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# Nuclear-Spin-Lattice Relaxation of Solid Hydrogen at Low Temperatures*

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We report systematic measurements of the nuclear-spin-lattice relaxation times $T_1$ in the ordered phase of solid hydrogen. The dependence of $T_1$ on temperature $T$ and on the ortho content $X$ is found to be described by $T_1 = AX^4T^{-1}e^{B/T}$, where $A = 1.0 \pm 0.3$ min, $B \simeq [0.4(1.8X-1)+0.24]$ °K for $X > 0.56$ and $B \simeq 0.24$ °K for $X < 0.56$. This functional dependence is in qualitative agreement with that calculated from the rotational correlation times of the quantum crystal lattice. The applied field was 75 kG and the temperature range investigated was 0.075 to 1.5 °K.

## I. INTRODUCTION

The quantum properties of solid mixtures of ortho-para hydrogen have received considerable attention in recent years both experimentally and theoretically. For ortho concentrations greater than 60% these properties lead to a singularity in the specific heat[1-4] and a change in the profile of the NMR absorption line.[5-7] It is now generally accepted that these are associated with the cooperative ordering of the rotational degrees of freedom arising from their collective molecular quadrupolar interactions.

NMR affords a direct means of investigating the rotational excitations arising from these interactions. First, as a consequence of the quenching of the rotational molecular motion the intramolecular magnetic dipole-dipole interaction does not average to zero, and this results in a fine structure which is a direct measure of the orientational order parameter.[8] Second, thermal equilibrium between the nuclear spins and the quantum-crystal lattice is established by the modulation of the intramolecular magnetic dipolar couplings. The correlation times of these thermal fluctuations, given by the rapid transitions between the orientational states, determine the nuclear-spin-lattice relaxation times.

Following a brief theoretical survey in Sec. II, the experimental method is outlined in Sec. III and the results are discussed in Sec. IV. Section V summarizes the conclusions that can be drawn from the results.

## II. THEORETICAL SURVEY

### A. Molecular Orientational Ordering

X-ray diffraction[9,10] has shown that a crystal lattice change occurs at a temperature close to that of the order-disorder transition. Studies of neutron diffraction[11] and ir absorption spectra[12] have shown that the low-temperature face-centered cubic (fcc) phase is represented by the space group $Pa^3$ in agreement with the classical calculations of Felsteiner.[13] This space group is a fcc lattice with four distinct simple cubic sublattices such that in each sublattice the equilibrium direction of the molecules is aligned along a threefold axis, one of the body diagonals of the fcc lattice. The electric field at a given molecular site, due to the quadrupoles of its neighbors, has axial symmetry, thereby lifting the degeneracy of the $J = 1$ state. The states $J_z = \pm 1$ are separated from the ground state $J_z = 0$ by an energy gap $\Delta$. One of the four body diagonals forms the quantization axis for each of the four sublattices for the intermolecular interactions.

The orientational ordering of solid hydrogen on this lattice has been studied theoretically by many investigators.[13–19] Self-consistent molecular-field theories, such as that using the temperature-dependent Green's-function technique of Raich and Etters,[16] lead to a first-order phase transition at a critical temperature $T_c$ given by

$$T_c = \tfrac{1}{4}(19X\Gamma)\ln 2 \ ,$$

where $X$ is the fractional ortho content and $\Gamma = 0.69$ °K[20] is the quadrupolar coupling constant. Below $T_c$ the orientational order parameter $\langle O_2^0\rangle$, given by the statistical ensemble average $\langle 3J_z^2 - 2\rangle_T$ taken over the states $J_z$, is nonzero and the excited states $J_z = \pm 1$ are separated from the ground state $J_z = 0$ by an energy gap $\Delta$. The temperature dependence of the order parameter is given implicitly by

$$3\epsilon \coth(\tfrac{1}{2}\beta\epsilon) = \epsilon - 24\gamma X \ ,$$

where $\epsilon = \frac{1}{2}\gamma X\langle O_2^0\rangle$, $\gamma = \frac{1}{12}\,19\Gamma$, $\beta^{-1} = kT$, and $\langle J_z\rangle = 0$. The values of $T_c$ disagree with the observed data by a factor of approximately 2 and offer no explanation for the vanishing of the transition when $X \lesssim 60\%$.

