Deuteron NMR and a model for phase transitions in monoclinic RbD_2PO_4

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The quadrupole-perturbed deuteron NMR spectra and spin-lattice relaxation times of monoclinic RbD_2PO_4 have been measured and the electric-field-gradient tensors at the deuteron sites have been determined in phase I at 110 °C, phase III at 80 °C, and phase III at 40 °C. The results are incompatible with a location of the D(2) and D(3) deuterons in the center of the corresponding H bonds. They show that these deuterons are disordered between two off-center sites in phases I and II, whereas they are ordered in phases III and IV. A four-sublattice model accounting for all four phase transitions in monoclinic RbD_2PO_4 is proposed.

I. INTRODUCTION

$RbH_{2x}D_{2(x-1)}PO_4$ is known to crystallize at room temperature in two different modifications.[1] The tetragonal form, which is isomorphous to KH_2PO_4, is stable for low deuterium concentrations whereas the monoclinic form is stable for high deuterium concentrations.[2] Samita *et al.*[2] have discovered that monoclinic RbH_2PO_4 undergoes with decreasing temperature phase transitions from phase I ($z=2$) to phase II ($z=4$) at $T_{c1}=104$ °C, and from phase II ($z=4$) to phase III ($z=8$) at $T_{c2}\approx 44$ °C. The sequence of succesive phases with decreasing temperature they found is[3,4]

$$P2_1/m\,(a_0,b_0,c_0)\rightarrow P2_1/c\,(a_0,b_0,2c_0)\rightarrow P2_1(2a_0,b_0,2c_0),$$

where $2a_0=17.352$ Å, $b_0=6.184$ Å, $2c_0=9.566$ Å, and $\beta=\sphericalangle(a,c)=108.8°$ with b being the unique monoclinic axis.

The high-temperature paraelectric phase I has the same space group as pseudo-one-dimensional monoclinic paraelectric CsH_2PO_4.[5] The transition from phase I to phase II is connected with the appearance of a superlattice along the c axis and the change of the mirror plane into a glide plane.[3,4] The transition from phase II to phase III is connected with the appearance of another superlattice along the a axis and—according to these authors[3,4]—the loss of the center of symmetry. Phase III was thus considered to be ferrielectric rather than antiferroelectric.

Very recently it has been shown,[6] however, that the spontaneous polarization does not appear at T_{c2} but at $T_{c3}=T_{c2}-5$ K. The spontaneous polarization

$$\Delta P_s=P_{sa}-P_{sb}=0.02\ \mu\text{C/cm}^2$$

is small as compared to the sublattice polarization

$$P_{sa}\approx -P_{sb}=1.8\ \mu\text{C/cm}^2$$

at 303 K.[6] Thus, there seems to be four, and not three, different phases in this system. Phase III is, according to this model, strictly antiferroelectric with a centric space group. The loss of the center of symmetry occurs only in phase IV.

The isotope shifts[7] in T_c connected with an increase in the deuterium content in $RbH_{2x}D_{2(1-x)}PO_4$ show that the O—H $\cdots$ O hydrogen bonds play a significant role in the III-II phase transition at T_{c2} but not in the I-II phase transition at T_{c1}.

The microscopic nature of all these transitions is not yet completely clear. The PO_4 tetrahedra are here—in contrast to KH_2PO_4—connected with three different kinds of hydrogen bonds.[3] One of them—associated with D(1)—has an O—O length of 2.519 Å in phase II and forms chains along the c axis. It is ordered in all phases. The other two chains of H bonds associated with D(2) and D(3) have in phase II O—O distances[3] 2.497 and 2.514 Å and run along the b axis. Here the H atoms display extremely large thermal amplitudes[3] of about 0.5 Å both in phase I and phase II. The deuterons are located either in the center of the H bonds or more between two equivalent off-center sites.

Komukae and Makita[7] have proposed a quasi-one-dimensional Ising model with two sublattices which predicts a ferrielectric phase transition at T_{c2} but makes no attempt to explain the transition at T_{c1} and T_{c3}. To throw some additional light on the microscopic nature of these phase transitions, we decided to perform a deuteron NMR study of monoclinic RbD_2PO_4. This study is complementary to our previous ^{87}Rb NMR study.[8] Our principal aim was to determine:

(i) Are the deuterons located in the center of the O—D(2) $\cdots$ O and O—D(3) $\cdots$ O bonds in phases II and III, or do they move between two equivalent off-center sites?

(ii) What is the microscopic nature of the structural changes at T_{c1}, T_{c2}, and T_{c3}? Is the transition at T_{c2} an order-disorder transition as in CsH_2PO_4, or do we deal with an displacive transition? What is the relation between the order parameters of the transitions at T_{c1}, T_{c2},

and T_{c3}, and can one construct a unified model of all these phase changes?

