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Deuteron NMR and the local symmetry of the H bond in $Rb_3D(SO_4)_2$

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The temperature and angular dependencies of the deuteron NMR spectra of $Rb_3D(SO_4)_2$ have been measured and the electric-field gradient (EFG) tensors at the deuteron sites have been determined both above and below the antiferroelectric transition temperature T_c. In contrast to the ^{87}Rb $\frac{1}{2}\rightarrow-\frac{1}{2}$ NMR spectra no pronounced deuteron line splitting has been found at T_c. This seems to show that there is a center of symmetry at the midpoint of the O-D$\cdots$O bond. The above results are compatible with the centrosymmetric space group $A2/a$ and a doubling of the unit-cell axes along the b and c directions below T_c. The appearance of a small, but definite, anomaly in the deuteron spin-lattice relaxation T_1 at T_c on the other hand suggests that the deuteron motion between the two off-center sites in the O-D$\cdots$O bond is connected with electric-field gradient tensor fluctuations. The H-bond potential must be thus slightly asymmetric so that the true space group is $A2$ both above and below T_c. The deviations from $A2/a$ must be, however, rather small. The H-bond asymmetry fluctuates in space and time due to deuteron motion so that the time- and space-average crystal symmetry seen by x rays is indeed $A2/a$. [S0163-1829(99)04317-9]

I. INTRODUCTION

$Rb_3H(SO_4)_2$ and $Rb_3D(SO_4)_2$ belong to the $M_3H(XO_4)_2$ ($M=$K, Rb, Cs and $X=$Se, S) family of H-bonded crystals which shows unique isotope effects on replacing hydrogen by deuterium.[1,2] Whereas $Rb_3D(SO_4)_2$ undergoes an antiferroelectric phase transition at $T_c=82$ K, $Rb_3H(SO_4)_2$ remains paraelectric down to the lowest temperatures where measurements have been made. The structure of these systems consists of isolated H-bonded dimeric units $[(SO_4)\text{-}H\cdots SO_4)]^{3-}$ separated by Rb ions. The length of the H-bond in $Rb_3H(SO_4)_2$ at room temperature is 2.485 Å[3] whereas the O-D$\cdots$O bond in $Rb_3D(SO_4)_2$ is slightly longer. According to x-ray diffractions the room-temperature structure of both $Rb_3H(SO_4)_2$ and $Rb_3D(SO_4)_2$ is monoclinic with the space group $A2/a$ and four formula units per unit cell ($Z=4$). It should be noted that there are, in fact, two formula units per primitive cell but that a unit cell with $Z=4$ is chosen for sake of convenience. This structure, which also agrees with the number of observed Rb $\frac{1}{2}\rightarrow-\frac{1}{2}$ lines in single crystal ^{87}Rb NMR experiments,[4,5] implies that there exists a center of inversion symmetry at the midpoint of the O-D$\cdots$O or O-H$\cdots$O hydrogen bonds. The protons and deuterons should be thus either statistically or dynamically disordered between the two potential minima in the O-H$\cdots$O bonds, or alternatively, located at the center of the H bond.

The low-temperature space group of $Rb_3D(SO_4)_2$ is not yet known. For $Rb_3D(SeO_4)_2$ at $T<T_c=25$ K the space group is $A2$ ($Z=16$) (Ref. 6) and not $P2_1/a$ as suggested previously for $K_3D(SO_4)_2$.[7] The $A2$ space group in the general case predicts the observation of 24 Rb lines in $Rb_3D(SO_4)_2$ and implies the absence of the center of symmetry in the middle of the H bond.

Recent inelastic neutron-scattering experiments have suggested[8] that the H bond in $M_3H(SO_4)_2$-type compounds is even at room temperature not really symmetric but rather of the asymmetric double-minimum type. The O-H$\cdots$O double-minimum potential could be symmetric only on the space and/or time average.