Attempts have been made to improve on these rigid-lattice calculations by using models of librational excitations[14,15,17–19] analogous to the spin-wave theory of antiferromagnetism. The dispersion relations of the excitations exhibit eight modes with mean energy $\Delta \approx 19\Gamma$ and a broad bandwidth of approximately $16\Gamma$, whose spectral shape depends on the calculational approximations used. The deviations from the molecular-field-theory results for the transition temperature and the temperature dependence of the orientational order parameter are astonishingly small. The effect of the zero-point motion is to reduce the order parameter at $T = 0$ by the factor[16] $(1 - 0.025/X)$. A further refinement due to the anisotropic interaction between the lattice vibrations and the rotational excitations has been calculated by Harris.[20,21]

Direct observations of the relative spacings of the librational energy levels by ir absorption studies[12,13] are in quantitative agreement with the theories if the anharmonic interactions between the librational waves are taken into account.[22–24] Measurements[25,26] of $(\partial P/\partial T)_V$ in ordered solid hydrogen and solid deuterium suggest that the concentration dependence of the energy gap $\Delta$ is given by

$$\Delta \approx 12(2.05X - 1)\,°\mathrm{K} \ .$$

This concentration dependence is not predicted by the linear theories and is probably related to higher-order calculations; for example, Coll and Harris[22] have shown that cubic anharmonic interactions can reduce $\Delta$ by $4.5\Gamma$. This dependence of $\Delta$ and the bandwidth of the excited states on the ortho content play an important role in determining the fine structure of the NMR spectrum and the nuclear-spin-lattice relaxation times.

### B. NMR Spectra and Relaxation Times

The perturbation of the nuclear Zeeman energy levels of an ortho molecule by the intramolecular magnetic dipole-dipole interaction can be shown[27] to lead to a doublet NMR absorption-line structure with frequency spacings between levels of

$$\nu = a \pm \tfrac{3}{2} d\langle 1 - \tfrac{3}{2}J_z^2\rangle_T (3\cos^2\theta - 1) \ , \qquad (1)$$

where $a = 4.25776$ kHz/kG, $d = 57.7$ kHz, and $\theta$ is the angle between the rotational quantization axis and the external magnetic field. [This value of $d$ is that appropriate to the free molecule, but comparisons of the vibrational spectra of the gaseous and solid phases of hydrogen by E. J. Allin, T. Feldman, and H. W. Welsh, J. Chem. Phys. 24, 1116 (1956), show that in the solid $d$ is reduced by less than 0.3% of the free molecular value.] It is assumed that transitions between the orientational states occur rapidly compared to the resulting doublet spacing.

The spectral intensity contributed by a given molecule[5] is proportional to $\sec\theta$ which is singular at $\theta = \frac{1}{2}\pi$. The line shape obtained by averaging over all directions $\theta$ for a polycrystalline specimen displays two cusps $(\theta = \frac{1}{2}\pi)$ with a frequency spacing of

$$\nu_{DD} = 3d\langle 1 - \tfrac{3}{2}J_z^2\rangle_T \ . \qquad (2)$$

This fine structure provides a direct measure of the molecular order parameter $\langle 3J_z^2 - 2\rangle_T$.

The thermal modulation of the intramolecular magnetic dipolar couplings by the collective rotational excitations is the dominant mechanism providing nuclear-spin-lattice relaxation in the ordered phase. As shown by Abragam[28] the modulation of the nonsecular terms of this dipolar coupling contributes to the spin-lattice relaxation rate by an amount

$$T_1^{-1} = 6\pi^2 d^2[\mathcal{J}_2^1(\omega) + 4\,\mathcal{J}_2^2(2\omega)] \ ,$$

where $\omega = 2\pi\nu$ and $\mathcal{J}_L^M(\omega)$ is the spectral density of the correlation function $\langle Y_L^M(0)Y_L^{M*}(t)\rangle$ of the spherical harmonic $Y_L^M(\omega)$.