II. EXPERIMENT

The angular dependences of the quadrupole-perturbed deuteron NMR spectra have been measured for three mutually perpendicular rotations around the a^*, b, and c axes at $\nu_L = 41.45$ MHz using the pulse Fourier transform technique. Here a^* is perpendicular to the (b,c) plane. The electric field gradient (EFG) tensors have been determined by the method of Volkoff.[9] Single crystals grown from a 99.8% deuterated solution have been used.

The spin-lattice relaxation times T_1 have been measured by a 180°-τ-90° pulse sequence. The conductivity was measured in the frequency range 30 Hz–100 kHz.

III. RESULTS AND DISCUSSION

The angular dependences of the quadrupole perturbed deuteron NMR spectra at $T = 110\,°C$ (phase I), $T = 80\,°C$ (phase II), and $T = 40\,°C$ (phase III) are shown in Figs. 1(a)–1(c). The deuteron quadrupole coupling constants e^2qQ/h and asymmetry parameters of the EFG tensors $\eta = (V_{XX} - V_{YY})/V_{ZZ}$ are collected in Tables I and II together with the direction cosines of the principal axes of the deuteron EFG tensors with respect to the crystal a^*, b, and c axes. The direction cosines of the largest principal values V_{ZZ} for the various deuterons agree within the limits of experimental uncertainty with the directions of the O—D · · · O hydrogen bonds determined by x rays for phase II. This allows for a definite assignment of the EFG tensors to the D(1), D(2), and D(3) deuterons.

The dependence of the deuteron quadrupole splitting on temperature for the b and c chains at $\mathbf{b} \perp \mathbf{H}_0$ is shown in Fig. 2. For $\mathbf{b} \perp \mathbf{H}_0$, we see above T_{c1} two sets of NMR lines belonging to b- and c-chain deuterons. The b-chain deuteron line splits at T_{c1} and the c-chain deuteron line at T_{c2}. The temperature dependences of the spin-lattice relaxation times T_1 for the c-chain and b-chain deuterons between 10° and 120 °C at $\mathbf{b} \perp \mathbf{H}_0$, are shown in Fig. 3. No soft-mode-type anomalies are seen at the transition temperatures.

For the c-chain deuterons—D(1)—the electric quadrupole coupling constant e^2qQ/h in phases I and II equals 150 kHz in good agreement with the value expected[10] for an asymmetric location of the deuteron in an O—D · · · O bond of $R(\text{O—O}) \approx 2.52$ Å. For the b deuterons—D(2) and D(3)—where the O—O distance is shorter, the value of e^2qQ/h is—as expected[10]—significantly lower. In phase I it amounts to 113 kHz for both D(2) and D(3), and in phase II to 121 kHz for D(3) and 119 kHz for D(2). These values are of the same order of magnitude as in tetragonal KD_2PO_4 (Ref. 11) where the deuteron moves between two equivalent off-center sites separated by about 0.4 Å. The quadrupole coupling constants are significantly higher than that expected[10] for a symmetric location of the deuteron in the middle of the H bond, i.e., for an O · · · D · · · O bond[11] where $e^2qQ/h \cong 56$ kHz. The extremely large thermal amplitudes of D(2) and D(3) thus show—together with the deuteron NMR data—that the b chains are indeed disordered in phases I and II and that the deuterons move between two off-center sites in the H bonds similarly as in the paraelectric phase of KD_2PO_4.

In phase I one observes, at a general orientation, three sets of deuteron lines which is in agreement with the space group $P2_1/m$. There are just two sets of chemically nonequivalent deuterons formed by the c chains and b chains. For a general orientation we have one c-chain deuteron line and two b-chain deuteron lines. The c-chain deuterons—D(1)—lie on the mirror plane and are all equivalent: $e^2qQ/h = 150$ kHz, $\eta = (V_{XX} - V_{YY})/V_{ZZ} = 0.04$. One of the principal axes of the D(1) EFG tensor is thus perpendicular to the mirror plane (Table I) whereas the other two lie in the mirror plane and make an angle of 12° with the a^* and c axes. There is a center of inversion in the middle of the O—D(2) · · · O and O—D(3) · · · O bonds. The b-chain deuterons—D(2) and D(3)—are here related by the mirror plane. Therefore D(2) and D(3) are chemically equivalent but physically nonequivalent; they have the same quadrupole coupling constant $e^2qQ/h = 113$ kHz and asymmetry parameter $\eta = 0.035$, but different directions of the principal axes of the EFG tensors.