In order to check on the local symmetry of the H bonds and the origin of the isotope effects in $Rb_3D(SO_4)_2$ we decided to perform a deuteron NMR study of $Rb_3D(SO_4)_2$. The nuclear electric quadrupole interaction of the deuteron ($I=1$) is namely one of the most sensitive probes of the structure and local symmetry of O-D$\cdots$O bonds as shown in numerous experiments in KH_2PO_4-type H-bonded crystals.[9]

II. EXPERIMENT

Crystals were grown from aqueous solutions by the evaporation method and were oriented by x-ray diffractions. A rectangular laboratory frame $\tilde{a}\perp\tilde{b}\perp\tilde{c}$ was chosen for crystal rotations. The deuteron NMR spectra have been measured at a Larmor frequency $\nu_L=58.34$ MHz. The occurrence of the phase transition was checked by ^{87}Rb NMR at $\nu_L=124.33$ MHz. The $90^\circ_x-90^\circ_y$ quadrupolar solid echo sequence has been used.

III. RESULTS

The temperature dependence of the deuteron quadrupole perturbed NMR frequencies in $Rb_3D(SO_4)_2$ at $\tilde{c}\perp B_0$, $\angle(\tilde{a},B_0)=0°$ is shown in Fig. 1. Two doublets (i.e., four lines) corresponding to two magnetically nonequivalent deuteron sites in the unit cell are found both above and below T_c. There is no change in the multiplicity of the spectra and no line splitting at T_c in contrast to the ^{87}Rb case where the three ^{87}Rb $\frac{1}{2}\rightarrow-\frac{1}{2}$ NMR lines split on cooling below T_c into 12 lines at the same orientation (Fig. 2). There is, however, a sharp increase [Fig. 3(a)] in the width of the deuteron lines below T_c which might indicate the presence of unresolved deuteron line splittings. The width of the ^{87}Rb lines in $Rb_3D(SO_4)_2$, on the other hand, is practically the same below T_c as above T_c [Fig. 3(b)]. The peak in the Rb linewidth at T_c may be the result of inhomogeneous broadening be-

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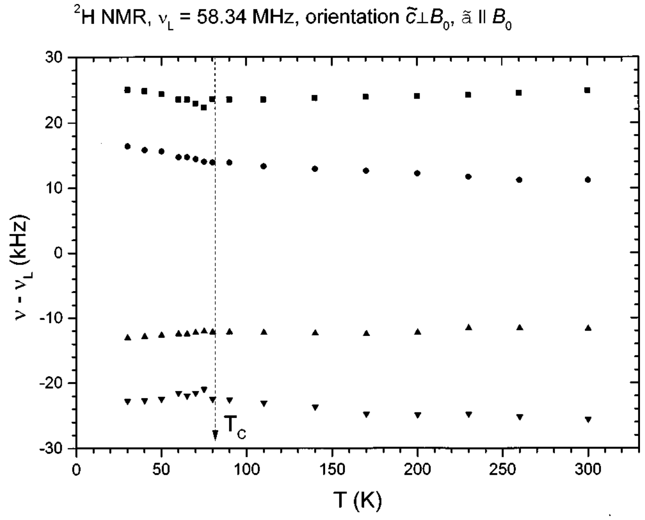

FIG. 1. Temperature dependence of the ^{2}H NMR lines in $Rb_3D(SO_4)_2$ at $\tilde{c}\perp B_0$, $\angle(\tilde{a},B_0)=0°$ between room temperature and 30 K.

cause of overlapping lines connected with the transition to the low-temperature phase. It should be also noted that in $Rb_3H(SO_4)_2$ as well three ^{87}Rb $\frac{1}{2}\rightarrow-\frac{1}{2}$ NMR lines are seen (Fig. 4) in the whole temperature interval between room temperature and 4 K. This is compatible with the space group $A2/a$. There is no sign of a phase transition in the protonated compound which thus seems to be isomorphous with the high-temperature phase of $Rb_3D(SO_4)_2$.

The deuteron angular rotation patterns in $Rb_3D(SO_4)_2$ for three mutually perpendicular orientations have been measured at room temperature as well as just above and below T_c and the electric-field gradient (EFG), respectively, the quadrupole coupling tensors have been determined. The changes in the deuteron quadrupole coupling on cooling are rather small (Fig. 5). The results are collected in Tables I and II.

