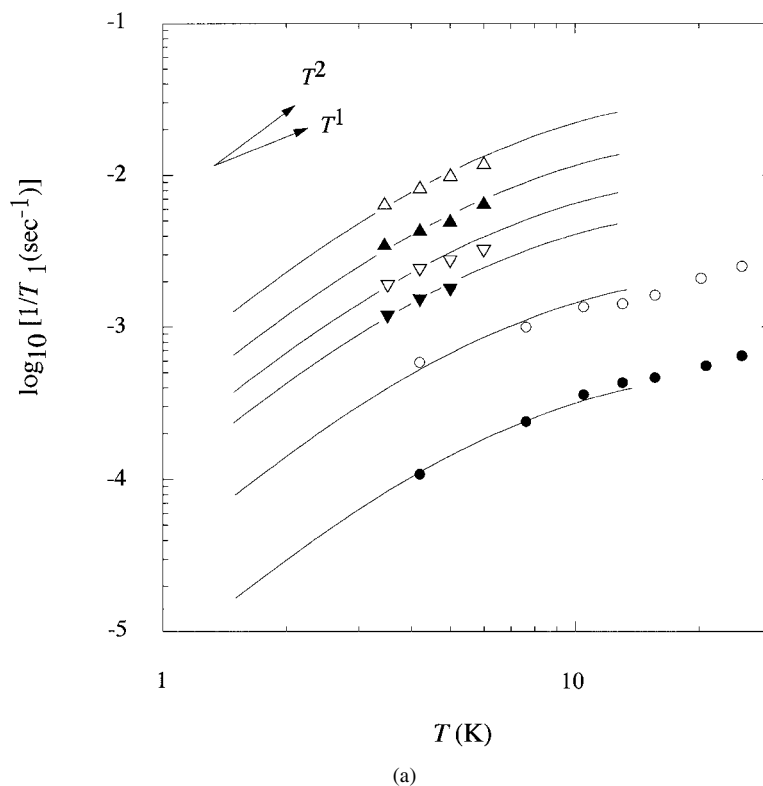


Figure 6. Log–log plot of the nuclear spin relaxation rate $1/T_1$ of ^1H in glycerol against temperature. (a) Below 25 K measured by using SQUID NMR at the Larmor frequency of 236 kHz (Δ), 494 kHz (\blacktriangle), 1.01 MHz (∇) and 1.62 MHz (\blacktriangledown) together with the relaxation rate at the Larmor frequencies of 4.01 MHz (\circ) and at 21.0 MHz (\bullet) obtained by pulsed NMR. (b) From 4.2 K to below 200 K at the Larmor frequency of 4.01 MHz (\circ) and at 21 MHz (\bullet). Solid curves below 25 K indicate the relaxation rates expressed by equation (9), $1/T_1 \propto (T^2/\omega^\beta) \int_0^{6/T} [(x dx)/\sinh x]$, deduced from the spin–lattice relaxation induced by the Raman process [13] induced by the coupling between TLS and a phonon system. Solid arrows in both figures denote the slope of the expression (9) in a log–log plot as $1/T_1 \propto T$ at the higher-temperature limit and as $1/T_1 \propto T^2$ at the lower-temperature limit.

- (3) The relaxation rates obtained from 236 kHz to 21.0 MHz at low temperatures do not behave monotonically with temperature especially below around 25 K.
- (4) The spin–lattice relaxation times at 4.2 K increase as the Larmor frequencies from 236 kHz to 21 MHz but do not simply and linearly depend on frequency but change gradually with slope less than unity especially at lower frequencies.

Such a unique dependence of relaxation rate on temperature and frequency at low temperatures far below T_g cannot be interpreted by the usual BPP theory, although the relaxation rate above T_g can be described by the modified BPP process with a Cole–Davidson type distribution of correlation times for thermally activated classical molecular reorientational motion [30].

Therefore we need to establish a theoretical model for the dynamic structure of glassy glycerol at low temperatures far below T_g that can interpret the above experimental results of the nuclear spin–lattice relaxation.

