Proton spin-lattice relaxation and local symmetry of the H bond in Rb₃H(SO₄)₂

U. Mikac, B. Zalar, J. Dolinšek, J. Seliger, V. Žagar, O. Plyushch,* and R. Blinc

J. Stefan Institute, University of Ljubljana, Ljubljana, Slovenia

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A rather strong and unusual temperature and frequency dependence of the proton spin-lattice relaxation time T_1 has been observed in a Rb₃H(SO₄)₂ single crystal in the temperature interval between 300 and 10 K. Below 10 K the proton T_1 becomes temperature independent but still exhibits a rather strong Larmor frequency dependence. At higher temperatures the spin-lattice relaxation is determined by a modulation of the Rb-proton and/or proton-proton dipolar coupling due to thermally activated jumping of the proton between the two equilibrium sites in the H bond whereas at low temperatures phonon-assisted proton incoherent tunneling takes over. The results thus show that the double-minimum potential of the H bond in Rb₃H(SO₄)₂ is locally asymmetric in the temperature range investigated. There is no evidence for a change from a double to a single minimum type H-bond potential down to 4 K.

I. INTRODUCTION

Preliminary measurements[1] on Rb₃H(SO₄)₂ powder samples have shown a surprisingly strong temperature dependence of the proton spin-lattice relaxation time T_1. The proton T_1^{-1} at 37 and 18 MHz strongly decreases with decreasing temperature between 300 and 10 K and becomes temperature independent below 10 K. The activation energy for this motion is significantly lower than the activation energy 0.82 eV found for the deuteron inter-H-bond motion[2]—connected with DSO₄ reorientation—in Rb₃D(SO₄)₂. Two-dimensional (2D) deuteron NMR exchange measurements[2] have further shown that the correlation frequency for the deuteron inter-H-bond motion is as low as 2.16 Hz at 290 K. It would become astronomically slow below 100 K. This means that HSO₄ rotation and proton inter-H-bond motion cannot be responsible for the observed strong temperature dependence of the proton T_1 in Rb₃H(SO₄)₂ below 300 K and that this temperature dependence very probably arises from proton intra-H-bond motion.

In order to check on the nature of the anomalous proton T_1 in a Rb₃H(SO₄)₂ we decided to perform proton relaxation rate measurements on a rather pure Rb₃H(SO₄)₂ single crystal at higher Larmor frequencies up to 270 MHz. We hoped to obtain some information on the local symmetry of the O-H···O bond and the possibility of phonon-assisted proton incoherent tunneling at low temperatures.

We also wished to compare the local symmetry of the O-H···O bond in Rb₃H(SO₄)₂ with the symmetry of the O-D···O bond in Rb₃D(SO₄)₂ above and below the antiferroelectric transition at $T_c = 82$ K.[2,3,4,5]

II. STRUCTURAL BACKGROUND

Rb₃H(SO₄)₂ and related A_3H(XO_4)₂ compounds (A = K, Rb, Cs; X = Se, S) consist of isolated [(XO_4) -H···(XO_4)]³⁻ dimers separated by A^+ ions and are thus often described as ''zero-dimensional'' H-bonded systems.[6] The isotope effects on replacing hydrogen by deuterium[7] are here so large that the protonated compounds remain paraelectric as $T \to 0$ whereas the deuterated ones exhibit an

antiferroelectric transition at $T_c \approx 100$ K. The space group of the protonated compounds and the high-temperature space group of the deuterated ones are generally assumed[8,9,10,11] to be $A2/a$ implying the existence of a center of symmetry at the midpoint of the O-H···O bond [Fig. 1(a)]. The origin of the anomalous isotope effect is usually explained by the geometrical isotope effect.[12] The protonated H bond is somewhat shorter than the deuterated one. Due to thermal contraction and the corresponding decrease in the lattice parameters, the O-H···O bond length of the protonated compound is temperature dependent and assumed to cross at approximately 100 K the critical bond length of $R_{O\cdots O} = 2.47$ Å, where the symmetric double-minimum type potential transforms into a single minimum one with the proton at the center of the H