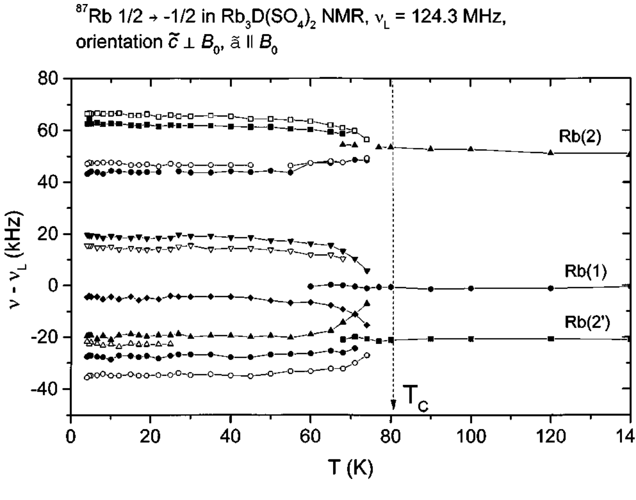

FIG. 2. Temperature dependence of the ^{87}Rb $\frac{1}{2}\leftrightarrow-\frac{1}{2}$ NMR lines in $Rb_3D(SO_4)_2$ at $\tilde{c}\perp B_0$, $\angle(\tilde{a},B_0)=0°$ between room temperature and 4 K. The Rb(2) and Rb(2′) sites are connected via glide reflection and are thus chemically equivalent but magnetically nonequivalent. The Rb(1) site is nonequivalent with the Rb(2) and Rb(2′) sites.

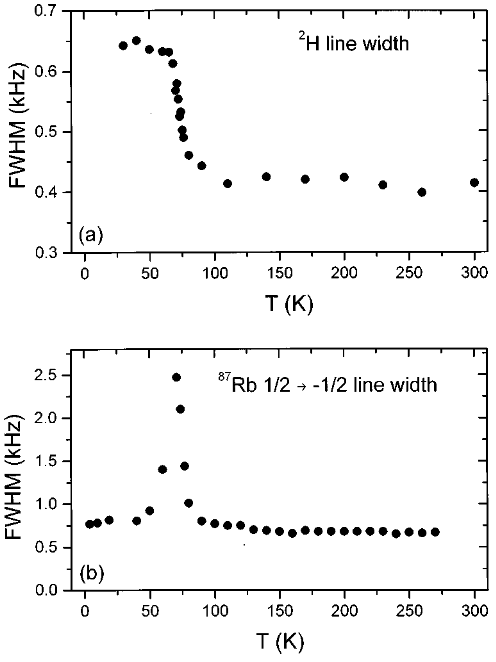

FIG. 3. (a) Temperature dependence of the deuteron NMR linewidths, (b) temperature dependence of the ^{87}Rb $\frac{1}{2}\leftrightarrow-\frac{1}{2}$ NMR linewidths.

The temperature dependence of the deuteron spin-lattice relaxation time T_1 is shown in Fig. 6(a). It increases with decreasing temperature and shows a rather small but distinct anomalous drop at T_c. Below T_c it again increases with decreasing temperature and shows signs of becoming temperature independent below 50 K. In contrast to the deuteron T_1 the two ^{87}Rb inverse spin-lattice relaxation rates W_1^{-1} and W_2^{-1} show a very pronounced anomalous drop at T_c [Fig. 6(b)]. Here too the inverse relaxation rates increase below T_c with decreasing T and tend to become temperature independent below 10 K. It should be noted that there is no

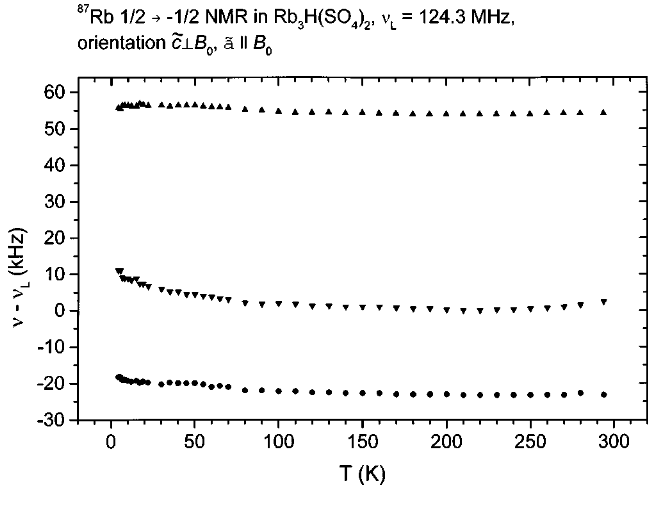

FIG. 4. Temperature dependence of the ^{87}Rb $\frac{1}{2}\leftrightarrow-\frac{1}{2}$ NMR lines in $Rb_3H(SO_4)_2$ at $\tilde{c}\perp B_0$, $\angle(\tilde{a},B_0)=0°$ between room temperature and 4 K.