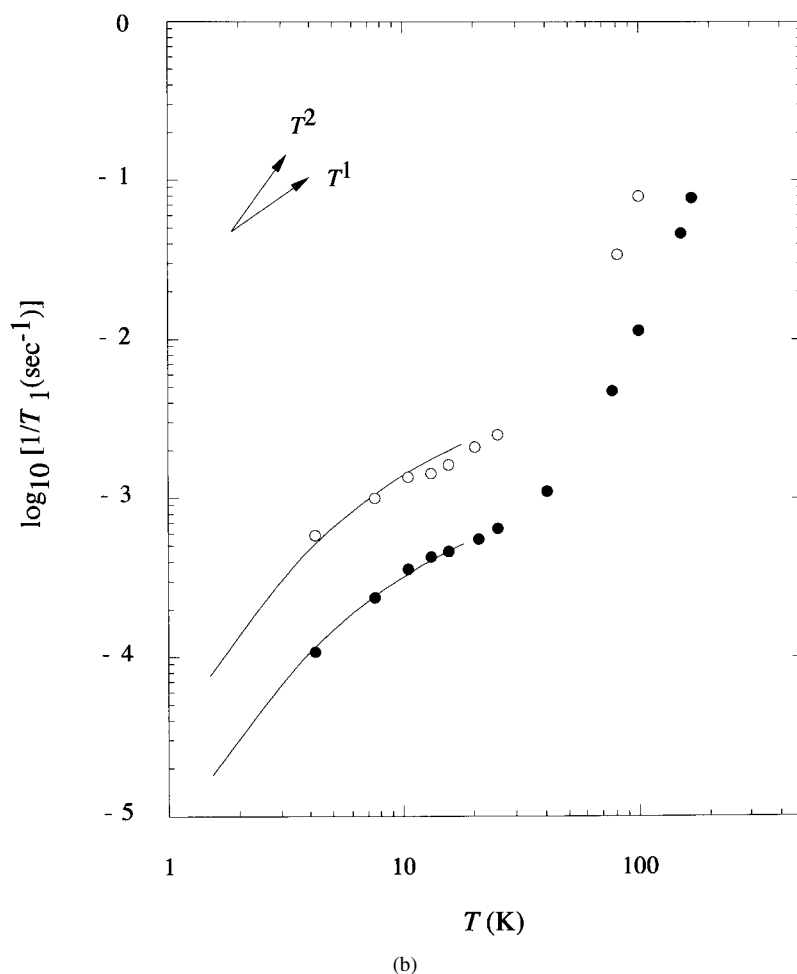


Figure 6. (Continued)

It has long been recognized that any unique frequency dependence of the relaxation rate in glassy materials is related to some specific type of distribution [31–36] of the correlation time for the molecular motional process. From a microscopic point of view, a distribution of the correlation time might come from a distribution of the height of the potential energy barrier that hinders the molecular motion. In the case of nuclear magnetic relaxation due to the molecular motion in glassy material it was shown that the Cole–Davidson distribution [37], originally presented to interpret the dielectric behaviour of glassy materials in a supercooled state, can also account for the unique spin–lattice relaxation of organic glasses at lower temperatures below T_g .

The Cole–Davidson distribution in the limiting case of $\omega\tau^* \gg 1$ leads to a relaxation rate as

$$\frac{1}{T_1} = C \sin(\gamma\pi/2) \tau^{*-\gamma} \omega^{-(1+\gamma)} \quad \text{for } 0 < \gamma \leq 1 \quad (3)$$

where τ^* is called the upper cutoff of the correlation time, γ is a parameter which represents the extent of the distribution of the correlation time for molecular motion and C a constant