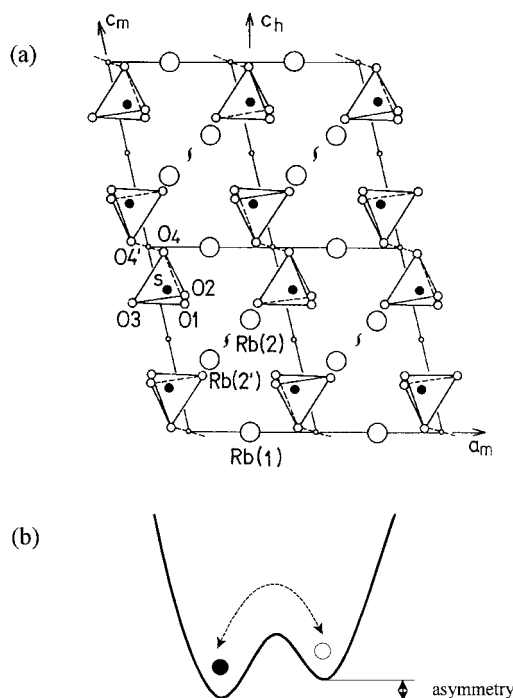FIG. 1. (a) Structure of Rb₃H(SO₄)₂ and (b) the schematic presentation of the asymmetric double-well potential of the O-H···O bond as a function of the space coordinate.

bond.[10] The O-H···O dipole moment thus vanishes and no antiferroelectric transition can take place. In the deuterated compound, on the other hand, the crossing of the critical bond length does not occur. The antiferroelectric transition is thus preserved.

The above hypothesis of a transition from a double to a symmetric single minimum type H-bond potential on cooling does not seem to be supported by Raman-scattering data in $K_3D_{1-x}H_x(SO_4)_2$ type crystals.[13] The data were rather interpreted as pointing to the existence of a double-minimum H-bond potential in the protonated compound even at 20 K. A deuteron spin-lattice relaxation time anomaly recently observed at T_c in $Rb_3D(SO_4)_2$ was similarly interpreted as being incompatible with the existence of a center of symmetry in the middle of the O-D···O bond.[3] Infrared measurements as well have not shown the expected change in the OH stretching band on going from an asymmetric to a symmetric H-bond potential with decreasing temperature.[14] The true local symmetry group in $Rb_3D(SO_4)_2$ should be thus even above T_c $A2$ rather than $A2/a$ (Refs. 2, 4, and 5) and the H-bond potential could be asymmetric because of deuteron self-trapping.[15] Deuteron motion between the two off-center sites in the H bond averages out the asymmetry as seen by x rays.[11] The space and time averaged H-bond potential is thus of the symmetric double minimum above T_c and asymmetric below T_c. The average space group in $Rb_3D(SO_4)_2$ is $A2/a$ above T_c and $A2$ below T_c. The incoherent neutron-scattering data[16] in $Rb_3H(SO_4)_2$ seem to show that even in the protonated compound there is locally no center of symmetry in the midpoint of the O-H···O bond because of self-trapping. The O-H···O bond potential with the self-trapped proton could be thus strongly asymmetric and the surrounding lattice rather distorted so that the true space group is $A2$. In order to retain the average $A2/a$ symmetry seen by x rays the two localized self-trapped proton states at the ''right'' and ''left'' off-center sites in the O-H···O bond must be equivalent on the space and time average. They may not be equivalent at any instant of time. Transition between them may occur via phonon-assisted tunneling at low temperatures.

III. THEORY

In order to discriminate between the above two possibilities, i.e., the proton being centered in the O-H···O bond or moving between two asymmetric off-center sites—in $Rb_3H(SO_4)_2$ at low temperatures, we decided to study the temperature and frequency dependence of the proton and ^{87}Rb spin-lattice relaxation rates T_1^{-1} in a $Rb_3H(SO_4)_2$ single crystal.