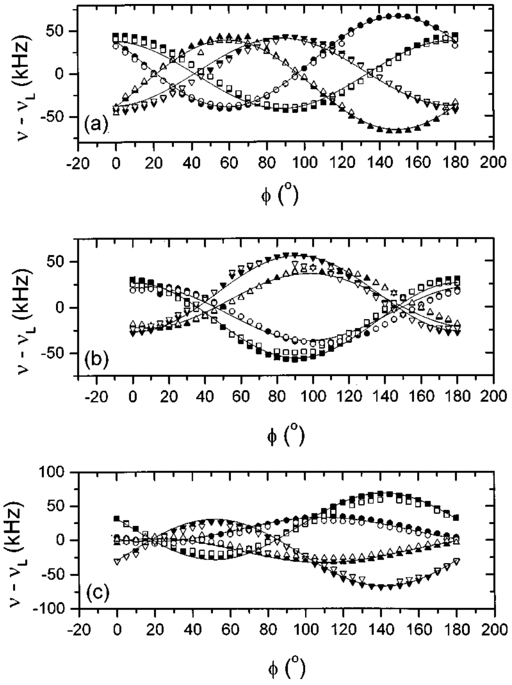

FIG. 5. Angular dependence of the deuteron quadrupole splitting in $Rb_3D(SO_4)_2$ (a) rotation around the laboratory $\tilde{a}$ axis at $T = 300\ K > T_c$ (solid circles) and $T = 72\ K < T_c$ (open circles), (b) rotation around the laboratory $\tilde{b}$ axis at $T = 300\ K > T_c$ (solid circles) and $T = 72\ K < T_c$ (open circles), and (c) rotation around the laboratory $\tilde{c}$ axis, which is perpendicular to the $\tilde{a}\tilde{b}$ plane at $T = 300\ K > T_c$ (solid circles) and $T = 72\ K < T_c$ (open circles).

Rb spin-lattice relaxation rate anomaly in the undeuterated compound where there is no structural phase transition.[4,5]

IV. DISCUSSION

There are two conflicting explanations of the isotope effects in $Rb_3H(SO_4)_2$ and $Rb_3D(SO_4)_2$. According to the first—which is based on x-ray diffractions[10]—the crystal lattice parameters and the H-bond contract with decreasing temperature. As a result of that it has been suggested that the double-minimum O-H···O potential in $K_3H(SO_4)_2$ crosses the critical bond length $R_{O\cdots O} = 2.47$ Å around 100 K and changes into a symmetric single-minimum-type potential. This would result in a vanishing of the O-H···O bond electric dipole moment before a phase transition could take place.[11]

In the deuterated compound, on the other hand, the H bond is longer and the phase transition takes place before the O-D···O bond contracts below the critical value where the double-minimum potential would change into a symmetric single-minimum one.

TABLE I. Deuteron quadrupole coupling constant $(e^2qQ/h)_D$ and asymmetry parameter η for the two magnetically nonequivalent but chemically equivalent deuterons in $Rb_3D(SO_4)_2$ at 300 K, 84 K, and 72 K.

	$T = 300$ K	$T = 84\ K > T_c$	$T = 72\ K < T_c$
e^2qQ/h	96 kHz	87 kHz	87 kHz
η	0.06	0.09	0.09

