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EVIDENCE FOR ANISOTROPIC DIFFUSION OF MU
IN ICE AND IMPLICATIONS FOR H

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Abstract

Muonium has been studied in single crystals of H₂O and D₂O. Orientation dependent precession frequencies reveal anisotropy in the hyperfine tensor of muonium. The axial symmetry suggests that Mu atoms diffuse preferentially along the c-axis channels of the ice lattice. It is expected to behave the same way.

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Despite the fundamental importance of both hydrogen atoms and frozen aqueous systems, little is known about the diffusion and chemical reactions of H in ice. ESR detection of trapped hydrogen atoms was first reported in 1954 for γ -irradiated acidic ices at 77 K [1], and in 1959 for pure ice at 4.2 K [2], but it was not until 1976 that Shiraishi *et al.* [3] published the first, and only, study of H atoms in neutral ice at high temperatures. They used continuous electron irradiation, but they were only able to detect H in pure ice *above* 160 K, where motional line narrowing and chemically induced spin polarization [4] serve to enhance signal intensities. Thus there exists a considerable range of temperature, ~ 50 K-160 K for which direct study of H in pure ice has not been possible.

In contrast to H, it is a relatively simple matter to study the lighter isotope muonium ($\text{Mu} \equiv \mu^+e^-$) [5] by muon spin rotation (μSR) [6], provided only that a suitable beam of spin polarized muons is available. At first, muonium in ice was only studied at 77 K [7-9], but the temperature range up to the melting point has since been covered [10,11], and the work reported here includes measurements down to 4.2 K.

In previous muonium studies the ice samples were polycrystalline. As far as we know this is also the case for ESR of H, although OH has been studied in a single crystal at 77 K [12]. Single crystal experiments provide valuable information in magnetic resonance, and this is also true for μSR [13-18]. Of most relevance to the research reported here is the work of Brewer *et al.* on muonium in single crystals of quartz [16-18]. At room temperature the usual triplet precession signal was found to be split into two frequency components separated by δ

reveals the muon and muonium precession frequencies. Full details of sample preparation, experiments and data analysis will be given in a later publication.

Two-frequency muonium precession was observed for both H₂O and D₂O crystals in a 10 G magnetic field transverse to the beam direction. An example is given in fig. 1, which shows the muon asymmetry for a D₂O crystal at 146 K oriented with its c-axis parallel to the field. The beat pattern represents a splitting of 1.2 MHz. This value was also found for H₂O. A Zeeman splitting of this magnitude would require a field of 38 G (based on the splitting observed by Gurevich at 77 K and 98 G [8]), whereas at 10 G the Zeeman splitting is minor (<0.1 MHz). An experiment at 5 G gave the same result, but at higher fields the Zeeman effect was apparent, as explained below. The frequencies were independent of temperature but varied with crystal orientation, indicating that our findings stem from the same phenomenon as occurs in quartz.

The spectra of muonium in single crystal ice are all consistent with an axially symmetric spin Hamiltonian:

$$\hat{H} = \omega_e \hat{S}_z - \omega_\mu \hat{I}_z + \hat{S} \cdot \hat{T} \cdot \hat{I} \quad (2)$$

where the hyperfine tensor T has the form

$$T_c = h \begin{pmatrix} A_\perp & 0 & 0 \\ 0 & A_\parallel & 0 \\ 0 & 0 & A_\parallel \end{pmatrix} \quad (3)$$

when written in the principal axis system of the crystal. The electron and muon Larmor frequencies, ω_e and ω_μ , are proportional to the strength of the external field, whose direction defines the z-axis of the laboratory co-ordinate system. The Hamiltonian (2) results in precession

much as 0.8 MHz [16]. The splitting was apparent at fields much lower than that required for the well known "two-frequency precession" [8] due to the Zeeman effect. Furthermore the splitting was shown to depend on crystal orientation [16]. The results are consistent with a small anisotropy in the muonium hyperfine interaction. The axial symmetry found at high temperature is lost below 130 K, where three frequencies are observed in zero field [18]. Comparison of the Mu results with the ESR of H in quartz suggests that the atoms occupy similar sites in the crystal at low temperature. At high temperatures Mu is thought to diffuse up and down the c-axis channels of the lattice, but this has not yet been observed for H [19].

The crystal structure of ice Ih is similar to that of quartz in that both are threaded by hexagonal channels parallel to the unique axis. It therefore seemed to us worthwhile to reexamine muonium in ice, but using single crystals.