If the proton is located in the midpoint of the H bond at the center of symmetry or moving in a symmetric double-minimum potential between two off-center sites related by inversion symmetry, the proton intra-H-bond motion should not be effective in producing spin-lattice relaxation via a modulation of the dipole-dipole or chemical shift interactions. As a result of that the proton T_1 should become very long when the proton interbond motion, connected with rotations of the SO_4 tetrahedra, freezes out. The proton T_1 should be in this case at low temperature determined by spin diffusion and dipolar coupling to paramagnetic impurities.[17]

Spin diffusion is nearly temperature independent and characterized by a $\sqrt{\omega_L}$-type dependence on the Larmor frequency. If, however, the proton moves between two off-center sites in a locally asymmetric H-bond potential, the proton motion should produce spin-lattice relaxation via the modulation of the ^{87}Rb-proton and/or proton-proton dipolar coupling $\mathcal{H}_D$ as well as via a modulation of the proton chemical shift anisotropy tensor $\Delta\sigma$.[17] Here we have

$$\frac{1}{T_1'} = \left(\frac{1}{T_1}\right)_D + \left(\frac{1}{T_1}\right)_{\Delta\sigma}, \tag{1}$$

where

$$\left(\frac{1}{T_1}\right)_D = \langle|\Delta\mathcal{H}_D|^2\rangle\left(\frac{1}{3}\frac{\tau}{1+(\omega_{LI}-\omega_{LS})^2\tau^2} + \frac{\tau}{1+(\omega_{LI}\tau)^2}\right.$$
$$\left. + \frac{2\tau}{1+(\omega_{LI}+\omega_{LS})^2\tau^2}\right) \tag{2a}$$

and

$$\left(\frac{1}{T_1}\right)_{\Delta\sigma} = \langle|\Delta\sigma H_0|^2\rangle\frac{\tau}{1+\omega_{LI}^2\tau^2}. \tag{2b}$$

Here $\omega_{LI} = \gamma_H H_0$ is the proton Larmor frequency and $\omega_{LS} = \gamma_{Rb} H_0$ is the ^{87}Rb Larmor frequency whereas τ is the effective correlation time. $\Delta\mathcal{H}_D$ is the fluctuation in the Rb-H dipolar interaction and $\Delta\sigma$ the fluctuation in the ^{1}H chemical shift anisotropy tensor due to proton motion between the two equilibrium sites in the O-H···O hydrogen bond potential. H_0 is the magnitude of the external magnetic field. In the slow motion limit at low temperatures where $\omega_{LI}\tau \gg 1$ we thus have

$$\left(\frac{1}{T_1}\right)_D \approx \frac{\langle|\Delta\mathcal{H}_D|^2\rangle}{\tau}\left[\frac{1}{3(\omega_{LI}-\omega_{LS})^2} + \frac{1}{\omega_{LI}^2} + \frac{2}{(\omega_{LI}+\omega_{LS})^2}\right]$$
$$= f(\omega_{LI}) \tag{3a}$$

and

$$\left(\frac{1}{T_1}\right)_{\Delta\sigma} \approx \frac{\langle|\Delta\sigma|^2\rangle}{\tau} \neq f(\omega_{LI}). \tag{3b}$$

In the fast motion limit at higher temperatures, the limit $\omega_{LI}\tau \ll 1$ should apply so that

$$\left(\frac{1}{T_1}\right)_D \approx \langle|\Delta\mathcal{H}_D|^2\rangle\tau \neq f(\omega_{LI}) \tag{4a}$$

and

$$\left(\frac{1}{T_1}\right)_{\Delta\sigma} \approx \langle|\Delta\sigma|^2\rangle H_0^2\tau = f(\omega_{LI}). \tag{4b}$$

Since τ increases with decreasing temperature T_1 should become larger at lower temperatures if we are in the slow motion limit, $\omega_{LI}\tau \gg 1$, [Eqs. (3a) and (3b)], whereas it should become shorter if we are in the fast motion limit, $\omega_{LI}\tau \ll 1$, [Eqs. 4(a) and 4(b)]. If we are in the slow motion limit and dipolar coupling is rate determining, T_1^{-1} is proportional to the square of the Larmor frequency, whereas it is Larmor

frequency independent in this limit if chemical shift anisotropy fluctuations are rate determining.

