THE EFFECT ON T_1 OF CORRELATED WATER
MOTIONS IN THE POLAR PHASE OF COLEMANITE

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1. Introduction

Proton magnetic resonance in the ferroelectric colemanite, $CaB_3O_4(OH)_3.H_2O$, is dominated by the dynamical motion of the water molecules. Absorption lineshape [1] and spin lattice relaxation studies [2,3] have shown that in the non polar phase (above 270 K) the water molecules undergo two kinds of reorientational motion; a 180° flipping motion about the H-O-H bisectrix which merely exchanges the hydrogen positions, together with a jumping motion in which one of the water hydrogens takes up one of two possible sites. This latter motion is also accompanied by a jump of some of the hydroxyl hydrogens between two possible sites.

In the polar phase, as illustrated by the hydrogen positions in Fig. 1, the jumping motion freezes out accompanied by a slight rearrangement of the heavy atom network [4]. The predominant lineshape and relaxation mechanism in this phase is the remaining 180° flipping motion of the water groups. This accounts very well for most of the observed features of the absorption lineshape and BPP type temperature dependence of the spin lattice relaxation time (Fig. 2). However there still remains a small discrepancy between the 0.13±0.01 s value observed for the T_1 minimum at a Larmor frequency of 30 MHz and the 0.09 s value predicted by this model.
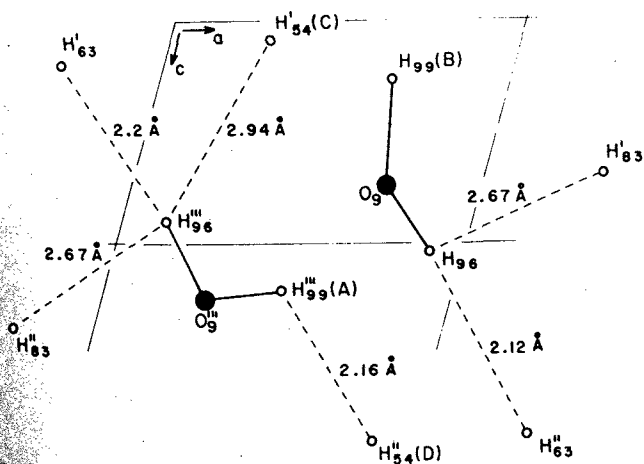

Fig. 1: Projection along the b axis of colemanite showing the relative configuration of a pair of water molecules and neighbouring hydroxyl hydrogens. The smaller water hydrogen - hydroxyl hydrogen distances, which make a significant contribution to the relaxation, are labelled.
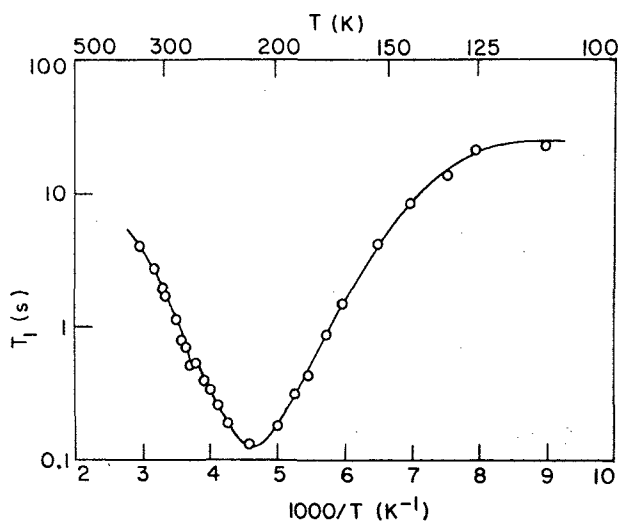

Fig. 2: Temperature dependence of the proton spin lattice relaxation time in powdered colemanite at a Larmor frequency of 30 MHz.

Although experimental values for the T_1 minimum smaller than model predictions can usually be accounted for by additional mechanisms not included in the model, this is clearly not the situation here and the interpretation is not so straightforward. It appears that the flipping mechanism in the theoretical model, assuming this motion is an appropriate one, is not as effective as it should be. One possible reason for this reduced efficiency is that since the water molecules occur in adjacent pairs their flips are correlated with each other. That is to say that a flip of one water molecule is accompanied by a simultaneous flip of the other one in the pair. Such a correlation would result in the number of intermolecular configurations available to the proton pairs being reduced over those available in uncorrelated motion. It would seem reasonable then that the corresponding reduction in the fluctuations of the intermolecular dipole interaction could lead to a reduction in relaxation time. We have therefore extended the theoretical model for water flipping to include correlations within adjacent water pairs. The goal was to see whether such correlations would lead to an increase of the theoretical T_1 and if so whether this could, by itself, account for the larger value observed.

2. Model Calculation

The spin lattice relaxation time resulting from the reorientations of the water molecules is given by [5,6]

$$\frac{1}{T_1} = \frac{9}{8}\gamma^4\hbar^2 \sum_{i \neq j}^{N} \left[J_{ij}^{(1)}(\omega_0) + J_{ij}^{(2)}(2\omega_0) \right]$$

where the $J(\omega)$'s represent the spectral density of the fluctuating dipolar interaction between protons i and j, and ω_0 is the Larmor frequency.