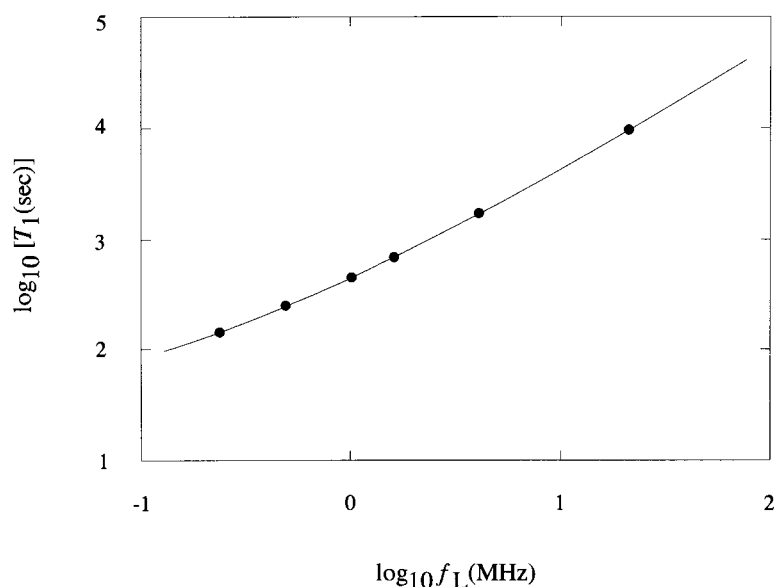


Figure 7. Log–log plot of the nuclear spin relaxation time T_1 of ^1H in glycerol at 4.2 K against the ^1H Larmor frequency measured by a SQUID NMR below 1.62 MHz and by a pulsed NMR above 4.01 MHz. Spin–lattice relaxation time T_1 does not linearly depend on frequency but changes with its slope less than unity especially at lower frequencies. The solid curve is a guide to the eyes.

corresponding to the strength of the nuclear magnetic dipole–dipole interaction between protons.

Equation (3) was applied successfully to the relaxation data for some organic glass formers [38, 39]. In the present study on glassy glycerol we found that the observed spin–lattice relaxation rate above about 77 K can well be reproduced by equation (3) using the parameter $\gamma = 0.3$. On the other hands, at 4.2 K, we extracted the value of γ to be 0.07 ± 0.02 by fitting equation (3) to the observed $1/T_1$ and obtained the activation energy of 3.3 kJ mol^{-1} , which is larger by about two orders of magnitude than the apparent activation energy of 80 J mol^{-1} deduced directly from figure 6(b) below 25 K. Therefore it becomes clear that equation (3) cannot account for a very weak temperature dependence of spin–lattice relaxation rate observed experimentally below 25 K. It is thus concluded that the original BPP theory and its modifications assuming any specific distribution of the motional correlation time cannot describe the proton spin–lattice relaxation process. It is therefore considered that the relaxation in glassy glycerol at very low temperatures is caused probably by some specific molecular dynamics other than simple stochastic molecular motion or motions.

In a number of amorphous inorganic and organic glasses it has been pointed out that there should be some entities that can undergo quantum-mechanical tunnelling motion at low temperatures which causes anomalous behaviour of the heat capacity, the ultrasonic velocity and the thermal conductivity in amorphous materials. Rubinstein *et al* [10, 11] and Szeftel *et al* [11, 12] took into account the coupling between the nuclear spin system and the LFE mode arising from TLS as a driving force for the nuclear relaxation in amorphous materials based on the theoretical works on TLS by Phillips [8] and Anderson *et al* [9]. Estalji *et al* [20] assumed the distribution of the correlation time τ for the TLS excitation as a result of a thermally activated classical rate-process model introduced by Phillips [40] in an asymmetric-double-well (ASDW) potential. Application of the fluctuation–dissipation theorem in the presence of

the ASDW potential to the nuclear spin relaxation gives rise to a specific expression for the spin–lattice relaxation rate as [11, 18–21]

$$\frac{1}{T_1} = \delta \int_0^{\Delta_m} d\Delta \int_0^{V_m} dV \frac{P(\Delta)g(V)}{\cosh^2[\Delta/2kT]} \int_{-\infty}^{+\infty} f(\tau/\tau_c) \exp(-i\omega_0\tau) d\tau \quad (4)$$

where δ is the mean coupling energy between the spin ensemble and a single ASDW potential configuration, ω_0 the Larmor frequency and Δ_m and V_m the upper limit of Δ and V , the energy difference and the barrier height between the wells, respectively.

In equation (4), $f(\tau/\tau_c)$ is the time dependent part of the correlation function for the tunnelling motion. It should be noted that the assumption of an exponential decay of $f(\tau/\tau_c)$ is valid for uncorrelated ASDW potential fluctuation and it leads to a normal relaxation behaviour as described by the BPP theory. However, the incorporation of the mutual coupling between the motions of the tunnelling entities gives rise to a stretched exponential decay of Williams–Watts–Kohlrausch type as [41]

$$f(\tau/\tau_c) = \exp[-|\tau/\tau_c|^\beta] \quad \text{for } 0 < \beta \leq 1. \quad (5)$$