The effective correlation time τ consists of two contributions. At higher temperatures it is determined by thermally activated proton hopping across the potential barrier, τ_{Ar}, whereas it is at lower temperatures determined by phonon-assisted tunneling τ_T:[18]

$$\frac{1}{\tau} = \frac{1}{\tau_{Ar}} + \frac{1}{\tau_T}. \tag{5}$$

It is well known that the classical Arrhenius hopping rate in an asymmetric double well [Fig. 1(b)] is

$$\tau_{Ar}^{-1} = 2\tau_\infty^{-1} \exp(-E_a/k_B T) \cosh\left[\frac{A}{2k_B T}\right], \tag{6a}$$

whereas the phonon-assisted tunneling rate is given by

$$\tau_T^{-1} = \tau_0^{-1} \sqrt{1 + (A/\Gamma)^2} \coth\left(\frac{\sqrt{A^2 + \Gamma^2}}{2k_B T}\right) \tag{6b}$$

and is finite as $T \to 0$. This means that the decrease in the proton T_1^{-1} will level off at low temperature as the temperature dependence of the tunneling time τ_T is much weaker than that of the Arrhenius hopping time τ_{Ar}. Here E_a is the activation energy, A is the asymmetry of the double-well H-bond potential, Γ represents the tunneling matrix element of the ground-state doublet, τ_∞ is the Arrhenius correlation time at $T \to \infty$, and τ_0 is proportional to Γ^3.

The effective correlation time τ depends on the H-bond asymmetry A, which is because of the self-trapping randomly distributed over the H-bond network in the crystal. For a Gaussian asymmetry distribution function $\rho(A)$ with a variance σ_A, the proton spin-lattice relaxation time is obtained by integrating the spectral density over the distribution function $\rho(A)$. Thus we get the expression for the proton spin-lattice relaxation time

$$\frac{1}{T_1} = \int_{-\infty}^{\infty} \rho(A)(1 - p^2)\frac{1}{T_1'} dA, \tag{7}$$

where $1/T_1'$ is given by Eq. (1). p is the local polarization of the H bond and depends on the H-bond asymmetry A, tunneling matrix element Γ, and temperature as[18]

$$p = \left(\frac{A}{\sqrt{A^2 + \Gamma^2}}\right) \tanh\left(\frac{\sqrt{A^2 + \Gamma^2}}{2k_B T}\right). \tag{8}$$

It should be noted that the biasing factor $1 - p^2$ occurring in Eq. (7) stays finite at $T = 0$ because of quantum effects,

$$(1 - p^2)_{T=0} = \frac{\Gamma^2}{A^2 + \Gamma^2} \tag{9}$$

whereas it vanishes in the classical limit where $\Gamma \to 0$.

This together with the finite value of τ_T allows for a finite proton spin-lattice relaxation rate at $T = 0$ in case of phonon-assisted proton tunneling in contrast to the classical ''hopping motion'' case where $1 - p^2$ vanishes as $T \to 0$ and T_1 goes to infinity in this limit.
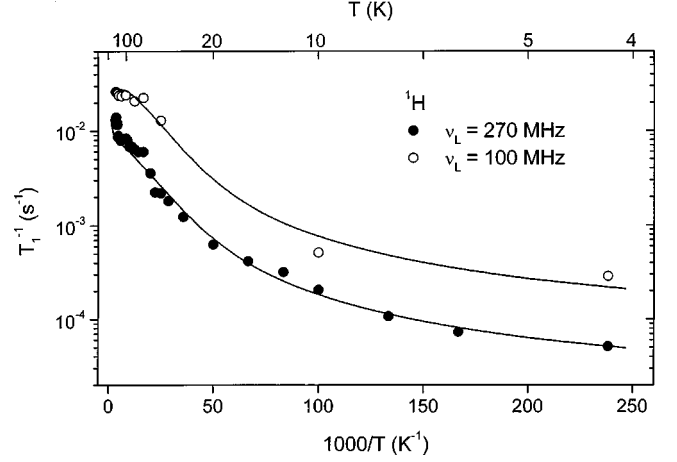

FIG. 2. Temperature dependence of the proton spin-lattice relaxation rate T_1^{-1} in a $Rb_3H(SO_4)_2$ single crystal at 100 and 270 MHz. The low-temperature part is dominated by the phonon-assisted proton tunneling. The solid lines represent a fit to Eqs. (1), (2), and (5)–(9).