In the formalism which we will adopt the water dynamics are described by a dimensionless transition matrix [7]

$$X = \frac{\Lambda}{\omega_0}$$

where the matrix Λ has elements λ_{ij}, $i \neq j$, which are the probabilities/unit time of the interproton vector $\vec{r}_i$ making a transition to $\vec{r}_j$ among the n possible position vectors (λ_{ii} is chosen so that $\sum_j \lambda_{ij} = 0$).

In a similar way the proton dipolar interaction is described by a geometrical matrix A with elements given by

$$a_{ij} = \frac{1 - 3\cos^2\alpha_{ij}}{r_i^3 r_j^3}$$

where $r_i, r_j = |\vec{r}_i|, |\vec{r}_j|$ and α_{ij} is the angle between $\vec{r}_i$ and $\vec{r}_j$.

X has eigenvalues x_i and is diagonalized with a matrix T. i.e.

$$X_T = TXT^{-1} \quad \Rightarrow \quad (X_T)_{ij} = x_i\delta_{ij}$$

If A is then transformed by the same matrix T,

$$A_T = TAT^{-1}$$

the spin lattice relaxation time can be written as

$$\frac{1}{T_1} = \frac{3\gamma^4\hbar^2}{20\omega_0 n}\left[M(\omega_0) + 2M(2\omega_0) \right]$$

where

$$M(\omega_0) = \sum_{i=1}^{n} \frac{x_i}{1 + x_i^2}(A_T)_{ii}$$

In a 180° flip of a water molecule the intramolecular proton-proton vector merely changes sign leaving its contribution to the dipolar interaction invariant and hence contributing nothing to the relaxation. As a result only the intermolecular couplings need be considered, of which there are two dominant kinds; the interaction between water pairs and the water-hydroxyl interaction.

In uncorrelated water motions each water-water interproton vector can occupy the four positions illustrated schematically in Fig. 3 and labelled, arbitrarily 1,2,3 and 4. The transition matrix is then

$$\Lambda = \lambda \begin{bmatrix} -2 & 0 & 1 & 1 \\ 0 & -2 & 1 & 1 \\ 1 & 1 & -2 & 0 \\ 1 & 1 & 0 & -2 \end{bmatrix}$$

where λ is the probability/unit time of any water molecule, all assumed dynamically equivalent, making a 180° flip. However, if the water motions are correlated in the sense that the water molecules in each pair reorient in unison then the transition matrix for the same inter-water proton vectors becomes

$$\Lambda = \lambda \begin{bmatrix} -1 & 1 & 0 & 0 \\ 1 & -1 & 0 & 0 \\ 0 & 0 & -1 & 1 \\ 0 & 0 & 1 & -1 \end{bmatrix}$$
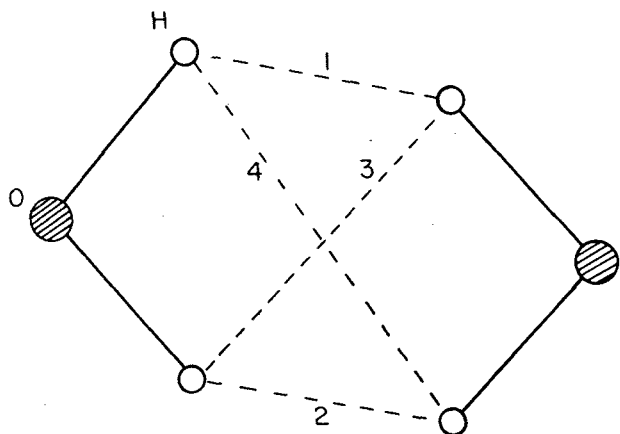
Fig. 3: Schematic representation of a pair of water molecules showing the four positions occupied by each inter proton vector between water molecules during uncorrelated motions. The choice of label numbers is arbitrary.

In either case the water-hydroxyl interproton vectors have only two values for each water-hydroxyl group and their corresponding transition matrix is given by

$$\Lambda = \lambda \begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix}$$

In fact, for correlated water motions the water-water interproton vectors can be partitioned into two sets {1,2} and {3,4} each of which has a transition matrix of the simple 2×2 form above. Applying the diagonalization and transformation procedure described previously to these matrices produces the following expression for T_1 resulting from correlated $180°$ flips of the water molecules,

$$T_1^{-1} = 7.0 \left[\frac{\omega_0 \tau}{1 + (\omega_0 \tau)^2} + \frac{4\omega_0 \tau}{1 + 4(\omega_0 \tau)^2} \right]$$

where $\tau = 1/\lambda$ is the correlation time for the $180°$ flip motion.

This gives a T_1 minimum of 0.10s for a Larmor frequency of 30 MHz which is greater than that for uncorrelated motion by about 10% but still significantly short of the 0.13s observed. It appears that at least the simple correlated model considered here is inadequate to fully account for the minimum in T_1 and that some other mechanism is presumably in effect.

In colemanite, as shown by Fig. 1, some hydroxyl hydrogens are quite close to the water molecules and there are only two water hydrogens for every three hydroxyl hydrogens in each molecular unit. As a result the hydroxyl-water coupling and the water-water coupling make comparable contributions to the proton relaxation. Since the hydroxyl-water contribution is independent of any correlations in the water dynamics it seems reasonable that there is not a large difference in the overall T_1 between the correlated and uncorrelated motions, but it is gratifying that the change is in the right direction and is consistent with the reduction in the dipolar fluctuation discussed earlier.

References

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