Under the conditions on temperature that $T < V_m/k$ and $T < \Delta_m/k$, equation (4) can be approximated by a power law as given by [41]

$$\frac{1}{T_1} \propto T^{1+\alpha}/\omega^\beta. \quad (6)$$

The reduced form of the nuclear relaxation rate as given in equation (6) was applied successfully to the system of poorly conducting oxide glasses at temperatures below 100 K as well as at higher temperatures at which the motion of large ions takes place in a conducting glass [21]. However, it is not fully applicable to our present relaxation data because the factor α in equation (6) should be a function of temperature in the present experimental result of glycerol especially below 10 K. We should further clarify the model which can account for the present temperature dependence of the spin–lattice relaxation at low temperatures.

In order for the relaxation to be explicitly temperature dependent at low temperatures, it is natural to take into account the Raman process caused by a coupling between a TLS and a specific phonon system [40] as the spin–lattice relaxation scheme [13]. Applying the second-order perturbation theory to the magnetic dipolar interaction, the nuclear spin–lattice relaxation is given by

$$\frac{1}{T_1} \propto \int_{-\infty}^{+\infty} d\tau e^{-i\omega\tau} f(\tau/\tau_c) |h_{D1,2}|^2 [(\Delta_0/\hbar\omega)^2 G_z^2 + (\Delta/\hbar\omega)^2 G_x^2] \frac{E}{\sinh(2E/kT)} \quad (7)$$

where h_D denotes the off-diagonal elements of the dipolar interaction Hamiltonian between neighbouring protons under study. The integration in time domain extracts the power spectrum which is responsible for the spin–lattice relaxation. Also, G_x and G_z represent elastic terms [13, 14] of the forms $(1/E)(-\partial\Delta/\partial e)\Delta_0 + (\partial\Delta_0/\partial e)\Delta$ and $(1/E)(-\partial\Delta/\partial e)\Delta + (\partial\Delta_0/\partial e)\Delta_0$, respectively, where e is the strain caused by a phonon, Δ_0 the ground-state splitting for $\Delta = 0$ and $E = (\Delta_0^2 + \Delta^2)^{1/2}$, corresponding closely to the energy of phonon modes with $\hbar\omega$. The above treatment is based on a fundamental assumption that Δ and Δ_0 are distributed uniformly up to their individual cut-off values just as in the case of distribution of Δ and V . The distribution function, $P(\Delta, \Delta_0)$, for Δ and Δ_0 in the TLS is defined as a simple rectangular function without any correlation between the two quantities according to Phillips [8].

In a usual amorphous material, Δ and Δ_0 may widely be distributed corresponding to highly disordered structure. This means that there would be a broad distribution of the relaxation rates. It should be necessary to average the value of $1/T_1$ over Δ and Δ_0 in order

to obtain an observable relaxation rate [14]. In this situation we suppose that the most of the nuclear spins relax through spin diffusion to the spins which relax faster by interacting directly and strongly with the coupled TLS and with a specific phonon system, as in the case of the very fast relaxation process which has often been encountered in high polymers [42] or aliphatic compounds [43]. It is noted that in each of these complex organic systems the magnetization recovers exponentially just as in the present experimental results on glycerol, being different from the case of quadrupolar nuclei such as ^{23}Na and ^{27}Al in, e.g., vitreous sodium β -alumina [21] and ^2H in glycerol below T_g [26, 44].

Upon choosing the energy E and a parameter $r = (\Delta_0/E)^2$, instead of Δ and Δ_0 , as adjustable variables and using a corresponding distribution function $P(E, r)$ [14] in place of the original $P(\Delta, \Delta_0)$, the relaxation rate can be given by

$$\frac{1}{T_1} \propto T^2 |h_{D1,2}|^2 \int_{-\infty}^{+\infty} d\tau e^{-i\omega\tau} f(\tau/\tau_c) \int_0^{x_M} \frac{x dx}{\sinh x} \quad (8)$$

where x denotes the quantity $2E/kT$, x_M the cut-off value of x and $f(\tau/\tau_c)$ is supposed to be a function which decays in a stretched manner as $\exp[-(\tau/\tau_c)^\beta]$ as pointed out earlier.