In phase II the number of pairs of deuteron lines observed at a general orientation increases to six, which is compatible with the space group $p2_1/c$. All c-chain deuterons are still chemically equivalent but are now divided into two physically nonequivalent subsets. This reflects the change of the mirror plane into a glide plane and the doubling of the unit cell in the c direction. The number of D(1) deuteron lines observed for a general orientation of the magnetic field with respect to the crystal axes now equals two. This is compatible with the space group $P2_1/c$ and not with $P2_1/n$, which would predict for such an orientation four D(1) lines. For the b-chain deuterons we have here four deuteron lines for a general orientation as expected for $P2_1/c$. There is no crystallographic center of inversion in the middle of the O—D(2) · · · O and O—D(3) · · · O H bonds anymore, but there may still be approximate inversion symmetry. D(2) and D(3) are now chemically nonequivalent with $e^2qQ/h = 119$ kHz, $\eta = 0.073$, and $e^2qQ/h = 121$ kHz, $\eta = 0.071$. Each of these two groups now contains two physically nonequivalent subsets.

According to Refs. 3 and 4—where phase III is considered to be ferrielectric—one expects eight c-chain and eight b-chain deuteron lines for a general orientation. This follows from the loss of the center of symmetry and the doubling of the unit cell in the a direction for the space group $P2_1$. In fact, only eight lines are observed. This supports the results of Ref. 6 and seems to show that $P2_1$ is not the proper space group for phase III. There are now two chemically nonequivalent groups of c-chain deuterons—D(1) and D(1)′—with $\eta = 0.093$ and $\eta' = 0.082$, each of which contains two physically nonequivalent subsets. The changes for the b-chain deuterons—where the O—D · · · O deuteron motion between the two off-center sites in the H-bonds should freeze out—are much smaller. The quadrupole coupling

