PHYSICAL REVIEW B VOLUME 48, NUMBER 1 1 JULY 1993-I

^{1}H-^{75}As nuclear-quadrupole double-resonance study of the high-temperature phase transition in TlH_2AsO_4

J. Seliger, V. Žagar, and R. Blinc
J. Stefan Institute, University of Ljubljana, Ljubljana, Slovenia

(Received 25 February 1993)

The ^{75}As nuclear-quadrupole-resonance frequency has been measured around the high-temperature phase transition in TlH_2AsO_4 with a proton-arsenic cross-relaxation technique. The experimental results are analyzed within an order-disorder model where above the high-temperature phase transition each AsO_4 group forms four dynamically disordered symmetric double-minimum-type O—H · · · O hydrogen bonds, whereas below the high-temperature phase transition two of the four hydrogen bonds become asymmetric and ordered. The temperature dependence of the order parameter associated with the high-temperature phase transition is calculated from the nuclear-quadrupole-resonance data.

I. INTRODUCTION

TlH_2AsO_4 undergoes structural phase transitions at $T_c=251$ K (Ref. 1) and at $T_c'=363$ K (Ref. 2). Whereas the ferroelectric phase transitions in tetragonal KH_2PO_4 and KH_2AsO_4 are relatively well understood,[3] very little is known about the structural phase transitions in TlH_2PO_4 and TlH_2AsO_4. The role of the O—H · · · O hydrogen bonds at the phase transitions in these systems is of particular interest.

TlH_2PO_4, which we suppose to be closely related to TlH_2AsO_4, undergoes a slightly discontinuous antiferroelectric phase transition at $T_c=230$ K.[4] In the deuterated compound—TlD_2PO_4—an equivalent phase transition occurs at $T_c=350$ K. This shows that the O—H · · · O hydrogen bonds play an important role at the phase transition. Below T_c the PO_4 groups are linked by three types of asymmetric O—H · · · O hydrogen bonds. The shorter hydrogen bonds ($R_{O—O}=0.243$ and 0.247 nm) become symmetric above T_c whereas the longest hydrogen bonds ($R_{O—O}=0.250$ nm) remain asymmetric above T_c.[4–6]

With increasing temperature TlH_2PO_4 undergoes a high-temperature phase transition at $T_c=357$ K. Yoshida *et al.*[7] concluded on the basis of dielectric and optical measurements that the room-temperature phase of TlH_2PO_4 is ferroelastic and that on going into the high-temperature phase at $T_c=357$ K, the spontaneous shear strain χ_{5S} vanishes. The structure of the high-temperature phase, and in particular the O—H · · · O hydrogen bonding in this phase, are not known.

Only a few experimental data are published on TlH_2AsO_4. X-ray diffractions show that at room temperature both TlH_2PO_4 and TlH_2AsO_4 have monoclinic structures.[2] The unit-cell parameters of TlH_2AsO_4 at room temperature are $a=1.464$ nm, $b=0.462$ nm, $c=0.675$ nm, $\beta=94.81°$, and $Z=4$. On going into the high-temperature phases the crystal structures of both compounds change from monoclinic to orthorhombic and the unit-cell parameters of TlH_2AsO_4 change to $a=1.458$ nm, $b=0.478$ nm, $c=0.674$ nm, and $Z=4$. At room temperature both compounds crystallize in the space group $C_{2h}^{5}(P2_1/c)$.[8]

Milia[1] has measured the ^{75}As nuclear-quadrupole-resonance (NQR) frequencies in the low-temperature phase of TlH_2AsO_4. At 77 K she observed two inequivalent arsenics with the frequencies 38.475 and 37.760 MHz. These data show that there are two slightly inequivalent AsO_4 groups in the low-temperature phase. The NQR frequencies (~ 38 MHz) are characteristic for AsO_4 groups which have two hydrogens in the "close" (As—O—H) positions and two hydrogens in the "far" (As—O · · · H) positions.[9] Blinc *et al.*[10] concluded from proton spin-lattice relaxation measurements that at room temperature—which is above T_c—the ^{75}As NQR frequency is below 10 MHz. Such a large change of the ^{75}As NQR frequency is related to the changes in the O—H · · · O hydrogen bonding. Namely, in the case of an AsO_4 group, which forms four dynamically disordered symmetric double-minimum-type O—H · · · O hydrogen bonds, the NQR frequency is expected to be around 4 MHz.[11]

Since ^{75}As NQR proved to be a sensitive technique for the study of hydrogen bonding in KH_2AsO_4-type systems we decided to perform ^{75}As NQR measurements around the high-temperature phase transition temperature T_c' in order to get an insight in the hydrogen bonding structures of both the room-temperature phase and the high-temperature phase of TlH_2AsO_4.