IV. RESULTS AND DISCUSSION

The temperature dependence of the proton T_1 of a $Rb_3H(SO_4)_2$ single crystal is shown in Fig. 2 for $\mathbf{a} \| \mathbf{H}_0$, $\mathbf{c} \perp \mathbf{H}_0$ at 270 and 100 MHz. Except for a shoulder around 80 K, T_1 increases with decreasing temperature in the temperature range between 300 and 7 K. Between 7 and 4 K it gradually becomes temperature independent. In the whole measured temperature interval the proton T_1 is Larmor frequency dependent. The results are similar to the proton T_1 data obtained[1] in powdered $Rb_3H(SO_4)_2$ except for the frequency dependence above 50 K. Namely, in the powdered sample the proton T_1 measured at 18 and 37 MHz is frequency independent above 50 K and frequency dependent below this temperature. Here the frequency independence of the proton T_1 at higher temperatures has been ascribed to cross relaxation with the quadrupole perturbed $^{85,87}Rb$ spin system. This mechanism cannot explain our single-crystal results as no level crossing or frequency matching between the quadrupole perturbed $^{85,87}Rb$ Zeeman energy levels and the proton Zeeman energy levels can take place at 100 and 270 MHz.

The increase in the proton T_1 with decreasing temperature between 100 and 4 K (Fig. 2) means that we are in the slow motion regime $\omega_L \tau \gg 1$ in most of the investigated temperature interval. According to expression (3a) T_1 should be Larmor frequency dependent if it is mainly determined by Rb-H dipolar coupling fluctuations involving proton transfer from one equilibrium site in the asymmetric H-bond potential to another whereas it should be Larmor frequency independent if it is determined by chemical shift tensor fluctuations.
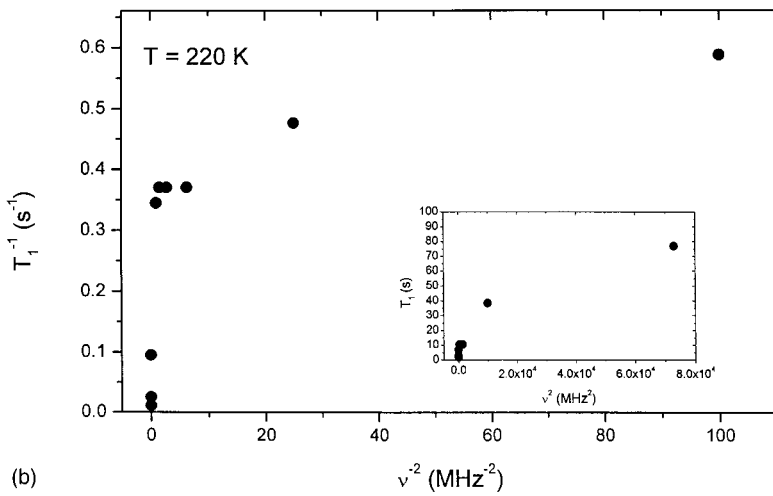
The observed frequency dependence of the proton spin-lattice relaxation rate T_1^{-1} at 4 K [Fig. 3(a)] can be fitted to the expression