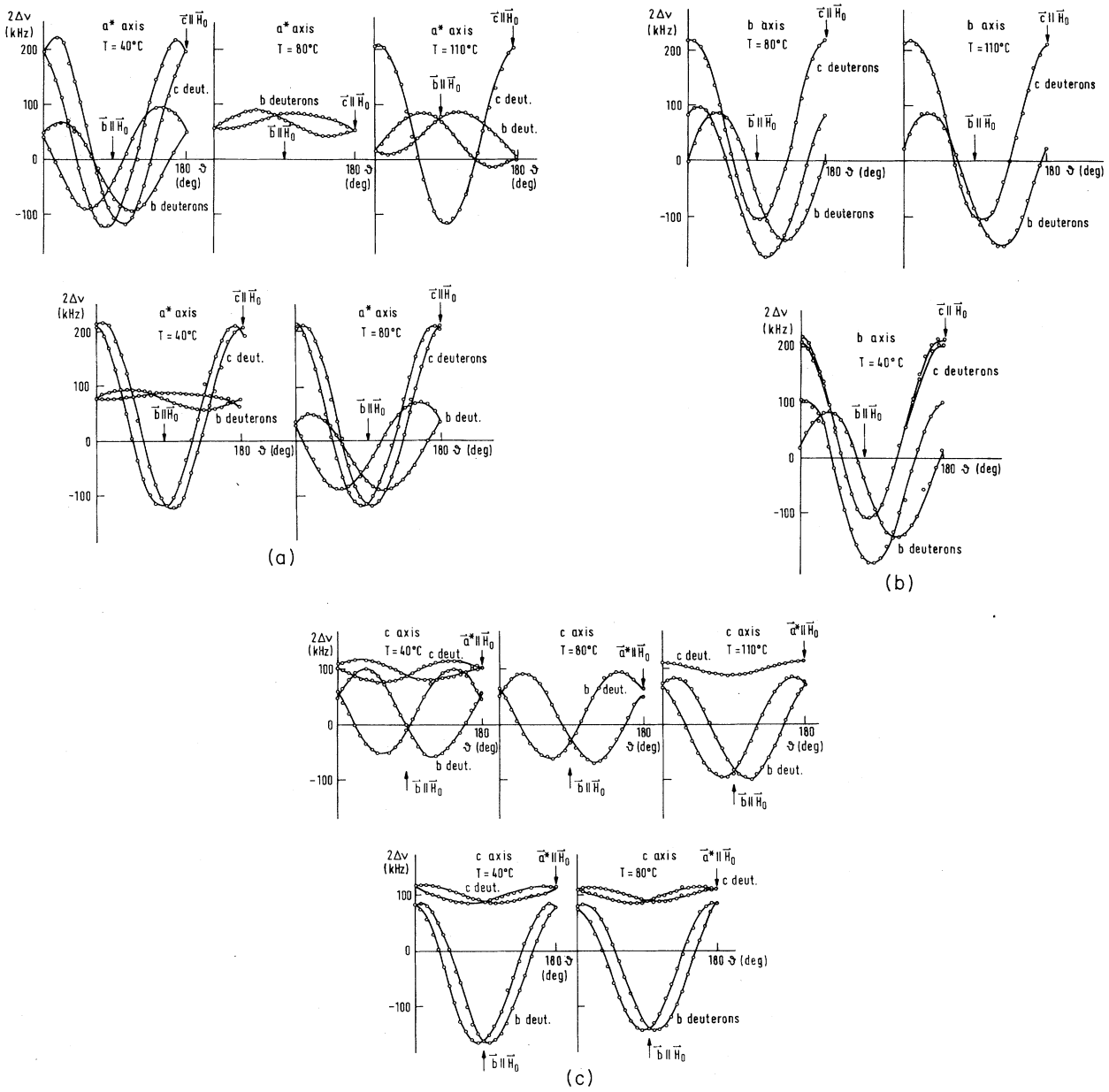

FIG. 1. Angular dependence of the deuteron NMR spectra of monoclinic RbD_2PO_4 at 110°, 80 °C, and 40 °C for a^*, b, and c rotations. The rotation patterns in (a) and (c) are separated into two different plots for temperatures 80 °C and 40 °C for sake of clarity because of a large number of lines. The assignation of the rotation patterns to b and c deuterons is indicated in the figures.

constants and asymmetry parameters are somewhat larger in phase III than in phase II: 123 and 128 kHz and 0.092 and 0.12, respectively. There is, however, no additional line splitting at T_{c2} (Fig. 2) as observed[11] at the paraelectric-ferroelectric transition in KD_2PO_4 and tetragonal RbD_2PO_4, where the deuterons order into one of the two off-center sites in the O—D $\cdots$ O bonds. Similarly, there is no corresponding anomaly or minimum in the D(2) or D(3) spin-lattice relaxation time T_1 (Fig. 3)—induced by the freeze out of the deuteron motion—as seen[12] in KD_2PO_4 or tetragonal RbD_2PO_4. Such a T_1 anomaly is, however, observed in monoclinic RbD_2PO_4 (Ref. 8) at T_{c2} in the ^{87}Rb spin-lattice relaxation time.

It is well known[10] that the second-largest principal axes V_{YY} of the deuteron EFG tensor is normal to the P—O—D $\cdots$ O′ plane in linear H bonds with an off-center location of the deuterons. In case of fast deuteron exchange between the two possible positions in a double-minimum potential, V_{YY} should fluctuate between both respective plane normals and the mean value should point in the direction of the bisectrix. This behavior is observed in KD_2PO_4,[11] for instance. When the deuterons in KD_2PO_4 order, the direction of V_{YY} alters strongly and points in the direction of the normal to the P—O—C $\cdots$ O′ plane, thus allowing for a determination of the

TABLE I. Quadrupole-coupling constants, asymmetry parameters, and the direction cosines of the principal axes V_{ZZ}, V_{YY}, and V_{XX} with respect to the a^*, b, and c crystal axes for the c-chain deuterons in monoclinic RbD_2PO_4.

T (°C)	e^2qQ/h (kHz)	η		Direction cosines with respect to the a^*, b, and c axes cosα	cosβ	cosγ
110	150	0.04	V_{ZZ}	0.2100	0	0.9777
			V_{YY}	0	−1	0
			V_{XX}	−0.9777	0	0.2100
80	150	0.053	V_{ZZ}	0.2049	±0.1023	0.9734
			V_{YY}	0.0897	∓0.9923	0.0845
			V_{XX}	∓0.9747	−0.0689	±0.2123
40	150	0.093	V_{ZZ}	0.2087	±0.1411	0.9713
			V_{YY}	0.4933	∓0.8698	−0.0038
			V_{XX}	∓0.8445	−0.4789	±0.2379
40	155	0.082	V_{ZZ}	0.2073	∓0.1727	0.9629
			V_{YY}	∓0.1693	0.9643	±0.2082
			V_{XX}	0.9645	±0.2010	−0.1716

deuteron position. No such behavior is seen in RbD_2PO_4.

All preceding data and differences fro KD_2PO_4 and tetragonal RbD_2PO_4 can be explained by a model where the D(2) and D(3) deuterons move in phases III and II between two off-center sites in H bonds with at least approximate centers of inversion in the middle of the O—D · · · O bonds. In contrast to KD_2PO_4, the D(2) and D(3) EFG tensors are within the limits of experimental error identical at the two off-center sites. This is supported by the fact that the angle between the P—O—D · · · O′ and P—O′—D · · · O planes is practically zero. In phase III the deuteron motion freezes out, but the center of inversion is still preserved. The transfer of the deuteron from one off-center site to the other across the "local" center of inversion does not change the deuteron EFG tensor and can therefore not represent a spin-lattice relaxation mechanism for this deuteron. The freeze out of such a motion can similarly not produce any deuteron line splitting. This is in sharp contrast to KD_2PO_4 or tetragonal RbD_2PO_4 where there is no center of inversion in the middle of the O—D · · · O bond. According to this model, phase III is, in fact antiferroelectric, with a centrosymmetric space group and does not belong to the acentric space group $P2_1$.