The correlation times $\tau$ of these rotational correlation functions can be estimated from the relaxation times measured in the hexagonal phase[27,29–31] by recalling from the pioneer studies of Bloembergen, Purcell, and Pound[32] that

$$\mathcal{J}(\omega) = 2\tau/[1 + (\omega\tau)^2] \ .$$

Harris and Hunt[27] estimate $\tau = 10^{-12}$ sec in contrast to the value of $10^{-4}$ sec suggested by Reif and Purcell.[5] The latter choice is certainly not consistent with the observation that $T_1$ is frequency independent and decreases linearly with temperature in the range $1.6 < T < 10$ °K.[27,29-31] Furthermore, correlation times of the order of picoseconds are anticipated from the magnitude of the cooperative molecular interactions.

These deductions for the hexagonal structure do not apply to the cubic structure. The rotational correlation times in the ordered lattice can be calculated from the rate $W$ at which thermally excited collective librational excitations occur at temperature $T$. $W$ is calculated from the quadrupolar coupling[8] between the ortho molecules. We estimate

$$\tau \simeq W^{-1} \simeq 1.0\ 10^{-6} X^4 T^{-1} e^{\beta E_0}\ \text{sec} \ , \tag{3}$$

where $E_0$ represents the energy of the lower band edge of excited states.

For the current experiments $\omega\tau \gtrsim 10^2$, and the spin-lattice relaxation time is therefore

$$T_1 = \frac{5}{12\pi^2}\left(\frac{\omega}{d}\right)^2 \tau \simeq 51 X^4 T^{-1} e^{\beta E_0}\ \text{sec °K} \tag{4}$$

at the Larmor frequency $\nu = 310$ MHz.

## III. EXPERIMENTAL METHOD

The NMR absorption was observed with a bridge spectrometer at 311 MHz using audio-frequency magnetic modulation and phase-sensitive detection. Spectra were recorded at low rf levels to avoid saturation by scanning the frequency with a mechanically swept uhf frequency generator whose output was monitored by a frequency counter. The bridge was composed of a quadrature hybrid-tee stripline coupler of which one arm, terminated in the characteristic impedance (50 Ω), was balanced against the conjugate arm, impedance matched to a resonant cavity containing the specimen. This NMR system will be described in greater detail elsewhere.[33]

Samples were prepared by condensing a purified mixture of room-temperature hydrogen (75% ortho) into the uhf cavity which formed an integral part of the mixing chamber of a dilution refrigerator. Possible traces of oxygen were removed from the hydrogen by passage through a catalytic deoxidizer and a liquid-nitrogen trap.

The dilution refrigerator was operated at the high-flow rates $[(0.6-4.0)\times 10^{-4}$ mole/sec$]$ required to maintain temperatures below 100 m °K under the ortho-para conversion heat load of the hydrogen samples. This heating was approximately 1100 erg/sec for a cavity filling factor of 25%. The sensitivity of the spectrometer enabled us to achieve adequate signal-to-noise ratios for data analysis with filling factors as low as 5%, and under these conditions a limiting temperature of 65± 5 m °K was realized. This limit is contributed, in part, by viscous heating in the sintered copper heat exchangers at these flow rates. This heating could not be easily alleviated by reducing the fluid flow impedance of the heat exchangers without excessive loss of surface exchange area, since the size of the heat exchangers is constrained by the available free volume in the bore of the superconductive magnet.

In the high-field low-temperature regime of these experiments ($H/T \sim 10^6$ Oe °K$^{-1}$) the NMR spectra of the ordered phase of solid hydrogen provide direct measurements of the temperatures of the samples. The relative intensities of the components of the doublet are given by the difference in the thermal population of the pertinent nuclear Zeeman levels, and the ratio of these intensities is therefore $e^{h\nu/kT}$. For example, the sample temperature deduced from the spectral asymmetry of the derivative absorption line shown in Fig. 1 is 73± 5 m °K. At temperatures higher than 100 m °K the temperature was monitored by a Speer carbon-resistance thermometer (220-Ω nominal impedance, grade 1002) affixed to the exterior wall of the cavity.