II. EXPERIMENTAL

^{75}As has a spin $I=\frac{3}{2}$ and thus in zero magnetic field two doubly degenerated quadrupole energy levels with the resonance—NQR—frequency ν_Q:

$$\nu_Q=\tfrac{1}{2}eQV_{ZZ}\sqrt{1+\eta^2/3}\ . \tag{1}$$

Here eQ is the quadrupole moment of an ^{75}As nucleus, V_{ZZ} is the largest principal value of the electric-field-gradient (EFG) tensor at the site of the nucleus and the asymmetry parameter η, $\eta=(V_{XX}-V_{YY})/V_{ZZ}$ is the difference of the two smaller principal values of the EFG tensor ($|V_{XX}|\leq|V_{YY}|\leq V_{ZZ}|$) divided by V_{ZZ}. The EFG tensor $\underline{V}$ is a second-rank tensor composed of the second derivative of the electrostatic potential V with respect to the coordinates, $(\underline{V})_{ik}=\delta^2V/\delta x_i\delta x_k$.

Around the high-temperature phase transition in TlH_2AsO_4 the ^{75}As NQR frequency is expected to be lower than 10 MHz. We therefore decided to perform the measurements of the ^{75}As NQR frequency with a nuclear-quadrupole double technique base on magnetic-field cycling.

In a magnetic-field cycle (Fig. 1) the hydrogen (proton) spin system is first polarized in a high static magnetic field B_0. Then the static magnetic field is adiabatically reduced to a low value B. After the demagnetization the proton spin temperature T_S is equal to $T_S=T_L(B/B_0)\ll T_L$. Here T_L is the temperature of the sample. The proton magnetization is immediately after the demagnetization by a factor $B_0/B\gg 1$ larger than the equilibrium magnetization in the static magnetic field B at the temperature T_L. The sample then remains for a time τ in the low static magnetic field B. After this time the proton magnetization is by a factor $\exp(-W_H\tau)$ smaller than at the beginning. Here W_H is the proton spin-lattice relaxation rate in the low static magnetic field B. Then the static magnetic field is adiabatically increased to the initial value B_0 and the proton NMR signal following a 90° pulse is measured. It is proportional to the remaining proton magnetization and decreases with τ as $\exp(-W_H\tau)$.

In samples containing quadrupole nuclei, the proton relaxation rate W_H in the low static magnetic field B can be increased by the application of a strong phase modulated rf magnetic field with the frequency close to a NQR frequency.[12] This technique works when $B<1$ mT.

In a nonzero static magnetic field B a strong rf magnetic field B_1 induces simultaneous transitions in the proton and quadrupole spin systems when its frequency ν is equal to $\nu=\nu_Q\pm\nu_H$. Here ν_Q is a NQR frequency and ν_H is the proton Larmor frequency. This effect is the so-called solid effect.[13] In the ν dependence of the proton NMR signal at the end of the magnetic-field cycle doublets are observed around the NQR frequencies at $\nu_Q+\nu_H$ and $\nu_Q-\nu_H$. In a special case when the spin-lattice relaxation rate of the quadrupole nuclei is high and when the probability per unit time for a solid-effect transition is higher than the proton spin-lattice relaxation rate, the quadrupole nuclei polarize the proton spin system in a low static magnetic field. This is called the dynamic polarization.[13] The dynamic polarization is effective in polycrystalline samples when $B\sim 1$ mT.

When the magnetic-field cycles are repeated with no rf irradiation at different values of the low static magnetic field B a faster spin-lattice relaxation of the proton spin system is often observed also when the proton Larmor frequency ν_H, $\nu_H=\gamma_H B/2\pi$, matches a NQR frequency. In such a situation the two spin systems resonantly couple and—if the quadrupole nuclei have a high spin-lattice relaxation rate—the proton spin-lattice relaxation rate increases.