Below T_{c3} in phase-IV, where ferrielectric behavior along the b axis sets in, the center of symmetry is lost and the space group is predicted[6] to become $P2_1$. In view of the smallness of the observed spontaneous polarization, the breaking of the approximate inversion symmetry between the two off-center sites in the b-chain H bonds should be rather small. The transfer of the deuteron from one off-center site to the other may thus produce only a very small change in the deuteron EFG tensor, thus explaining the absence of a T_1 anomaly at T_{c3}. A measurement of the angular dependence of the D(2) and

TABLE II. Quadrupole-coupling constants, asymmetry parameters, and the direction cosines of the principal axes V_{ZZ}, V_{YY}, and V_{XX} with respect to the a^*, b, and c crystal axes for the b-chain deuterons in monoclinic RbD_2PO_4.

T (°C)	e^2qQ/h (kHz)	η		Direction cosines with respect to the a^*, b, and c axes cosα	cosβ	cosγ
110	113	0.035	V_{ZZ}	±0.8107	−0.2381	∓0.5349
			V_{YY}	−0.5247	±0.1099	−0.8442
			V_{XX}	0.2598	±0.9650	−0.0359
80	121	0.071	V_{ZZ}	±0.9176	−0.1525	∓0.3670
			V_{YY}	−0.3823	∓0.0859	−0.9200
			V_{XX}	0.1088	±0.9846	−0.1371
80	119	0.073	V_{ZZ}	±0.6700	−0.1512	∓0.6558
			V_{YY}	0.6026	±0.7708	0.2066
			V_{XX}	−0.4436	±0.6336	−0.7261
40	128	0.12	V_{ZZ}	±0.9445	−0.1108	∓0.3049
			V_{YY}	−0.3090	±0.0217	−0.9508
			V_{XX}	0.1119	±0.9936	−0.0142
40	123	0.092	V_{ZZ}	−0.6139	±0.3916	0.6855
			V_{YY}	0.6561	±0.7359	0.1672
			V_{XX}	±0.4389	−0.5524	±0.7057

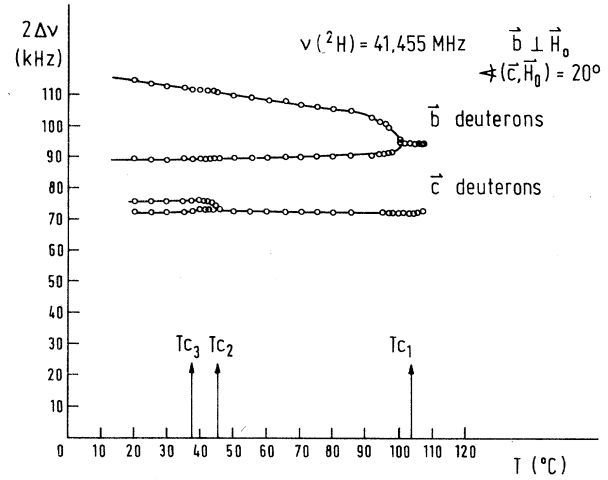

FIG. 2. Temperature dependence of the quadrupole splitting of the *b*- and *c*-chain deuterons in RbD_2PO_4 for $\mathbf{b}\perp\mathbf{H}_0$, $\sphericalangle(\mathbf{c},\mathbf{H})=20°$.

D(3) deuteron spectra at low enough temperatures should show the 16 deuteron lines predicted for the space group $P2_1$ at a general orientation. No systematic search for this effect—which should be hard to detect—has been made as yet. At $\mathbf{b}\perp\mathbf{H}_0$ (Fig. 2) there should be at T_{c3}—in agreement with experiment—no line splitting for the *b*-chain deuterons.

It should be further stressed that both the *c*-chain and the *b*-chain deuteron spin-lattice relaxation times are