In equation (8) at higher temperatures where $2E/kT < 1$, we have $1/T_1 \propto T/\omega^\beta$. In the present situation of an organic glassy material the tunnelling entity is a nucleus itself which constitutes a part of the molecule and so its number amounts to $\sim 10^{21} \text{ cm}^{-3}$ or more. This situation also supports the stretched exponential decay model where TLSs are abundant and thus correlate strongly with each other. At lower temperatures where $x_M = 2E_M/kT > 1$, we have $1/T_1 \propto T^2/\omega^\beta$ which cannot be deduced employing the simple approach expressed by equation (4) based on the direct process [10]. In the present study of glassy glycerol at low temperatures below 25 K where the value of the parameter β is around 0.9, our experimental results of the proton spin–lattice relaxation rate can be represented satisfactorily as shown in figure 6

$$\frac{1}{T_1} \propto \frac{T^2}{\omega^\beta} \int_0^{6/T} \frac{x dx}{\sinh x} \quad (9)$$

if we assume that $2E_M/k = (6 \pm 2) \text{ K}$ in equation (8).

The characteristic energy E_M for TLS, $3kT$, can be understood as the maximum asymmetry of ASDW potential Δ_M because equation (8) is still valid if we replace E_M by Δ_M in the integral under the condition that $kT > \Delta_M$ [13]. This shows that the spin–lattice relaxation measurement can give us the information on the upper limit of the ASDW potential well.

4. Conclusion

The variation of nearly quadratic to linear dependence of the $1/T_1$ of protons on temperature from around 4.2 K to around 25 K as well as its unique frequency dependence in glassy glycerol below 25 K could be interpreted by the coupling between the phonon bath and the low-frequency excitation (LFE) based on the tunnelling two-level system (TLS). The possible existence of characteristic energy E_M/k of $(3 \pm 1) \text{ K}$ was pointed out and its validity was examined from the viewpoint of the perturbation or the modulation of magnetic dipolar interaction by a dynamically coupled TLS to a specific phonon process.

The characteristic energy of $E_M/k = (3 \pm 1) \text{ K}$ can be related to the asymmetry energy of the ASDW potential, Δ_M , as was discussed in [13]. A heat capacity measurement [5] showed that an anomalous linear term in the heat capacity becomes dominant below $T = 2.5 \text{ K}$, consistent with the present experimental results for the proton spin–lattice relaxation rate. Thus the measurement of the spin–lattice relaxation rate over a very wide range of frequency

using a SQUID magnetometer can be used to derive the detailed and quantitative information on the shape of the double-minimum potential well of the TLS. It can therefore be a very useful clue for understanding the structure and the dynamic properties of the glassy state of glycerol at low temperatures from the microscopic point of view.