However, this experiment is done in a nonzero magnetic field B, which in the case of a spin-$\frac{3}{2}$ nucleus, removes the degeneracies of the two quadrupole energy levels (Fig. 2). The upper, "$\frac{3}{2}$," energy level splits into two levels with the energies $E_{3/2}^{+}$ and $E_{3/2}^{-}$:

$$E_{3/2}^{+,-}=h\nu_Q/2\pm[h\nu_{LQ}\sqrt{F(\theta,\phi,q)}]/(1+q^2)\ . \tag{2}$$

Here $\nu_{LQ}=\gamma_Q B/2\pi$ is the Larmor frequency of the quadrupole nuclei

$$q=\eta/(\sqrt{3}+\sqrt{3+\eta^2}) \tag{3}$$

and

$$F(\theta,\phi,q)=\tfrac{1}{4}(3-q^2)^2\cos^2\theta + [3+q^2+2\sqrt{3}q\cos(2\phi)]q^2\sin^2\theta\ . \tag{4}$$

In expression (4), θ and ϕ are the polar and the azimuthal angles describing the orientation of the magnetic field B in the principal-axis-frame X, Y, and Z of the EFG tensor. θ is the angle between the magnetic-field direction and the Z axis, and ϕ is the angle between the projection of the magnetic-field direction on the X-Y plane and the X axis. Similarly the lower, "$\frac{1}{2}$," energy level splits into two levels with the energies $E_{1/2}^{+}$ and $E_{1/2}^{-}$:

$$E_{1/2}^{+,-}=-\tfrac{1}{2}h\nu_Q\pm[h\nu_{LQ}\sqrt{G(\theta,\phi,q)}]/(1+q^2)\ . \tag{5}$$

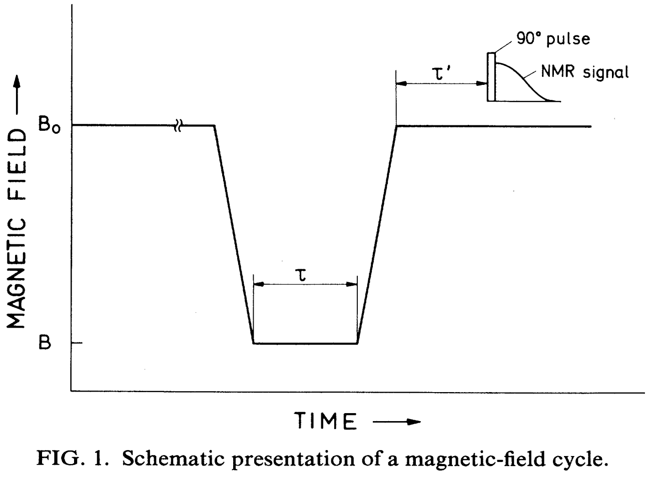

FIG. 1. Schematic presentation of a magnetic-field cycle.

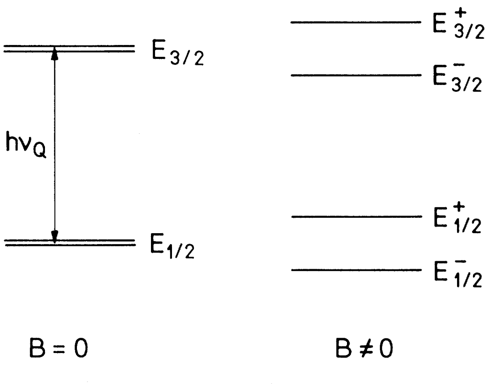

FIG. 2. Energy levels of a spin-$\frac{3}{2}$ nucleus in zero and nonzero magnetic field.

Here

$$G(\theta,\phi,q)=\tfrac{1}{4}(3-q^2)^2\cos^2\theta + [3q^2+1-2\sqrt{3}q\cos(2\phi)]\sin^2\theta\,. \qquad (6)$$

Both splittings are calculated in the first-order perturbation theory.

The Zeeman splittings of the quadrupole energy levels depend on the orientation of the magnetic field B. In a polycrystalline sample all the orientations of B are possible. Thus a broad region in the Larmor-frequency dependence of the proton spin-lattice relaxation rate is observed in which the quadrupole nuclei influence the proton spin-lattice relaxation. This regions starts at $(\nu_H)_{\min}$,

$$(\nu_H)_{\min}=\frac{1}{h}(E_{3/2}^{-}-E_{1/2}^{+})_{\min}=\nu_Q-2\nu_{LQ}/\sqrt{1+\eta^2/3}\,, \qquad (7)$$

and ends at $(\nu_H)_{\max}$,

$$(\nu_H)_{\max}=\frac{1}{h}(E_{3/2}^{+}-E_{1/2}^{-})_{\max}=\nu_Q+2\nu_{LQ}/\sqrt{1+\eta^2/3}\,. \qquad (8)$$