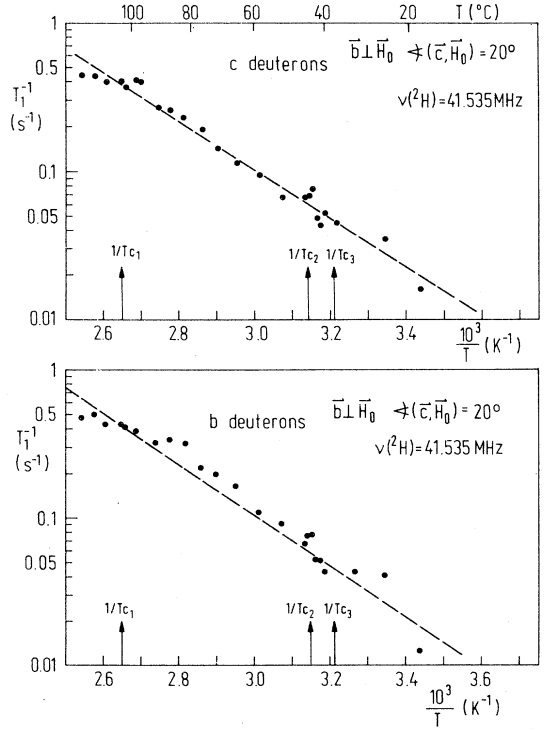

FIG. 3. Temperature dependence of the *b*- and *c*-chain deuteron spin-lattice relaxation times T_1 in monoclinic RbD_2PO_4 for $\mathbf{b}\perp\mathbf{H}_0$, $\sphericalangle(\mathbf{c},\mathbf{H})=20°$.

anomalously short and demonstrate the presence of a strong relaxation mechanism, the strength of which increases with increasing temperature.

The motion producing the spin-lattice relaxation is slow as compared to the Larmor frequency ω_L so that

$$T_1 \propto \omega_L^2 \tau,\ \omega_L \tau \gg 1\ ,$$

and the correlation time τ for this motion ($\tau > 10^{-7}$ s) decreases with increasing temperature. We believe that such a mechanism is proveded by deuteron interbond motion induced by D_2PO_4 rotations. This explains not only the observed T dependence of the deuteron T_1, but also the equality of the *b*- and *c*-chain deuteron relaxation rates. The relaxation data in Fig. 1 give an activation energy of 0.34 ± 0.02 eV for both *c* and *b* deuterons. This is a lower activation energy than the one observed for KD_2PO_4.[13] Therefore the deuteron interbond motion in RbD_2PO_4 is expected to be faster than in KD_2PO_4 at a given temperature, and the T_1 in RbD_2PO_4 is correspondingly shorter.

To get additional insight into the nature of the deuteron motion, the electrical conductivity σ was measured along the *a*, *b*, and *c* crystal axes as a function of temperature (Fig. 4). At the I-II phase transition (T_{c1}), where there is no change in the nature of the D(2) and D(3) deuteron intrabond motion, the $\sigma_i(T)$ curves do not reveal any anomalies. At the II-III phase transition (T_{c2}) to the antiferroelectric phase which is triggered by the ordering of the D(2) and D(3) deuteron, there is a sharp break in $\sigma_i(T)$ curves and the activation energy is doubled in the ordered phase. One possible explanation of this anomaly is that electrical conductivity here involves both reorientation of the PO_4 tetrahedra and deuteron transfer in the O—D(2) $\cdots$ O and O—D(3) $\cdots$ O bonds. There is no anomaly at T_{c3}. Around 500 K the crystal decomposes.

IV. MODEL FOR THE PHASE TRANSITIONS

In order to explain the phase transitions at T_{c1}, T_{c2}, and T_{c3}, as well as the temperature dependence of the deuteron data, we have to introduce four *b*-chain O—D $\cdots$ O sublattices instead of only two as has been done previously in a model explaining[7] the dielectric anomaly around T_{c2}. The necessity for the introduction of four sublattices has been already seen by Makita *et al.*[4] though they—for sake of convenience—worked with only two sublattices.[7]

There are two different types of order parameters in our problem. One of them is the polarization of the four sublattices P_{il}, $i=1,2$; $l=\alpha,\beta$. This order parameter is connected with the "longitudinal" ordering of the D(2) and D(3) deuterons into one of the two off-center sites in the O—D $\cdots$ O bonds along the chains running along the *b* axis. The second order parameter $\tilde{\eta}$ is connected with the "transverse" degree of freedom of these chains. It describes the reorientations of the PO_4 tetrahedra—and thus of the O—D(2) and O—D(3) bonds— in the *b*-*c* plane which alternate along the *c* axis, thus destroying the reflection symmetry and doubling the unit-cell parameter $c \rightarrow 2c$ below T_{c1}. Both the "longitudinal" as

well as the "transverse" order parameters represent the frozen-out eigenvectors of relaxational modes becoming soft at different points of the Brillouin zone boundary; the "transverse" mode leads to a doubling of the unit cell along the c and the "longitudinal" to a doubling along the a axis. The order parameter for the "ferrielectric" transition at T_{c3}, on the other hand, is connected with a zone-center mode as expected for a proper ferroelectric transition.