The nuclear-spin–lattice relaxation times were measured by recording the recovery of the signal intensity following partial saturation at fixed frequency. The saturating rf power levels were re-

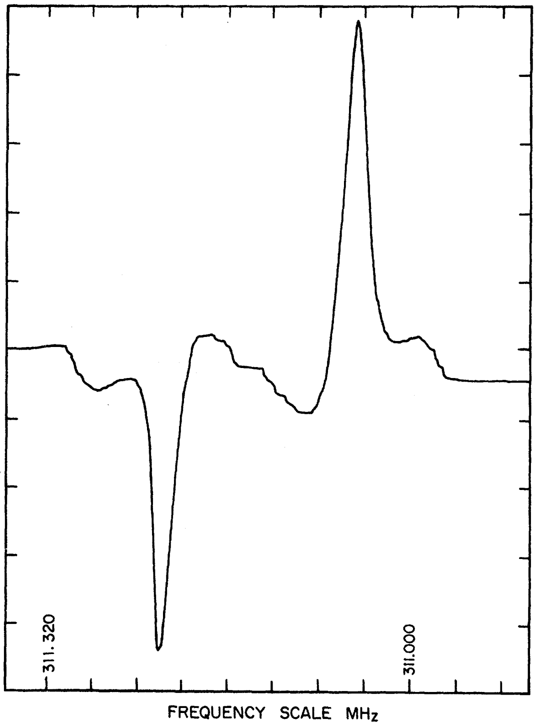

FIG. 1. Derivative absorption-line spectrum of solid hydrogen at 73 ±5 m °K.

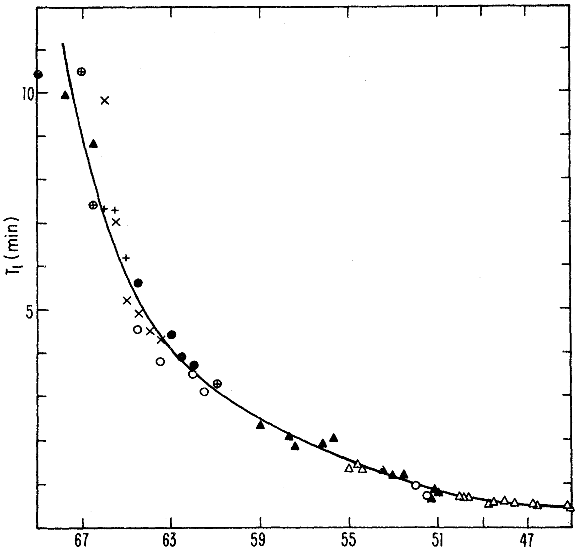

FIG. 2. Dependence of nuclear-spin-lattice relaxation time on ortho content at 85 ± 5 m °K. The legends refer to independently prepared samples.

stricted to 20 dB above those at which the spectra were observed in order to avoid excessive rf heating of the cavity. Possible saturation effects during the recording time were eliminated by an on-off sequence in which the observational rf level is switched on for a brief time $t_1$ and then off for a period of approximately $10t_1$. The signal intensity was plotted on an exponential time scale and the relaxation time taken from the resulting linear slope.

## IV. RESULTS

A strong dependence of $T_1$ on the ortho content of the sample was observed by taking successive measurements as a given sample aged at constant temperature. The results for several samples at $T = 85 \pm 5$ m °K are plotted in Fig. 2, where the ortho contents of the samples were estimated from their age assuming that the ortho-para conversion rate in the solid is that given by previous investigators[10,34,35]:

$$\dot{X} = -kX^2, \quad k = 1.9\%\,\mathrm{h}^{-1} \ .$$

The temperature dependence of $T_1$ for different samples of approximately constant ortho content ($X \simeq 0.67 \pm 0.02$) is illustrated in Fig. 3.