But ν_H and ν_{LQ} are proportional: $\nu_{LQ}=(\gamma_Q/\gamma_H)\nu_H$, and therefore

$$(\nu_H)_{\min}=\nu_Q/[1+2(\gamma_Q/\gamma_H)/\sqrt{1+\eta^2/3}\,]\,. \qquad (9)$$

When the NQR frequencies of different or inequivalent nuclei are well apart so that the cross-relaxation spectra do not overlap the lower edges of the cross-relaxation spectra, $(\nu_H)_{\min}$ can be used to determine the NQR frequencies ν_Q. The frequencies of these lower edges however slightly depend on the asymmetric parameter η. Thus in the case of ^{75}As $\nu_Q=1.34(\nu_H)_{\min}$ for $\eta=0$ and $\nu_Q=1.30(\nu_H)_{\min}$ for $\eta=1$. If η is not known, say from the crystal symmetry, we may use an average factor 1.32, which differs approximately 1.5% from the limiting values.

III. RESULTS AND DISCUSSION

In TlH_2AsO_4 the proton spin-lattice relaxation time was observed to be shorter than 100 ms in a magnetic field of a few mT or lower. Since the minimum time τ in the magnetic-field cycle, which we obtain with our magnetic-field cycling apparatus, is about 100 ms, the measurements of the ^{75}As NQR frequency with the application of the rf magnetic field failed. We therefore measured the proton-arsenic cross-relaxation spectra in order to determine the ^{75}As NQR frequency.

As a check of the accuracy of this technique we applied it to a similar system—KH_2AsO_4—where the ^{75}As NQR frequency can also be determined by the dynamic polarization measurements.

In Fig. 3(a) the proton-arsenic dynamic polarization spectrum of KH_2AsO_4 is shown. The measurements were performed at 23 °C in a low magnetic field of 1.5 mT. The irradiation time τ was 1 s and the proton NMR signals were measured at a time τ', $\tau'=1.5$ s $\approx 0.1T_{1H}$, after finishing the remagnetization. The ^{75}As NQR frequency in KH_2AsO_4 at 23 °C as determined by the dynamic polarization is $\nu_Q=(3.55\pm0.01)$ MHz.

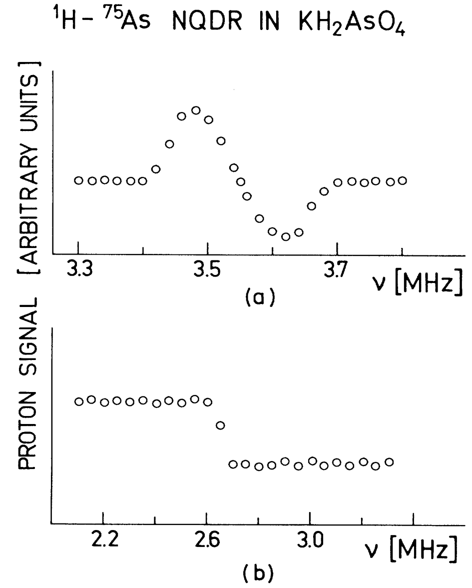

FIG. 3. Measurement of the ^{75}As NQR frequency in KH_2AsO_4 by (a) dynamic polarization and (b) proton-arsenic cross relaxation.

The proton-arsenic cross-relaxation spectrum in KH_2AsO_4 is shown in Fig. 3(b). The measurements were performed at 23 °C. In the magnetic-field cycles we have kept the time τ constant and equal to 0.5 s, whereas the low magnetic field B was changed in steps corresponding to the steps in the proton Larmor frequency ν_H of 50 KHz. The minimum proton Larmor frequency $(\nu_H)_{\min}$ at which the proton-arsenic cross-relaxation is observed is equal to (2.65 ± 0.05) MHz. Since in KH_2AsO_4 the asymmetry parameter η is known to be zero, we multiply $(\nu_H)_{\min}$ by a factor of 1.34 and obtain $\nu_Q=(3.55\pm0.07)$ MHz. This result is in excellent agreement with the one obtained by dynamic polarization.

The temperature dependence of the ^{75}As NQR frequency in TlH_2AsO_4 is shown in Fig. 4. The NQR frequencies are determined from the proton-arsenic cross-relaxation spectra by multiplying $(\nu_H)_{\min}$ with a factor of 1.32.

The transition temperature T_c' was observed as being 110 °C and not 90 °C as given in Ref. 2. The reason for this discrepancy is not known.