For the four sublattices, we introduce pseudospin variables $S^z_{il,m}$ $i=1-2, l=\alpha,\beta$ describing the deuteron motion in the double-well potentials of the O—D $\cdots$ O bonds forming chains along the b axis. The index $i=1,2$ describes two sublattices which become inequivalent in the c direction, whereas the index $l=\alpha,\beta$ describes sublattices which become inequivalent in the a direction. Our treatment is based on the quasi-one-dimensional Ising model where the short-range intrachain interactions of the pseudospins are taken into account exactly, and the long-range interchain interactions are approximated by a mean field.[14] The quasi-one-dimensional Ising model is analogous to the one for CsH_2PO_4.[15]

Within the mean-field theory the model can be represented by a Landau-type free-energy expansion

$$F(T,P_{1\alpha},P_{2\alpha},P_{1\beta},P_{2\beta},\tilde{\eta})=\tfrac{1}{2}a\tilde{\eta}^2+\tfrac{1}{4}b\tilde{\eta}^4+\tfrac{1}{2}a_1(P_{1\alpha}^2+P_{1\beta}^2)+\tfrac{1}{2}a_2(P_{2\alpha}^2+P_{2\beta}^2)+\tfrac{1}{4}b_1(P_{1\alpha}^4+P_{1\beta}^4)$$
$$+\tfrac{1}{4}b_2(P_{2\alpha}^4+P_{2\beta}^4)-f'(P_{1\alpha}P_{2\alpha}+P_{1\beta}P_{2\beta})+h(P_{1\alpha}P_{2\beta}+P_{2\alpha}P_{1\beta})$$
$$+h'_1P_{1\alpha}P_{1\beta}+h'_2P_{2\alpha}P_{2\beta}\ . \tag{1}$$

The model represents an extension of Kittel's two-sublattice model which allows only for a transition from the paraelectric to the antiferroelectric, or from the paraelectric to the ferroelectric phase but not the paraelectric-antiferroelectric-ferrielectric phase sequence (Fig. 5).

Minimizing F with respect to $\tilde{\eta}$, $P_{1\alpha}$, $P_{1\beta}$, $P_{2\alpha}$, and $P_{2\beta}$, we find four different phases (Fig. 5)

Phase I: $T>T_{c1}$:$\tilde{\eta}=0$, $P_{il}=0$, $i=1,2$, $l=\alpha,\beta$, (2)

Phase II: $T_{c2}<T<T_{c1}$:$\tilde{\eta}\neq 0$, $P_{il}=0, i=1,2$, $l=\alpha,\beta$, (3)

Phase III: $T_{c3}<T<T_{c2}$:$\tilde{\eta}\neq 0$, $P_{il}\neq 0$, $i=1,2$, $l=\alpha,\beta$, (4a)

$$\sum_{i,l}P_{il}=0\ , \tag{4b}$$

$$P_{1\alpha}=-P_{1\beta}\ , \tag{4c}$$

$$P_{2\alpha}=-P_{2\beta}\ , \tag{4d}$$

Phase IV: $T<T_{c3}$:$\tilde{\eta}\neq 0$, $\sum_{i,l}P_{i,l}\neq 0$, (5a)

$$P_{1\alpha}\neq -P_{1\beta}, P_{2\alpha}\neq -P_2\ . \tag{5b}$$

The above model thus shows that phase I is disordered with respect to the "longitudinal" as well as the "transverse" order parameters. In phase II antiferroelectric "transverse" ordering sets in, but there is still no longitudinal order. In phase III we have ferroelectric ordering of the b-chain deuterons in the c direction but antiferroelectric ordering in the a direction. The sublattices in the b-c layers are now ferroelectrically ordered but the sublattice polarization alternates along the a axis leading to zero total polarization. The compensation of the sublattice polarizations of alternating layers along the a axis is no longer complete below T_{c3} leading to a ferrielectric state with a small spontaneous polarization along the b axis. The dielectric properties and dynamics of this model will be described in detail in a subsequent paper.

V. CONCLUSIONS

The results for monoclinic RbD_2PO_4 obtained in this study can be summarized as follows.

(1) The directions of the largest principal axes of the deuteron EFG tensors agree with the directions of the O—D $\cdots$ O bonds predicted by x-ray structural studies thus confirming the H bonded network proposed by Makita *et al.*[3,4]

(2) The values of the deuteron quadrupole coupling constants for the D(2) and D(3) deuterons are incompatible with the possibility that these deuterons are located in the center of the O—D $\cdots$ O bonds. The quadrupole-coupling data strongly suggest that the D(2) and D(3) deuterons are disordered between two equivalent off-center sites in phases I and II and ordered into one of the two possible sites in phases III and IV. There is an approximate center of inversion in the middle of the O—D(2) $\cdots$ O and O—D(3) $\cdots$ O H bonds. The NMR data are compatible with the D(1) deuterons being ordered in an off-center site in all four phases.