We find that the empirical functional dependence of $T_1$ on temperature $T$ and fractional ortho content $X$ is given by

$$T_0 = AX^4T^{-1}e^{(B+0.24\,^\circ\mathrm{K})/T} \ , \tag{5}$$

where $A = 1.0 \pm 0.3$ min, $B \simeq 0.4(1.8X-1)$ °K for $X > 0.56$, and $B = 0$ for $X < 0.56$. This form for $T_1$ is in qualitative agreement with that predicted by Eq. (4). There is no abrupt change at $X \simeq 0.56$ and an energy gap $\Delta_c \simeq 0.24$ °K is required for $X < 0.56$ in order to explain the monotonic change of $T_1$ in that region.

Observations of the dependence of the fine-structure splitting $\nu_{DD}$ on ortho concentration, which we have reported elsewhere,[36] have shown that the *mean* energy gap is given by

$$\Delta = 11(1.8X-1) + 0.24\,^\circ\mathrm{K} \quad \text{for} \quad X > 0.56$$

and

$$\Delta_c = 0.24\,^\circ\mathrm{K} \quad \text{for} \quad X < 0.56 \ .$$

The quantity $B$ in Eq. (5) is the energy $E_0$ of the lower band edge of excited states and is therefore related to $\Delta$ by $2(\Delta - B) \approx$ (bandwidth of excited states). Although the concentration dependence of $B$ is the same as that of $\Delta$, its absolute value is smaller than that expected from the theoretical bandwidths.[14-17] However, as emphasized in Sec. II, this parameter depends strongly on the detailed spectral density of the low-energy rotational excitations. Since the critical temperatures $T_c$ at which rotational orderings occur are of the order of 1 °K and the bandwidths of the theoretically calculated excitation spectrum are almost as large as the mean energy of the excitations, it is not unreasonable to expect that $B \sim \frac{1}{2}T_c \sim 0.5$ °K.

The effect of saturation at a given frequency on the complete absorption spectrum was observed on a cathode-ray oscilloscope by sweeping through the spectrum with a frequency-modulated uhf generator in addition to the fixed-frequency oscillator. If the fixed frequency was selected to coincide with one of the cusps, the second cusp de-

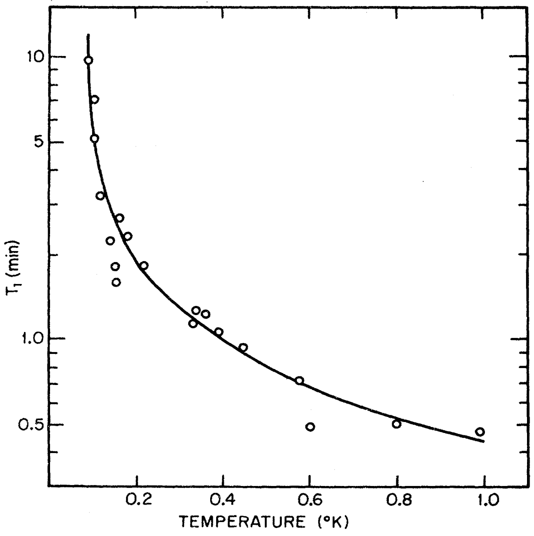

FIG. 3. Variation of nuclear-spin-lattice relaxation time with temperature at constant ortho content (67%).

creased in intensity by approximately 10% when the first cusp was reduced to 50% of its initial intensity. This response occurred in a time shorter than that which could be detected by the visual-display system. Saturation at the center of gravity of the spectrum resulted in a symmetrical reduction in intensity of the total absorption pattern. Since the two cusps are contributed by the class of molecules whose rotational wave functions have quantization axes normal to the external magnetic field, this cross relaxation is effected by adiabatic nuclear-spin flips arising from the nuclear spin-spin interactions between neighboring molecules which have the same orientation. The observations therefore indicate that, while the nuclear spin-spin interactions are weak, the role that they play in the establishment of an ensemble nuclear-spin temperature is not negligible in comparison with the spin-lattice interactions. In the latter regime (selective "hole burning"), reduction of the difference in thermal population of the Zeeman levels $I_z = 0, 1$ by partial saturation at one cusp (50% reduction in intensity) would result in an increased difference in population of the levels $I_z = -1, 0$ and an enhanced intensity at the other cusp (approximately 10%). The values of $T_1$ obtained were independent of the frequency within the linewidth at which saturation was effected.