References

- [1] Zeller R C and Pohl R O 1971 *Phys. Rev. B* **4** 2029
- [2] Phillips W A 1981 *Amorphous Solids, Low-Temperature Properties* ed W A Phillips (Berlin: Springer)
Phillips W A 1987 *Rep. Prog. Phys.* **50** 1657
Klinger M I 1988 *Phys. Rep.* **165** 275
- [3] Reese W 1966 *J. Appl. Phys.* **37** 3959
- [4] Tucker J E and Reese W 1967 *J. Chem. Phys.* **46** 1388
- [5] Leadbetter A J and Wycherley K E 1970 *J. Chem. Thermodyn.* **2** 855
- [6] Craig R S, Massena C W and Mallya R M 1965 *J. Appl. Phys.* **36** 108
- [7] Bonjour E, Calemczuk R, Lagnier R and Salce B 1981 *J. Phys. Coll.* **6** C6–63
- [8] Phillips W A 1972 *J. Low. Temp. Phys.* **7** 351
- [9] Anderson P W, Halperin B I and Varma C M 1972 *Phil. Mag.* **25** 1
- [10] Rubinstein M and Taylor P C 1974 *Phys. Rev. B* **9** 4258
- [11] Szeftel J and Alloul H 1975 *Phys. Rev. Lett.* **34** 657
Rubinstein M, Resing H A, Reinecke T L and Ngai K L 1975 *Phys. Rev. Lett.* **34** 1444
Rubinstein M and Resing H A 1976 *Phys. Rev. B* **13** 959
- [12] Szeftel J and Alloul H 1978 *J. Non-Cryst. Solids* **29** 253
- [13] Deville A, Gaillard B, Blanchard C and Livage J 1983 *J. Physique* **44** 77
- [14] Kurtz S R and Stapleton H J 1980 *Phys. Rev. B* **22** 2195
- [15] Greenbaum S G, Strom U and Rubinstein M 1982 *Phys. Rev. B* **26** 5226
- [16] Dobbs J N, Anderson A C and Hayes W 1983 *Phys. Rev. B* **28** 3559
- [17] Strom U, Ngai K L and Kanert O 1991 *J. Non-Cryst. Solids* **131–133** 1011
- [18] Kanert O, Steinert J, Jain H and Ngai K L 1991 *J. Non-Cryst. Solids* **131–133** 1001
- [19] Ngai K L, Strom U and Kanert O 1992 *Phys. Chem. Glasses* **33** 109
- [20] Estalji S, Kanert O, Steinert J, Jain H and Ngai K L 1991 *Phys. Rev. B* **43** 7481
- [21] Sieranski H, Kanert O, Backens M, Strom U and Ngai K L 1993 *Phys. Rev. B* **47** 681
- [22] Gibson G E and Giaque W F 1923 *J. Am. Chem. Soc.* **45** 93
- [23] Akagi Y 1983 *PhD Thesis* Osaka University
- [24] Webb R A 1977 *Rev. Sci. Instrum.* **48** 1585
Giffard R P, Webb R A and Wheatley J C 1972 *J. Low. Temp. Phys.* **6** 533
Meredith D J, Pickett G R and Symko O G 1973 *J. Low Temp. Phys.* **13** 607
Chamberlin R V, Moberly L A and Symko O G 1979 *J. Low Temp. Phys.* **35** 337
- [25] Abragam A 1980 *The Principle of Nuclear Magnetism* (Oxford: Oxford University Press)
- [26] Schnauss W, Fujara F and Sillescu H 1992 *J. Chem. Phys.* **97** 1378
- [27] Mansfield P and Powles J G 1962 *Proc. 11th Coll. Ampère (Bucharest, 1961)* p 194
- [28] Kintzinger J P and Zeidler M D 1973 *Ber. Bunsenges. Phys. Chem.* **77** 98
- [29] Koivula E, Punkkinen M, Tanttila W H and Ylinen E E 1985 *Phys. Rev. B* **32** 4556
- [30] Connor T M 1964 *Trans. Faraday Soc.* **60** 1574
Roeder S B W, Stejskal E O and Vaughan W E 1965 *J. Chem. Phys.* **43** 1317
Noack F and Preissing G 1969 *Z. Naturf. a* **24** 143
Müller-Warmuth W and Otte W 1980 *J. Chem. Phys.* **72** 1749
Kuhns P L and Conradi M S 1982 *J. Chem. Phys.* **77** 1771
- [31] Noack F and Preissing G 1969 *Z. Naturf. a* **24** 143
- [32] Kusumoto H and Gutowsky H S 1963 *J. Polym. Sci. A* **1** 2905
- [33] Fang P H 1961 *Physica* **27** 681
- [34] Cole K S and Cole R H 1941 *J. Chem. Phys.* **9** 341
- [35] Fuoss R and Kirkwood J 1941 *J. Am. Chem. Soc.* **63** 385
- [36] Hunt B I and Powles J G 1966 *Proc. Phys. Soc.* **88** 513
Torrey H C 1953 *Phys. Rev.* **92** 962
- [37] Davidson D W and Cole R H 1951 *J. Chem. Phys.* **19** 1484
- [38] Roeder S B W, Stejskal E O and Vaughan W E 1965 *J. Chem. Phys.* **43** 1317

- [39] Müller-Warmuth W and Otte W 1980 *J. Chem. Phys.* **72** 1749
- [40] Phillips W A 1990 *Phonons 89, Proc. 3rd Int. Conf. on Phonon Physics* vol 1, ed S Hunklinger, W Ludwig and G Weiss (World Scientific: Singapore) p 367
- [41] Kanert O, Küchler R, Dieckhöfer J, Lu X, Jain H and Ngai K L 1994 *J. Non-Cryst. Solids* **172–174** 1277
- [42] McCall D W and Douglass D C 1963 *Polymer* **4** 433
- [43] Anderson J E and Slichter W P 1965 *J. Phys. Chem.* **69** 3099
- [44] Schnauss W, Fujara F, Hartmann K and Sillescu H 1990 *Chem. Phys. Lett.* **166** 381