Single crystals of both H₂O and D₂O were grown by a method based on that of Jona and Scherrer [20]. Samples were cut from the centre of larger blocks. They were cuboid in shape, with sides typically 2-3 cm in length. The quality of the single crystals was checked under polarized light. Experiments were performed at TRIUMF using conventional μ SR apparatus and techniques. Precession frequencies were determined by fitting the appropriate theoretical function to the μ SR histogram, whose general form is

$$S(t) = B + N e^{-t/\tau_\mu} [1 + A(t)], \quad (1)$$

where B represents a small constant background count, N is a normalization factor, and A(t) is the muon asymmetry, whose time dependence

of the muon spin polarization in the x-y plane:

$$P_x = P_x + iP_y = \frac{1}{2} c^2 (e^{i\omega_{12}t} + e^{i\omega_{43}t}) + \frac{1}{2} s^2 (e^{i\omega_{23}t} + e^{i\omega_{14}t}). \quad (4)$$

The four precession frequencies are

$$\begin{aligned} \omega_{12} &= \omega_- - \Omega + \frac{1}{2} \delta\omega \\ \omega_{23} &= \omega_- + \Omega - \frac{1}{2} \delta\omega \\ \omega_{43} &= \omega_- - \Omega - \frac{1}{2} \delta\omega - \omega_t \\ \omega_{14} &= \omega_- + \Omega + \frac{1}{2} \delta\omega + \omega_t \end{aligned} \quad (5)$$

where ω_- is the usual muonium precession frequency

$$\omega_- = \frac{1}{2} (\omega_e - \omega_\mu), \quad (6)$$

and Ω corresponds to the Zeeman beat frequency [8]

$$\Omega = \frac{1}{2} \left\{ \omega_t^2 + (\omega_e + \omega_\mu)^2 \right\}^{1/2} - \omega_t, \quad (7)$$

but with the isotropic hyperfine frequency ω_0 replaced by the parameter ω_t :

$$\omega_t/2\pi = A_x + \frac{1}{2} (A_{||} - A_x) \sin^2\theta, \quad (8)$$

which depends on the anisotropy and the angle θ between the laboratory z axis and the unique (c) axis of the crystal. Finally, $\delta\omega$ is the additional, field-independent splitting due to the hyperfine anisotropy:

$$\delta\omega/2\pi = \frac{1}{2} (A_{||} - A_x) (3 \cos^2\theta - 1). \quad (9)$$

The intensities of the precession signals are given by

$$c^2 = \frac{1}{2} \left\{ 1 + \frac{(\omega_e + \omega_\mu)}{[(\omega_e + \omega_\mu)^2 + \omega_t^2]^{1/2}} \right\}, \quad c^2 + s^2 = 1. \quad (10)$$

However, the frequencies ω_{14} and ω_{43} are too high to be resolved by conventional μ SR apparatus so that their amplitudes are effectively zero.

Thus two frequencies remain, split by $(\delta\omega - 2\Omega)$ and centred about ω_- .

Experiments were performed at a variety of fields and crystal orientations to test the above equations. Since $\delta\omega$ is field independent, measurements at different fields but fixed orientation can be used to separate the two contributions to the measured splitting. The Zeeman splitting, 2Ω , can then be used to determine the hyperfine frequency ω_t . The result of such analysis are set out in table 1.

In the low field limit $\Omega \rightarrow 0$ and the frequency splitting should exhibit the characteristic $(3 \cos^2\theta - 1)$ dependence. This was confirmed for an H_2O crystal, as shown in fig. 2. The best fit of eq. (9) to the data reveals an anisotropy $|A_{||} - A_x| = 1.27 \pm 0.03$ MHz in complete agreement with the value 1.27 ± 0.01 MHz determined for D_2O (table 1). The sign ambiguity inherent in the low field results is resolved by the higher field experiments: $A_{||} > A_x$.