## V. CONCLUSION

The observed dependence of the splitting of the NMR spectrum[36] on ortho content at constant temperature provides a measure of the energy gap between the excited states and the ground state. For high ortho concentrations, $X > 0.56$, the gap is found to be $\Delta \approx 11(1.8X - 1)$ °K. For low ortho concentrations, $X < 0.56$, the rotational degeneracy is lifted by the rotational spin-lattice interaction $\Delta_c = 0.24$ °K, and the fine structure persists for $T < \Delta_c$.

The measured nuclear-spin-lattice relaxation times are consistent with those calculated from the rotational correlation times of the quantum crystal lattice. While the concentration dependence of the librational-excitation energies, which determine the correlation times, is the same as $\Delta$, the quantitative values of the energy gap which are consistent with the data are smaller. This is not satisfying and the discrepancy can only be resolved when improved calculations of the detailed spectral density of the excitations have been performed. The values of $T_1$ deduced from the theoretical spectral shapes are an order of magnitude larger than those observed. This is also the case for the relaxation times observed in the ordered phase of solid deuterium; for example, Smith *et al.*[37] find $T_1 = 195$ sec for $X$ (para fraction) = 0.93 at 2 °K and $T_1 = 130$ sec for $X = 0.87$ at 1.5 °K. The strong concentration dependence of their results is not inconsistent with ours.

As in the case of the spectra no abrupt change occurs for $X < 0.56$ and an energy gap $\Delta_c \simeq 0.24$ °K is predicted by the results.

Further studies are planned at lower temperatures in order to elucidate the temperature dependence of the relaxation times and the fine-structure splitting, and this will necessitate modifying the present dilution refrigerator. Further experiments should also be performed at different magnetic field values in order to verify the field dependence of the relaxation times.

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# Coherent- and Incoherent-Scattering Laws of Liquid Argon[†]

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The inelastic-scattering functions for liquid argon have been measured at 85.2 K. The coherent-scattering function was obtained from a measurement on pure $A^{36}$ and the incoherent-scattering function was derived from the result obtained from the $A^{36}$ sample and the result obtained from a mixture of $A^{36}$ and $A^{40}$ for which the scattering is predominantly incoherent. The data, which are presented as smooth scattering functions at constant values of the wave-vector transfer in the range 1.0–4.4 $Å^{-1}$, are corrected for multiple-scattering contributions and for resolution effects. Such corrections are shown to be essential in the derivation of reliable scattering functions from neutron-scattering data. The incoherent-scattering function is compared to recent molecular-dynamics results and the mean-square displacement as a function of time is derived. The coherent-scattering function is compared to molecular-dynamics results and also, briefly, to some recent theoretical models.

## I. INTRODUCTION

Although a considerable amount of insight into the dynamical behavior of atoms in liquids has been gained during recent years through the results obtained from inelastic-neutron-scattering experiments, earlier studies have been of limited utility because of various experimental uncertainties—most importantly, the effects of multiple scattering. The present report attempts to correct these deficiencies for liquid argon, and we describe in detail the data analysis leading to the corrected scattering laws presented. In spite of some remaining problems (principally connected with estimation of errors in the final results), we believe that the present results are sufficiently reliable to allow quantitative comparisons with both theory and molecular-dynamics results. An important feature of the present results is that the absolute normalization of the scattering functions has been obtained experimentally.

The theoretical description of the complex many-body problem which the liquid constitutes is conveniently made in terms of two functions. One of these is concerned only with the average motion of one atom among the other atoms (Van Hove self-correlation function) while the other function describes the relative motion of atoms (density-correlation function). In principle the neutron-scattering experiments allow a complete determination of both of these functions. In practice, however, competing requirements on intensity and