$$\frac{1}{T_1} = A + B\nu_L^{-2}, \tag{10}$$

where $A = 4 \times 10^{-6}$ s^{-1} measures the frequency independent contribution and $B = 1.6$ s^{-3} the frequency dependent one. A
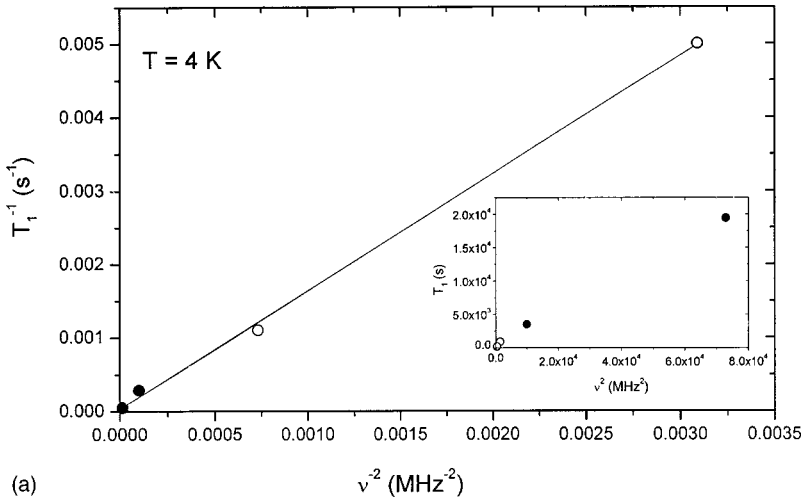
FIG. 3. Larmor frequency dependence of the proton T_1 at (a) $T = 4$ K and (b) $T = 220$ K. The solid line represents the fit to Eq. (10). The open symbols are the data from Ref. 1.

qualitatively similar Larmor frequency dependence has been also observed below 50 K in powdered $Rb_3H(SO_4)_2$ at $\nu_L = 18$ MHz and 37 MHz. This behavior agrees rather well with the predictions of Eqs. (1)–(8) and shows that Rb-H dipolar coupling mainly determines the proton T_1 at low temperatures.

Between 100 and 280 K the temperature dependence of the T_1^{-1} changes. At $\nu_L = 270$ MHz the T_1^{-1} versus $1000/T^3$ curve becomes nearly temperature independent whereas the change in the T_1^{-1} versus temperature slope is smaller at 100 MHz. This seems to suggest that relaxation via chemical shift tensor fluctuations becomes more important at higher temperatures and that we are approaching the crossover between the $\omega_L \tau \gg 1$ and $\omega_L \tau \ll 1$ regimes. At 220 K the Larmor frequency dependence is rather different [Fig. 3(b)] from the one at 4 K. At high Larmor frequencies, T_1 becomes less Larmor frequency dependent than at lower ones. This as well shows a significant chemical shift tensor fluctuation contribution to T_1^{-1}.

The temperature dependence of the proton T_1 below 50 K can as well be described by the above expressions provided that below 7 K phonon-assisted tunneling rather than thermally activated hopping between the two O-H$\cdots$O equilibrium sites becomes rate determining: $1/\tau_T \gg 1/\tau_{Ar}$. The obtained parameters from the fit are $E_a = 6.3$ meV, $\Gamma = 0.5$ meV, $\tau_\infty = 3.9 \times 10^{-6}$ s, $\tau_0 = 2.8 \times 10^{-4}$ s, and $\sigma_A = 0.6$ meV. It should be noted that the obtained activation

energy 6.3 meV is significantly lower than the activation energy 0.82 eV found for deuteron inter-H-bond motion in $Rb_3D(SO_4)_2$ by 2D exchange NMR.[2] It is however of the same order of magnitude as the one found for phonon-assisted O-H$\cdots$O proton tunneling in $Rb_{0.5}(NH_4)_{0.5}H_2PO_4$ proton glasses.[18] This seems to show that phonon-assisted proton tunneling between the two off-center sites in the O-H$\cdots$O bonds indeed takes place in $Rb_3H(SO_4)_2$ below 7 K.

As suggested by the different Larmor frequency dependence the relaxation via chemical shift anisotropy fluctuations must be taken into account at higher temperature. The shoulder in the temperature dependence of the proton T_1 about 80 K in particular cannot be explained just by the dipolar relaxation. If the above explanation is correct the chemical shift anisotropy fluctuation mechanism becomes less effective at lower temperatures and Rb-H dipolar coupling fluctuations take over.

The reasons for this crossover could be the following:

(i) There is a significant change in the H-bond potential at lower temperatures which diminishes the difference $\Delta\sigma$ in the chemical shift tensors between the two equilibrium sites in the H bond without affecting too much the Rb-H dipolar interaction.