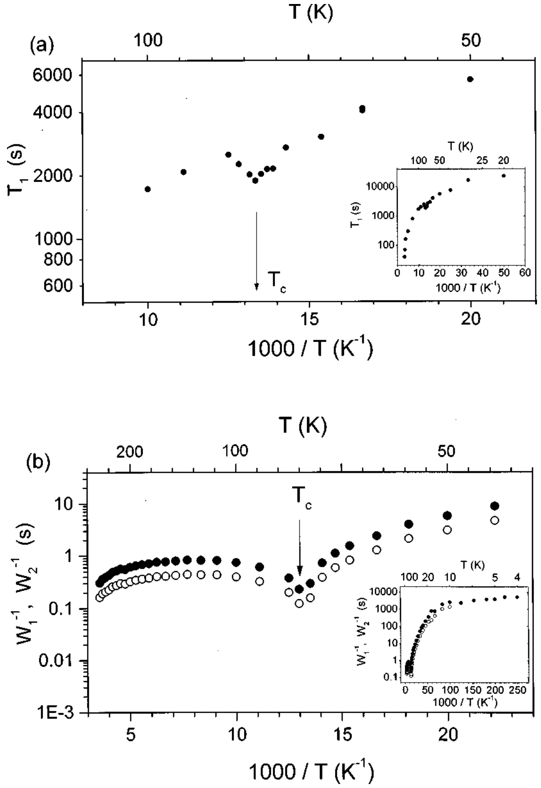

FIG. 6. Temperature dependence of (a) the ^2H spin-lattice relaxation time T_1 and (b) the ^{87}Rb $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ spin-lattice relaxation rates W_1^{-1} and W_2^{-1} in $Rb_3D(SO_4)_2$.

According to the second model, the H-bond contraction should have little or no role in the phase-transition mechanism. The isotope effect is here due to the mass difference between H and D resulting in different dynamical properties such as hydrogen tunneling or zero-point energy vibrations.[9] The pseudospin Ising model in a transverse field, in particular, predicts that the phase transition is suppressed if the tunneling matrix element becomes larger than the pseudospin coupling constant.

Let us now see what are the implications of the above deuteron NMR data for these two models. The first thing to be discussed is the spectroscopic evidence for the proposed change in the shape of the H-bond potential. The deuteron quadrupole coupling constant $(e^2qQ/h)_D$ is known to be a very sensitive indicator of the local symmetry and the length of the O-H and $R_{O\cdots O}$ bonds. In KD_2PO_4 where $R_{O\cdots O} = 2.49$ Å and $R_{O\text{-}D} \approx 1.05$ Å the deuteron quadrupole coupling constant is $(e^2qQ/h)_D \approx 120$ kHz, and in triglycine sulfate (TGS) where $R_{O\cdots O} = 2.44$ Å, $(e^2qQ/h)_D \approx 87$ kHz. In both of these systems the deuteron moves in a double-well potential. In the K-H maleate ion, on the other hand, where $R_{O\cdots O} = 2.40$ Å, $R_{O\text{-}D} = 1.20$ Å and the H bond is symmetric with the deuteron at the midpoint between the two oxygen, the deuteron quadrupole coupling constant is much lower $(e^2qQ/h)_D \approx 56$ kHz.

The observed magnitude of the deuteron quadrupole coupling constant, $(e^2qQ/h)_D \approx 96$ kHz in $Rb_3D(SO_4)_2$, at room temperature shows that the deuteron is not at the center of the H bond or close to it. The magnitude of $(e^2qQ/h)_D$ is

TABLE II. Deuteron quadrupole coupling tensors components (kHz) for the two magnetically nonequivalent deuterons of $Rb_3D(SO_4)_2$ at 300 and 84 K$>T_c$. The EFG tensor components at 72 K$<T_c$ are the same as the one at 84 K. The orientation of the EFG tensor is such that the largest principal axis V_{ZZ} is very nearly parallel to the O-D···O bond direction, the second principal axis V_{YY} is normal to the plane formed by the deuteron, the nearest oxygen and the S atom of the SO_4 group to which the deuteron is bonded, and the third axis V_{XX} is perpendicular to V_{ZZ} and V_{YY}.[9] The fits of the angular dependencies were corrected for crystal misalignments. Note that the quadrupolar coupling tensors are expressed in the laboratory $\tilde{a}$, $\tilde{b}$, $\tilde{c}$ frame and not in the crystal axes fixed a, b, c frame. The deviation of the monoclinic axis from $\tilde{b}$ direction is ≈25°.