Above T_c' the ^{75}As NQR frequency is equal to 5.3 MHz and is nearly temperature independent. Such a low ^{75}As NQR frequency is characteristic for an AsO_4 group forming four symmetric O—H $\cdots$ O hydrogen bonds.[11]

On going through T_c' from above a strong continuous increase of the ^{75}As NQR frequency is observed after passing T_c'. The temperature dependence of ν_Q below T_c' is nearly linear.

We assume that—similarly as in TlH_2PO_4—two of the O—H $\cdots$ O hydrogen bonds formed by an AsO_4 group become asymmetric and ordered below T_c' whereas the

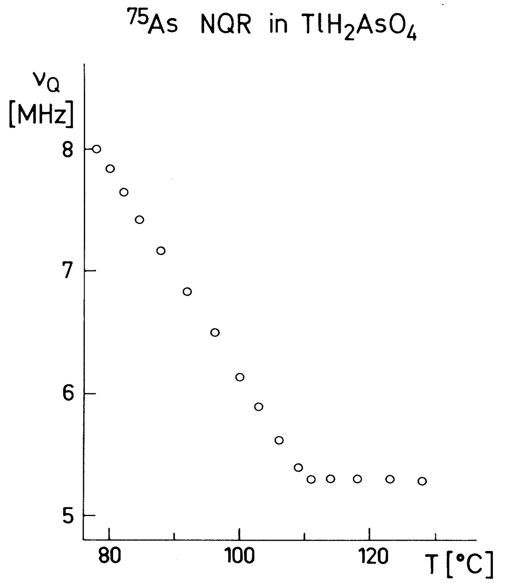

FIG. 4. Temperature dependence of the ^{75}As NQR frequency in TlH$_2$AsO$_4$.

other two remain symmetric and disordered below T_c' and become asymmetric and ordered in the low-temperature phase below T_c. Further we assume that the dynamic symmetry of the O—H · · · O hydrogen bonds is associated with the motion of hydrogens between two equilibrium sites in the O—H · · · O bonds as in other KH$_2$PO$_4$-type systems. In a symmetric double-minimum-type hydrogen bond the hydrogen moves between two equivalent equilibrium sites whereas in an asymmetric hydrogen bond it moves between two inequivalent equilibrium sites with the occupation probabilities $(1+S)/2$ and $(1-S)/2$. Here S is the order parameter of the hydrogen bond. The ordering of hydrogens around an AsO$_4$ group below T_c' is schematically presented in Fig. 5.

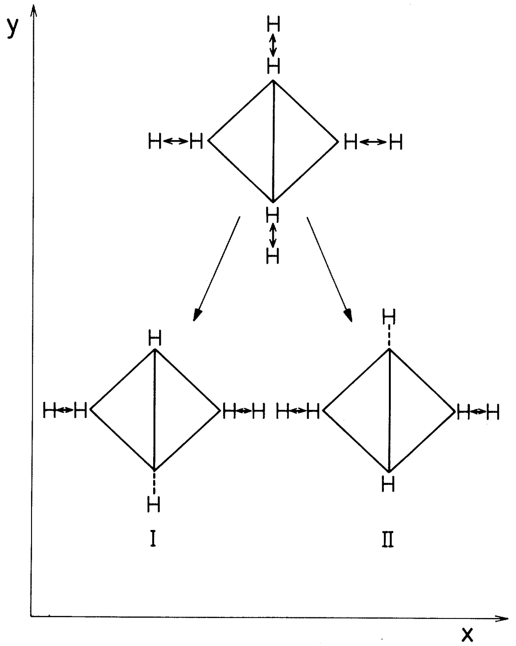

FIG. 5. Hydrogen ordering around an AsO$_4$ group below the high-temperature phase transition and the definition of the x-y coordinate system used in text.

We further assume that the EFG tensor at the arsenic site is mainly determined by the electric charge distribution within the AsO$_4$ group. This of course depends on the positions of the four hydrogens which are covalently or hydrogen bonded to the group. This assumption is based on the fact that in various dihydrogen arsenates the ^{75}As NQR frequencies at low temperatures only slightly depend on the type of cation.[1,9] A slightly more pronounced change of the ^{75}As NQR frequency is observed on deuteration and may be due to the fact that the O—D · · · O hydrogen bonds are longer and more asymmetric than the O—H · · · O hydrogen bonds.[14,15]

In the above model the EFG tensor at the arsenic site is above T_c' axially symmetric around the z axis, which is perpendicular to the x-y plane (see Fig. 5) to which the four hydrogen bonds surrounding an AsO$_4$ group are parallel. In the x,y,z coordinate system defined in Fig. 5 the EFG tensor $\underline{V}$ at the arsenic site above T_c' reads

$$\underline{V}=\begin{bmatrix} -a & 0 & 0 \\ 0 & -a & 0 \\ 0 & 0 & 2a \end{bmatrix} . \tag{10}$$

Here eQa/h is equal to 5.3 MHz.

