Cluster distribution in paraelectric KH_2AsO_4. I. Dispersion of the proton spin-lattice relaxation time

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The anomalous frequency dependence of the proton spin-lattice relaxation time in paraelectric KH_2AsO_4 is the result of proton-^{75}As level crossing in partially polarized regions where the As nuclear quadrupole resonance frequency matches the proton Larmor frequency. The experiment allows the determination of the short-range-order polarization distribution function even for strongly polarized regions which, in view of their small abundance, are hard to detect otherwise.

I. INTRODUCTION

The soft-mode dynamics in KH_2AsO_4 (KDA) and other H-bonded ferroelectrics is connected with the fast (10^{-11}–10^{-12} s) motion of protons between the two sites in the O—H—O hydrogen bonds.[1–13] The proton motion is basically determined by the short-range Slater-Takagi rules,[2,3] which can be, to a certain extent, represented by an Ising-type Hamiltonian.[1,4,5]

The appearance[6–8] of anomalous ^{75}As lines in KDA between $T_c = 96$ K and $T_c + 60$ K which display the symmetry of the ferroelectric phase well above T_c demonstrates the presence of quasistatically polarized clusters in the paraelectric phase.[8] The detailed nature of these clusters is not yet clear. They are—in contrast to those giving rise to the central peak in light scattering[9,10]—insensitive to crystal annealing.[8]

In order to throw some additional light on this problem, we decided to study the frequency dependence of the proton spin-lattice relaxation time in paraelectric KH_2AsO_4. We specifically hoped to be able to answer the question whether (i) the crystal indeed consists of unpolarized regions giving rise to the "paraelectric" As lines on one side and well-defined quasistatically polarized regions giving rise to symmetry-breaking "anomalous" As lines on the other side, or (ii) are we rather dealing with a continuous distribution of slowly fluctuating short-range-order polarizations with a zero mean value?

II. EXPERIMENTAL PROCEDURE

The frequency dependence of the proton spin-lattice relaxation time T_1 was studied by a field-cycling technique between $\nu_L = 15$ and 45 MHz. The T_1 values between 6 and 15 MHz were measured directly by a saturation technique using a frequency and field variable spectrometer. A single crystal was used where anomalous ^{75}As lines were detected by ^{75}As nuclear magnetic resonance. The temperature dependence of the proton spin-lattice relaxation time was studied at $\nu_L = 18.3$ MHz. The field cycling method could not be used below 15 MHz because the proton T_1 values were too short.

III. RESULTS

The proton T_1 in KDA is a factor 10^4–10^5 longer at 40 MHz than the proton relaxation time in the rotating ($T_{1\rho}$)

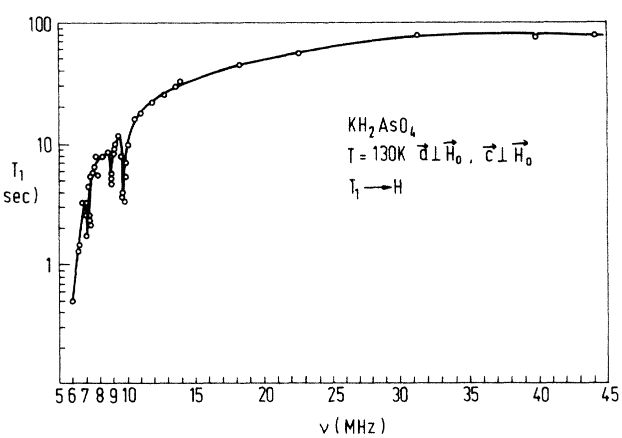

FIG. 1. Dispersion of the proton T_1 at $T = 130$ K and $\mathbf{c} \perp \mathbf{H}_0$, $\mathbf{a} \perp \mathbf{H}_0$ in KH_2AsO_4. The sharp dips are due to multiple quantum transitions.

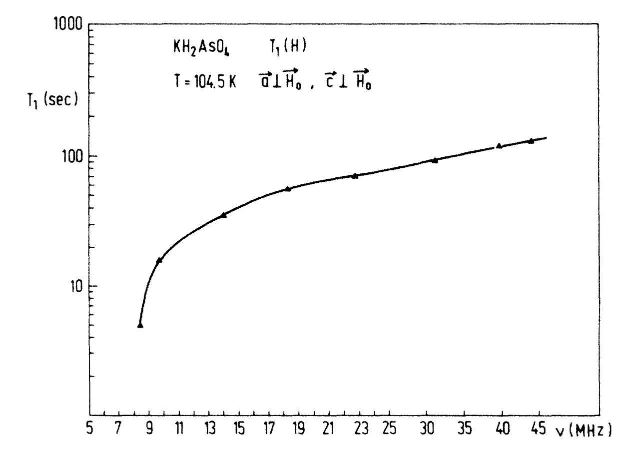

FIG. 2. Dispersion of the proton T_1 at $T = 104.5$ K.

or dipolar (T_{1D}) frames.[11] The form of the T_1-vs-T curve is analogous to that observed[12] in KH_2PO_4 (KDP) but there are two important differences.