$T=300$ K	qQV_{zz}/h	eQV_{yy}/h	eQV_{xx}/h	eQV_{xy}/h	eQV_{xz}/h	eQV_{yz}/h
^{2}H(1)	−40.3	−5	45.3	−65.3	22	−17.8
^{2}H(2)	−2.7	53.1	−50.5	4	1.1	64.9
$T=84$ K	eQV_{zz}/h	eQV_{yy}/h	eQV_{xx}/h	eQV_{xy}/h	eQV_{xz}/h	eQV_{yz}/h
^{2}H(1)	−32	−6.7	38.7	−59.5	24.7	−17.1
^{2}H(2)	1.1	46.1	−47.2	3.2	4.0	59.3

in between the values found in KD_2PO_4 and TGS. In spite of the relatively large temperature interval covered there is no significant decrease in the deuteron quadrupole coupling constant on cooling. At 84 K $(e^2qQ/h)_D \approx 87$ kHz and at 72 K $(e^2qQ/h)_D$ is as well 87 kHz. This causes some doubt on the proposed lengthening of the O-D bond and the gradual shift of the deuteron towards the center of the H bond with decreasing temperature. The fact that the deuteron quadrupole coupling constant is practically the same above as well as below T_c and close to the one found at room temperature, means that the deuteron is above T_c dynamically disordered between two distinct off-center sites and freezes into one of these two sites below T_c.

The second problem to be discussed is the proper space group and the existence or nonexistence of the center of symmetry at the midpoint between the two oxygen in the O-H···O bond. The exact space group of $Rb_3D(SO_4)_2$ and $Rb_3H(SO_4)_2$ and isomorphous compounds has been the subject of controversy for some time.

It should be stressed that the number of observed NMR lines can be smaller but never larger than predicted by the space-group symmetry. The space groups $P2_1/a$ $(Z=4)$ and later $A2$ $(Z=16)$ were reported[7,12] for $K_3D(SO_4)_2$ at $T<T_c$. It is now generally assumed that the proper space group for $K_3D(SO_4)_2$ above T_c is $A2/a$ $(Z=4)$ and below T_c $A2$ $(Z=16)$. It has been also suggested[13] that the phase transition in $Rb_3D(SeO_4)_2$ at $T_c=92$ K takes place without a change in the space group. The proper space group would be $A2/a$ both above and below T_c so that the center of symmetry would not be destroyed by the phase transition. Very recently it has been suggested[6] that the space group of $Rb_3H(SeO_4)_2$ is not $A2/a$ but rather $A2$. The only symmetry element of $A2$ is $\{C_{2z}|000\}$ so that there is no center of inversion. In $Rb_3D(SO_4)_2$, on the other hand, a doubling of the b and c axes—similar to the one reported for $K_3D(SO_4)_2$—occurs below T_c.

For $T>T_c$ $(Z=4)$ the $A2$ space group predicts two pairs of deuteron NMR lines and six ^{87}Rb $\frac{1}{2}\rightarrow-\frac{1}{2}$ NMR lines. The *A2/a* space group, on the other hand, predicts for $T>T_c$ $(Z=4)$ two pairs of deuteron NMR lines and three ^{87}Rb $\frac{1}{2}\rightarrow-\frac{1}{2}$ NMR lines. This is exactly what is observed in $Rb_3D(SO_4)_2$ above T_c. Three ^{87}Rb $\frac{1}{2}\rightarrow-\frac{1}{2}$ NMR lines are also observed in $Rb_3H(SO_4)_2$ over the whole temperature interval so that it indeed seems to be isomorphous with the high-temperature phase of $Rb_3D(SO_4)_2$.

For $T<T_c$ $(Z=16)$ the $A2/a$ space group predicts the existence of twelve ^{87}Rb $\frac{1}{2}\rightarrow-\frac{1}{2}$ NMR lines as indeed observed in $Rb_3D(SO_4)_2$ below T_c. The number of pairs of deuteron NMR lines should be eight whereas only two have been observed. In view of the observed increase in the deuteron NMR linewidth below T_c, it is, however, quite possible that we have, in fact, more than two deuteron lines but that they are not well resolved. The occurrence of the low-temperature space group $P2_1/a$ $(Z=4)$ for $T<T_c$ can be definitely excluded since it predicts six ^{87}Rb $\frac{1}{2}\rightarrow-\frac{1}{2}$ NMR lines whereas twelve lines have been observed below T_c.

On the first glance the NMR evidence thus speaks for the occurrence of the $A2/a$ space group in $Rb_3D(SO_4)_2$ both above and below T_c as indeed previously suggested for $Rb_3D(SeO_4)_2$. This group implies the existence of the center of symmetry in the midpoint of the O-D···O bond and thus also explains the absence of a splitting of the deuteron line at T_c, where the deuterons freezes out into one of the two off-center sites.