The two EFG tensors $\underline{V}_{\mathrm{I}}$ and $\underline{V}_{\mathrm{II}}$ corresponding to configurations I and II presented in Fig. 5 are related by a 180° rotation around the z axis. Thus they differ only in the signs of the xz and yz components. The x axis is still perpendicular to a local mirror plane of the AsO$_4$ group. Thus it is approximately a principal direction of the EFG tensor. Therefore the xz components of the EFG tensors $\underline{V}_{\mathrm{I}}$ and $\underline{V}_{\mathrm{II}}$ are approximately zero. In the order-disorder model, which we consider here, the average $\langle \underline{V} \rangle$ of the EFG tensors $\underline{V}_{\mathrm{I}}$ and $\underline{V}_{\mathrm{II}}$ $\langle \underline{V} \rangle = \frac{1}{2}(\underline{V}_{\mathrm{I}}+\underline{V}_{\mathrm{II}})$, is the EFG tensor $\underline{V}$ [expression (10)]. Thus the EFG tensors $\underline{V}_{\mathrm{I}}$ and $\underline{V}_{\mathrm{II}}$ are of the forms

$$\underline{V}^{\mathrm{I,II}}=\begin{bmatrix} -a & 0 & 0 \\ 0 & -a & \pm b \\ 0 & \pm b & 2a \end{bmatrix} . \tag{11}$$

Here $+b$ stands for configuration I and $-b$ stands for configuration II. If below T_c' an AsO$_4$ group is found in configuration I with the probability $(1+S)/2$ and in configuration II with the probability $(1-S)/2$, and if the exchange between the two configurations is fast on the NQR time scale, a time-averaged EFG tensor $\langle \underline{V} \rangle$ is observed of the form

$$\langle \underline{V} \rangle=\begin{bmatrix} -a & 0 & 0 \\ 0 & -a & Sb \\ 0 & Sb & 2a \end{bmatrix} . \tag{12}$$

The NQR frequency ν_Q for a spin-$\frac{3}{2}$ nucleus in an electric-field gradient $\underline{V}$ expressed in an arbitrary coordinate system x,y,z reads

$$\nu_Q=\frac{eQ}{h}\sqrt{(1/3)[(V_{xy})^2+(V_{xz})^2+(V_{yz})^2]-(1/3)(V_{xx}V_{yy}+V_{xx}V_{zz}+V_{yy}V_{zz})}\ . \tag{13}$$

In the case of the EFG tensor $\langle \underline{V} \rangle$ [expression (12)] this becomes

$$\nu_Q=\frac{eQ}{h}\sqrt{a^2+(1/3)S^2b^2}$$
$$=\sqrt{(5.3\ \text{MHz})^2+(1/3)(SeQb/h)^2}\ . \tag{14}$$

In order to determine the order parameter S from ν_Q we need to know eQb/h, which we can calculate if we consider the phase transition into the low-temperature phase. At this phase transition also the other two O—H ⋯ O hydrogen bonds, which are symmetric in the intermediate-temperature phase, become asymmetric. One of the two hydrogens freezes out in the close (As—O—H) position whereas another one freezes out in the far (As—O ⋯ O) positions. Similarly as the ordering of the first pair of hydrogens below T_c' introduces the term $+b$ in the yz position of the EFG tensor the ordering of the second pair of hydrogens below T_c introduces a term $+b$ at the xz position of the EFG tensor. The sign of the xz term ($+b$ or $-b$) depends on which of the two hydrogens remains close to the AsO_4 group. In case of a complete ordering of the four hydrogens surrounding an AsO_4 group the four possible EFG tensors read

$$\underline{V}=\begin{bmatrix} -a & 0 & \pm b \\ 0 & -a & \pm b \\ \pm b & \pm b & 2a \end{bmatrix}\ . \tag{15}$$

The NQR frequency ν_Q does not depend on the signs of the off-diagonal elements of the EFG tensors and is for the four possible EFG tensors (15) equal to

$$\nu_Q=\frac{eQ}{h}\sqrt{a^2+(2/3)b^2}$$
$$=\sqrt{(5.3\ \text{MHz})^2+(2/3)(eQb/h)^2}\ . \tag{16}$$

Within the accuracy of the above model we may for ν_Q take an average, 38 MHz, of the two ^{75}As NQR frequencies measured in TlH_2AsO_4 at 77 K (Ref. 1) and obtain $eQb/h=46$ MHz. The ^{75}As NQR frequency corresponding to a complete ordering of only two hydrogens surrounding an AsO_4 group is given by expression (14) in which we take $S=1$. As a result we obtain $\nu_Q=27$ MHz.