(ii) The second possibility is that there is a temperature-dependent shift in the position of at least one Rb ion and a corresponding decrease in the Rb-proton distance R resulting in an increase in $\langle |\Delta\mathcal{H}_D|^2 \rangle$,
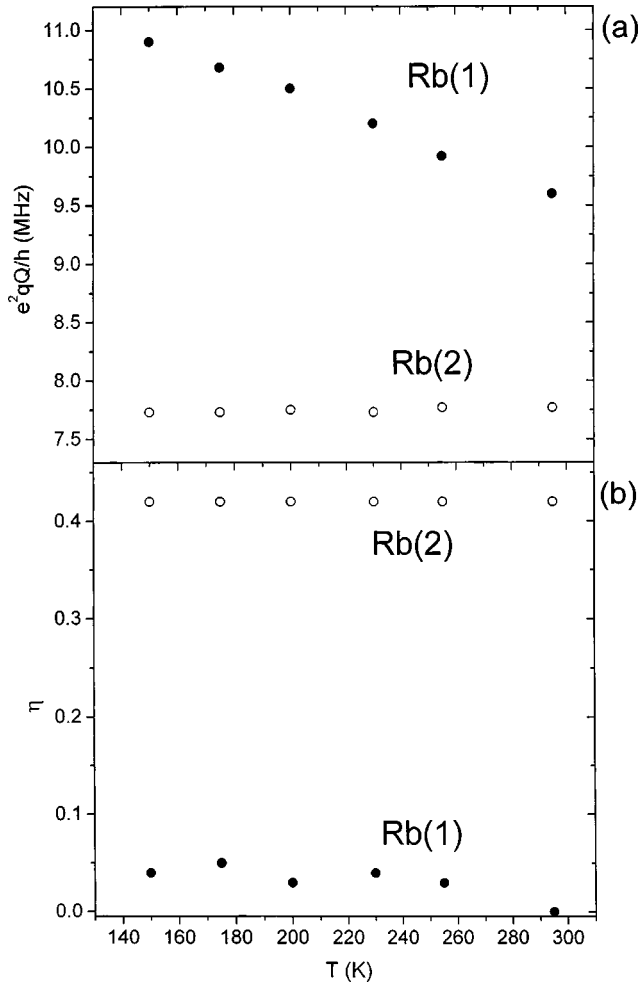
FIG. 4. Temperature dependence of Rb(1) and Rb(2) (a) quadrupole coupling constants e^2qQ/h and (b) asymmetry parameters η in $Rb_3H(SO_4)_2$ measured by proton-rubidium double nuclear-magnetic resonance in the laboratory frame.

$$\left(\frac{1}{T_1}\right)_D \propto \langle |\Delta\mathcal{H}_D|^2\rangle \propto \left\langle \left|\frac{1}{R^3}\left(\frac{\Delta l}{R}\right)\right|^2\right\rangle.$$

Here Δl is the distance between the two off-center sites in the H bond and R is a typical distance between a Rb site and the center of the H bond, which may depend on temperature.

Which of the above two possibilities is in fact realized cannot be decided on the basis of the above experiments alone. It should, however, be noticed that the temperature dependence of the quadrupole coupling constant of Rb(1)—which is close to the O-H··O bonded proton—is anomalously strong[4] so that the second possibility seems more likely. This is also supported by the fact that the Rb(2) quadrupole coupling constant is nearly temperature independent (Fig. 4). It should also be noted that the deuteron T_1 anomaly at T_c may as well be caused by a fluctuation in the Rb-deuteron dipolar coupling due to large fluctuations in the Rb(1) positions.[3]