This interpretation is, however, hard to reconcile with the observed small but definite deuteron T_1 anomaly at T_c. If there is a center of symmetry at the midpoint of the O-D···O bond, the motion of deuterons between the two off-center sites should produce no fluctuation in the deuteron electric-field gradient tensor or in the Rb-deuteron dipolar coupling. It should be, however, stressed that the anomaly in the deuteron spin-lattice relaxation time T_1 at T_c in $Rb_3D(SO_4)_2$ is significantly weaker than the one in KD_2PO_4,[9] where the deuteron motion between the two off-center sites freezes out below T_c, similarly as in $Rb_3D(SO_4)_2$, but there is no center of symmetry at the middle of the H bond. Here the deuteron transfer from one equilibrium site of the O-D···O bond to the other results in rotations of the two smaller principal axes for ±35°, resulting in significant fluctuations in the off-diagonal matrix elements of the electric-field gradient tensor.[14] There is no such rotation of the two smaller principal axes in $Rb_3D(SO_4)_2$ if there is a center of symmetry in the middle of the H bond.

One possible explanation of the T_1 anomaly at T_c [Fig. 6(a)] is that the proper space group of $Rb_3D(SO_4)_2$ is $A2$ both above and below T_c but that the deviations from the $A2/a$ space-group symmetry are rather small. In this case the H-bond potential would be slightly asymmetric as suggested by the neutron inelastic-scattering data[8] but the asymmetry could slowly fluctuate in time and space so that the time-average symmetry would be that of $A2/a$ space group above T_c—as suggested by x-ray diffractions—and of the $A2$ space group below T_c. A possible reason for the proposed asymmetry of the H-bond potential could be ''self-trapping'' of the proton due to the distortion of the SO_4 group to which it is temporarily attached. In such a case the deuteron T_1 anomaly at T_c would be produced by the condensation of a pseudospin soft mode which would result in the freezing out of the deuteron motion between the two off-center equilibrium sites below T_c. The deuteron motion between the two off-center sites would result in a rotation of the two smaller principal axes of the deuteron EFG tensor by an amount determined by the distortion of the SO_4 group. Since the presumed distortion is small it will result in a relatively small fluctuation in the electric quadrupole coupling. Such a change would not produce an observable splitting of the deuteron NMR lines at T_c but could be responsible for the increase in the linewidth and the decrease in T_1 at T_c.

The second explanation could be that the deuteron T_1 anomaly at T_c is caused by a fluctuation in the Rb-deuteron dipolar coupling due to large critical fluctuations in the Rb positions. The weak point of this explanation is that there is no structural evidence for such Rb displacements above or at T_c.

IV. CONCLUSIONS

From the above deuteron and ^{87}Rb NMR results we can conclude that:

(i) The deuteron NMR data are compatible with the deuteron motion in a double-minimum H-bond potential above T_c and a freeze-out of this motion below T_c.

(ii) There is no NMR evidence of a significant change in the shape of the O-D$\cdots$O H-bond potential between room temperature and $T_c = 82$ K or even below T_c.

(iii) The ^{87}Rb and deuteron NMR spectra and in particular the number of observed ^{87}Rb lines seem to suggest that the proper space group of $Rb_3D(SO_4)_2$ and $Rb_3H(SO_4)_2$ is $A2/a$ from room temperature down to 4 K but that a doubling of the unit-cell dimensions along the *b* and *c* axes takes place at T_c in $Rb_3D(SO_4)_2$ so that $Z=4$ changes into $Z=16$.

(iv) The observed deuteron T_1 anomaly in $Rb_3D(SO_4)_2$ at T_c is, however, incompatible with the $A2/a$ symmetry. This discrepancy could be resolved if the proper space group in $Rb_3D(SO_4)_2$ is $A2$ both above and below T_c but the deviations from $A2/a$ are small. The double-minimum-type H-bond potential is thus slightly asymmetric—possibly due to self-trapping of the deuteron—but the asymmetry may vary in space and time due to deuteron motions so that the average crystal symmetry would appear to be $A2/a$ as observed by x-ray diffractions.

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