(3) The quadrupole-coupling data show that the length of all O—D $\cdots$ O bonds is the shortest in phase I and significantly increases with decreasing temperature in

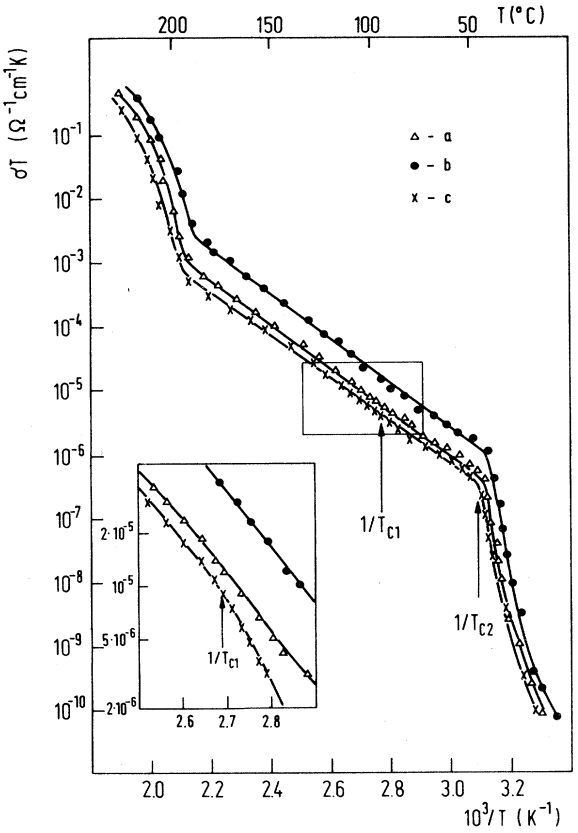

FIG. 4. Temperature dependence of the electrical conductivity of RbD_2PO_4 along the *a*, *b*, and *c* crystal axes.

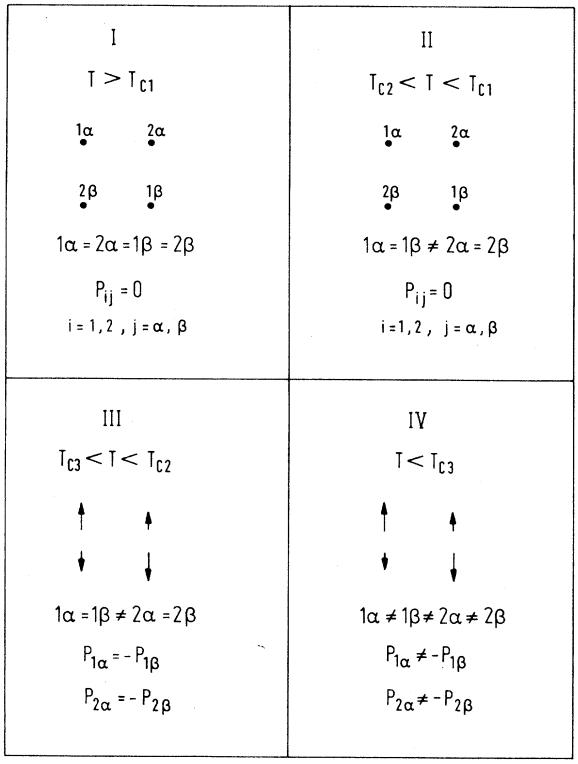

FIG. 5. Schematic arrangements of the four sublattices—formed by the *b*-chain hydrogen bonds—in monoclinic RbD_2PO_4.

phases II and III.

(4) The deuteron NMR data are compatible with the space group $P2_1/m$ for phase I and $P2_1/c$ for phase II. The number of observed deuteron lines in phase III is only half of that expected for the acentric space group $P2_1$. This is compatible with the suggestion[6] that phase III is strictly antiferroelectric and that only phase IV is acentric and ferrielectric, as suggested by spontaneous polarization and second-harmonic-generation data.[6]

(5) The data allow for the construction of a model accounting for all three observed phase transitions in monoclinic RbD_2PO_4. The model involves four sublattices of O—D $\cdots$ O bonded zig-zag chains running along the *b* axis and considers two different types of order parameters. The order parameter $\tilde{\eta}$, connected with the "transverse" degree of freedom of the *b* chains, accounts for the reorientations of the H_2PO_4 groups—and O—D bonds—which alternate in the *c* directions, whereas the "longitudinal" order parameters $P_{il}, i=1,2;\ l=\alpha,\beta$ describe the deuteron ordering in the O—D $\cdots$ O bonds resulting in the polarizations of the four *b*-chain sublattices. In phase I $\tilde{\eta}=0$, $P_{il}=0$, in phase II $\tilde{\eta}\neq 0$, $P_{il}=0$, in phase III $\tilde{\eta}\neq 0$, $P_{1\alpha}=-P_{1\beta}$, $P_{2\alpha}=-P_{2\beta}$ so that $\sum_{i,l}P_{il}=0$, whereas in phase IV $\sum_{i,l}P_i\neq 0$.

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