The temperature dependence of the order parameter S as obtained from the ^{75}As NQR frequency and by taking $eQb/h=46$ MHz is given in Fig. 6. The order parameter S is rather low. It has for example at 88 °C, which is 32 degrees below T_c' the value of 0.22. The temperature dependence of the order parameter S can be well described by the expression $S\propto(T_c'-T)^{0.55}$ An extrapolation of this temperature dependence to room temperature gives $S=0.35$ and an NQR frequency of 10.7 MHz.

This rather low value of the order parameter S shows that the ordered hydrogen bonds are in the intermediate-temperature phase only weakly asymmetric. This is, in fact, not surprising.

A neutron-diffraction study of TlH_2PO_4 at room temperature[4] showed that in the asymmetric O—H ⋯ O hydrogen bonds the O—H distance is 0.115 nm and the O ⋯ H distance is 0.136 nm. The distance 0.115 nm is much longer than 0.105 nm as expected for the O—H distance in an O—H ⋯ O hydrogen bond of the length of 0.250 nm.

Also the ^{17}O NQR in TlH_2PO_4 showed[6] that on going from the low-temperature phase to the intermediate-temperature phase some O—H ⋯ O hydrogen bonds still remain asymmetric. The difference of the ^{17}O quadrupole coupling constants corresponding to the O—H and O ⋯ H sites, which measures the asymmetry of the hydrogen bond, has been in the intermediate-temperature phase found to be much smaller than in the low-temperature phase. Thus the asymmetric O—H ⋯ O hydrogen bonds are in the intermediate-temperature phase significantly less asymmetric than in the low-temperature phase. The same seems to be true also in TlH_2AsO_4.

It is also not definitely known whether the hydrogens indeed move between two equivalent equilibrium sites above T_c and between two slightly inequivalent equilibrium sites below T_c or whether the high-temperature phase transition is associated with displacements of hydrogens from the central position in the O—H ⋯ O hydrogen bonds. Both mechanisms have a similar effect on the ^{75}As NQR frequency. Some experiments concerning the spin-lattice relaxation of ^{17}O in TlH_2PO_4 support the

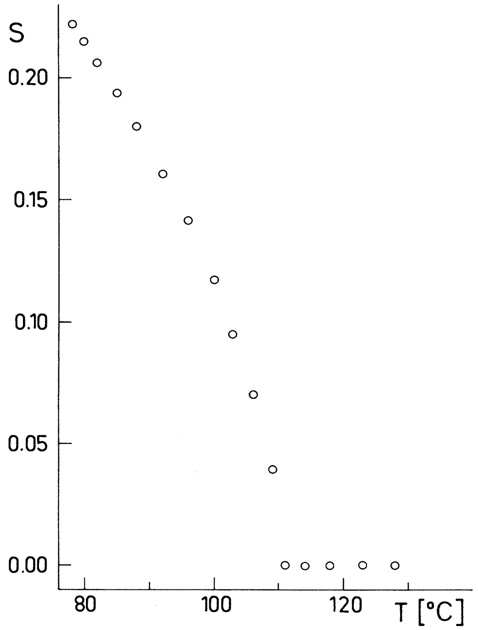

FIG. 6. Temperature dependence of the order parameter S of the asymmetric O—H ⋯ O hydrogen bonds in TlH_2AsO_4.

order-disorder mechanism. Namely, in the study of the ^{17}O NQR with the proton-oxygen double resonance[6] above the low-temperature phase transition, we observed oxygens from the asymmetric O—H · · · O bonds with the single-frequency rf irradiation. This technique works only when the oxygens relax fast. Slightly above room temperature we observed oxygen dips in the Larmor-frequency dependence of proton spin-lattice relaxation time. This shows that the spin-lattice relaxation time of oxygens is in the microsecond region. The positions of the oxygen dips (1.0 and 1.5 MHz) do not shift with increasing temperature. A reasonable explanation of these observations is that in the asymmetric hydrogen bonds hydrogens move between two inequivalent equilibrium sites with a much lower rate than in the symmetric hydrogen bonds. This motion does not shift the centers of the NQR doublets corresponding to the O—H and O · · · H sites. It only influences the splittings of the doublets. On the other hand it causes large fluctuations of the EFG tensors at the oxygen sites, which may result in a fast spin-lattice relaxation of oxygens as indeed observed.