In view of the small size of the anisotropy the values found for ω_t may be taken directly as determinations of the isotropic hyperfine constant A_0 . Combining results for H_2O and D_2O we find $A_0 = 4440 \pm 100$ MHz. This is consistent with the value 4791 ± 300 MHz for H_2O at 77 K reported by Gurevich *et al.* [8] and also with the vacuum hyperfine constant (4463.3 [21], indicating that the muonium atom experiences very little electronic interaction with atoms of the ice lattice. The hyperfine constants for H atoms in ice and vacuum are also very close to each other [3], and merely differ from the Mu value by the ratio of the proton and muon magnetic moments. In complete analogy with the work of Brewer *et al.* on quartz [17,18], we attribute the axial symmetry of the muonium hyperfine tensor in ice to rapid diffusion of the atom along the c-axis channels. Preliminary

Investigation suggests that the axial symmetry is preserved at temperatures right down to 4.2 K in D₂O, but it is too early to say whether it is due to rapid diffusion at low temperatures or if it is due to a feature of the trapping site. We hope to clarify this point with further studies. The suggestion that Mu, and by analogy H, diffuse anisotropically through the ice lattice has been made by others. Benderskii *et al.* [22] use the motion of H in a channel along the c-axis of ice as a model for H diffusion in liquid water. Application of their potential shows that diffusion of H is fast ($\tau_D \leq 1 \times 10^{-6}$ s) above 50 K, in agreement with studies of decay kinetics [23] and spin relaxation [3]. For muonium the isotope effect is expected to enhance both classical diffusion and tunnelling, which will be dominant at those temperatures, $T \leq 20$ K, where muonium would otherwise be localised.

The notion of anisotropic diffusion of hydrogen atoms in ice is strongly supported by experiments on the diffusion of He and Ne [24].

Whatever the source of the muonium hyperfine anisotropy, its discovery invites reinterpretation of previous work. The spectrum of muonium in polycrystalline ice will contain contributions from all possible crystal orientations, and thus the frequency splitting in low field will vary from $-\frac{1}{2}\delta\omega$ to $\delta\omega$. In the terminology of magnetic resonance this would be described as inhomogeneous line broadening. In μ SR it takes the form of relaxation of the single muonium precession frequency, ω_{μ} . An effective relaxation rate of about $2 \times 10^6 \text{ s}^{-1}$ was deduced by numerical simulation. In fact, such a rate of unknown origin was reported earlier [10]. It was characterized as isotope and temperature independent, and it was found to be the dominant contribution to

relaxation in D₂O and in H₂O above 160 K. The presence of inhomogeneous broadening explains why the ratio of observed relaxation rates in H₂O and D₂O is so much less than the expected ratio of 16 for rapid diffusion, and completely invalidates the conclusion of Gurevich *et al.* [9] that muonium does not diffuse in ice at 77 K.

ESR of H atoms in polycrystalline ice will also suffer from inhomogeneous line broadening. The effect should be minor for H₂O, except at high temperatures, but important for D₂O. If it is assumed that H has an anisotropy in its hyperfine tensor equivalent to that of Mu, then each hyperfine line will be broadened by as much as $(A_{\parallel} - A_{\perp})_H \approx 0.4 \text{ MHz}$. The results of Shiraishi *et al.* [3] show a line width close to this value in the high temperature limit. It is possible that the (usually characteristic) powder pattern line shape may have been obscured by a natural line width of similar magnitude, and by the presence of 100 kHz modulation sidebands. If inhomogeneous broadening is significant, then the activation energy for line narrowing above 160 K quoted by Shiraishi *et al.* should be revised upward.

An extensive study of muonium relaxation in H₂O and D₂O ice over a wide temperature range is being undertaken with a view to characterising the diffusional motion. It would be valuable if H were also investigated.

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Table 1

Determination of the hyperfine frequency from two-frequency precession^a

sample	field/G	$\delta\nu$	$\delta\omega/2\pi$	$2\Omega/2\pi$	$\omega_t/2\pi$
H ₂ O, arbitrary orientation	10	0.79 (2)	0.88(2)	4.20(16)	4460(180)
	70	-3.32(14)			
D ₂ O, arbitrary orientation	10	0.34 (1)	-0.25(1)	4.22(13)	4440(150)
	70	-4.47(12)			
D ₂ O, c//field	10	1.18 (1)	1.27(1)	0.80(3)	4410(170)
	30	0.47 (2)			

^aall frequencies in MHz; standard deviations in parentheses.

1. Muon asymmetry in a D₂O crystal at 146 K oriented with its c-axis parallel to the field of 10 G and perpendicular to the muon polarization. The precession signal contains a low frequency muon component in addition to the two beating muonium frequencies.

2. Muonium splitting in H₂O as a function of the angle between the crystal c-axis and the applied magnetic field (○ 5 G, ● 10 G, □ 20 G). The measured splittings have been corrected for Zeeman contributions. The solid line represents the best fit of eq. (9) to the data.