As already mentioned the proton T_1 at low temperatures is nearly temperature-independent as expected for phonon-assisted incoherent tunneling.[17] The observed Larmor frequency dependence of the T_1 (Fig. 3) at 4 K is—as discussed
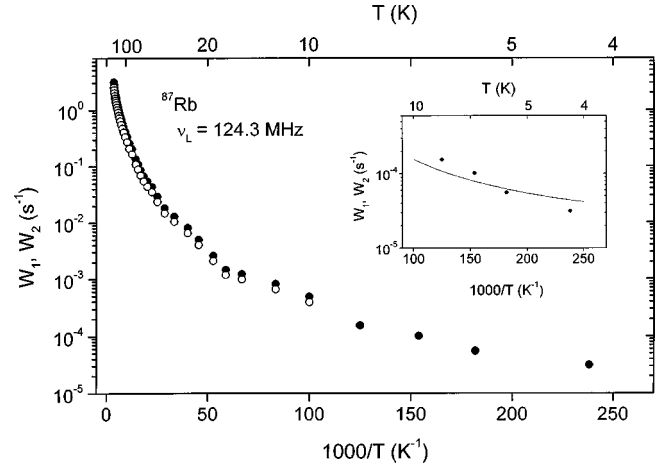

FIG. 5. Temperature dependence of the ^{87}Rb spin-lattice relaxation rates W_1 and W_2 in $Rb_3H(SO_4)_2$. Note the temperature-independent contribution at low temperatures. The solid line represents a fit to Eqs. (1), (2), and (5)–(9). The fit parameters are, apart from a scaling factor, the same as those for the proton T_1.

above—too strong for relaxation via spin diffusion to paramagnetic impurities. It is closer to the ω_L^2 expected for phonon-assisted incoherent tunneling than to the $\sqrt{\omega_L}$ law expected for relaxation via spin diffusion to paramagnetic impurities. Spin diffusion may however be responsible for the Larmor frequency independent contribution A at 4 K in addition to chemical shift tensor fluctuations. This is in agreement with measurements of rubidium spin-lattice relaxation rates in $Rb_3H(SO_4)_2$ and $Rb_3D(SO_4)_2$, where it was determined from the ratio $T_1(^{85}Rb)/T_1(^{87}Rb)$ that both spin-diffusion as well as electric quadrupolar relaxation due to phonon-assisted tunneling are present at temperatures below 17 K.[2]

The observed temperature and Larmor frequency dependence of the proton T_1 can be thus indeed quantitatively described by the relaxation via the modulation of the dipolar coupling and by phonon-assisted proton tunneling between the two asymmetric off-center sites in the H-bond potential even down to 4 K (Fig. 2). Previous ^{87}Rb NMR measurements[2,4,5] in $Rb_3H(SO_4)_2$ and $Rb_3D(SO_4)_2$ single crystals were interpreted as being incompatible with an asymmetric double-well H-bond potential—space group $A2$—above and below T_c. Deuteron spin-lattice relaxation time measurements in $Rb_3D(SO_4)_2$, however, have shown[3] that the proper space group is $A2$ in $Rb_3D(SO_4)_2$, both above as well as below T_c, but the deviations from $A2/a$ are small. The proton and deuteron NMR results would thus agree with the Rb NMR spectra if the deviations from the $A2/a$ space group are so small that the additional Rb lines in the NMR spectra cannot be resolved.

The results seem to agree qualitatively with the incoherent neutron-scattering data.[16] It should be noticed (Fig. 5) that the temperature dependencies of the ^{87}Rb spin-lattice transition rates W_1 and W_2 show at lower temperatures below 15 K a similar temperature-independent contribution as the proton T_1. This contribution can—apart from a scaling factor—be fitted by the same parameters as the temperature dependence of the proton T_1. It thus seems that this contri-

bution is due to Rb-proton dipolar coupling and that the temperature independence arises from the phonon-assisted proton tunneling between the two asymmetric off-center sites in the O-H$\cdots$O bond.

The above results thus show the following:

(i) There is no evidence for a change from the double to symmetric single minimum type H-bond potential in $Rb_3H(SO_4)_2$ down to 4 K.

(ii) The double-minimum potential is locally asymmetric so that the instantaneous space-group symmetry of $Rb_3H(SO_4)_2$ is $A2$ and the centrosymmetric space group $A2/a$, seen by x rays, is realized only on the space and time average.

(iii) Below 7 K phonon-assisted incoherent proton tunneling between the two locally asymmetric off-center proton sites in the O-H$\cdots$O bond becomes rate determining.

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*On leave from Institute of Physics of Solids and Semiconductors, Minsk, Belarus.

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