IV. CONCLUSIONS

The ^{75}As NQR frequency has been measured as a function of temperature around the high-temperature phase transition in TlH_2AsO_4 by a proton-arsenic cross-relaxation technique.

The accuracy of the technique has been checked in a similar system—KH_2AsO_4—in which the ^{75}As NQR frequency can also be measured by a more precise technique based on dynamic polarization.

In TlH_2AsO_4 above the high-temperature phase transition the ^{75}As NQR frequency was observed as being 5.3 MHz. Such a low value of the ^{75}As NQR frequency is characteristic for an AsO_4 group forming four dynamically disordered symmetric double minimum type O—H · · · O bonds.

Below the high-temperature phase transition—which we observed at 110 °C—the ^{75}As NQR frequency starts to increase continuously. We analyze the temperature dependence of the ^{75}As NQR frequency in an order-disorder model in which—similarly as in TlH_2PO_4—two of the four O—H · · · O hydrogen bonds formed by an AsO_4 group become asymmetric and ordered below the high-temperature phase transition whereas the other hydrogen bonds become ordered below the low-temperature phase transition. The order parameter S describing the ordering of hydrogens in the asymmetric hydrogen bonds below T_c' is calculated from the NQR data. It is proportional to $(T_c'-T)^{0.55}$. The values of the order parameter S are rather small, say 0.22 at $T_c'-32$ K, and that means that the two asymmetric hydrogen bonds are only slightly asymmetric. This agrees with the results of the neutron diffraction and ^{17}O NQR studies of TlH_2PO_4, which show that already above the low-temperature phase transition the O—H · · · O hydrogen bonds that remain asymmetric above T_c, exhibit a much lower asymmetry than in the low-temperature phase. It is still not completely clear whether the lower asymmetry of the hydrogen bonds in the intermediate-temperature phase is indeed a dynamic effect (hydrogen motion between two inequivalent equilibrium sites) or whether the hydrogen atoms are located close to the centers of the hydrogen bonds. Some experimental observations in TlH_2PO_4 support the dynamic model.

---

[1] F. Milia, Ferroelectrics **20**, 229 (1978).

[2] B. M. Zhigarnovskii, Yu. A. Polyakov, K. Rakhimov, V. I. Bugakov, V. Yu. Kozhenov, and M. A. Maifat, Izv. Akad. Nauk SSSR Neorg. Mater. **21**, 1802 (1985) [Inorg. Mater. (USSR) **21**, 1572 (1985)].

[3] See, for instance, R. Blinc and B. Žekš, *Soft Modes in Ferroelectrics and Antiferroelectrics* (North-Holland, Amsterdam, 1974).

[4] R. J. Nelmes and R. N. P. Choudhary, Solid State Commun. **38**, 321 (1981).

[5] Y. Oddon, A. Tranquard, and G. Pepe, Acta Crystallogr. B **35**, 542 (1979).

[6] J. Seliger, V. Žagar, R. Blinc, and V. H. Schmidt, J. Chem. Phys. **88**, 3260 (1988).

[7] H. Yoshida, M. Endo, T. Kaneko, T. Osaka, and Y. Makita, J. Phys. Soc. Jpn. **53**, 910 (1984).

[8] T. V. Narasaiah, R. N. P. Choudhary, and A. K. Pradhan, J. Mater. Sci. **22**, 3571 (1987).

[9] A. P. Zhukov, I. S. Rez, V. I. Pakhomov, and G. K. Semin, Phys. Status Solidi **27**, K129 (1968).

[10] R. Blinc, M. Rožmarin, F. Milia, and M. Melisaropoulou, Solid State Commun. **27**, 999 (1978).

[11] R. Blinc and J. L. Bjorkstam, Phys. Rev. Lett. **23**, 788 (1969).

[12] S. R. Hartmann and E. L. Hahn, Phys. Rev. **128**, 2042 (1962).

[13] M. Goldman, *Spin Temperature and Nuclear Magnetic Resonance in Solids* (Clarendon, Oxford, 1979).

[14] J. E. Tibbals, W.-L. Zhong, and R. J. Nelmes, J. Phys. C **15**, 4431 (1982).

[15] J. Seliger, V. Žagar, R. Blinc, and V. H. Schmidt, Phys. Rev. B **42**, 3881 (1990).