(i) In KDA, T_1 is 1–2 orders of magnitude shorter than in KDP.

(ii) In KDA there is a maximum in T_1 just above T_c, whereas T_1 decreases with decreasing temperature as $T \rightarrow T_c^+$.

The dispersion of the proton T_1 at $T=130$ K and $\mathbf{c}\perp\mathbf{H}_0$, $\mathbf{a}\perp\mathbf{H}_0$ is extremely strong and is presented in Fig. 1. T_1 is of the order of 0.5 s at 6 MHz and increases to more than 70 s at 40–45 MHz. The dispersion of the proton T_1 is similarly anomalous also at $T=104.5$ K (Fig. 2).

IV. DISCUSSION

Let us now discuss three possible mechanisms for proton spin relaxation in paraelectric KDA:

(A) Fluctuations in the proton dipole-dipole coupling.

(B) Fluctuations in the proton-As dipolar coupling.

(C) Proton-As relaxation via level crossing due to the presence of long-living (on the NMR time scale) clusters.

A. Fluctuations in the proton dipole-dipole coupling

The proton spin-lattice relaxation rate due to fluctuations in the proton-proton dipolar coupling is in the spin-temperature approximation ($[M_2(\text{H-H})]^{1/2} \gg T_{1\text{HH}}^{-1}$) obtained as

$$T_{1\text{HH}}^{-1} = 3\gamma_{\text{H}}^4 \hbar^2 I(I+1)[J_{\text{HH}}^{(1)}(\omega) + J_{\text{HH}}^{(2)}(2\omega)] , \tag{1}$$

where

$$J_{\text{HH}}^{(k)} = \frac{1}{N_{\text{H}}} \sum_{\substack{i,j \\ i<j}} \int_{-\infty}^{+\infty} \langle F_{ij}^k(0)[F_{ij}^k(t)]^* \rangle e^{ik\omega t} dt \tag{2}$$

stands for the local spectral density of the spatial part of the proton-proton dipolar coupling. Introducing the local order parameter $p_i(t)$ which fluctuates between $+1$ and -1 and which describes the position of the proton in the two equilibrium sites of the ith O—H···O bond, $F_{ij}(t)$ can be expressed as

$$F_{ij}(t) \approx \text{const} + \Delta F_{ij} p_i(t) + \Delta F_{ji} p_j(t) , \tag{3}$$

where

$$p_i(t) = p(t) + \Delta p_i(t) . \tag{4}$$

In expression (4), $\Delta p_i(t)$ describes the fast, "soft-mode" type of proton motion, whereas $p(t)$ describes the slow, quasistatic fluctuations of the polarization of the clusters.

Assuming that $\omega\tau_{\Delta p_i} \ll 1$ and $\omega\tau_p \gg 1$, as well as that $\langle p^2 \rangle_p \ll 1$ in the paraelectric phase well above T_c, and taking into account that[7,11]

$$|\Delta F^{(1)}|^2 = 0.24 \times 10^{-4} \text{Å}^{-6} , \tag{5a}$$

$$|\Delta F^{(2)}|^2 = 0.76 \times 10^{-4} \text{Å}^{-6} , \tag{5b}$$

we find

$$T_{1\text{HH}}^{-1} \approx (1.2 \times 10^7 \text{ s}^{-2}) \tau_{\Delta p_i} + (10^{-7} \text{ s}^{-2}) \langle p^2 \rangle_p / \tau_p (1/\omega^2) . \tag{6}$$

For $\tau_{\Delta p_i} \approx 10^{-12}$ s and $\tau_p > 10^{-6}$ s, this yields for $T \gg T_c$ with $\omega \approx 10^8 \text{ s}^{-1}$,

$$T_{1\text{HH}}^{-1} \approx \frac{1}{10^5 \text{ s}} + \frac{\langle p^2 \rangle}{10^3 \text{ s}} , \tag{7}$$

so that the proton T_1 due to the fluctuations in the proton-proton dipolar coupling should be of the order of 10^3–10^5 s—as indeed observed in KDP—and not of the order of 1–10^2 s as observed in KDA. Thus, this contribution cannot explain the experimental data.

B. Fluctuations in the proton-As dipolar coupling

Let us now investigate the proton relaxation rate $T_{1\text{HAs}}^{-1}$ induced by fast As spin fluctuations. For this process one finds

$$T_{1\text{HAs}}^{-1} = \tfrac{1}{2} M_2(\text{H-As}) \int_{-\infty}^{+\infty} e^{i\omega t} \langle S_{z\text{As}}(0) S_{z\text{As}}(t) \rangle dt . \tag{8}$$

Here, the H-As dipolar second moment amounts to $M_2(\text{H-As}) = 0.27 \text{ G}^2 = 1.93 \times 10^8 \text{ s}^{-2}$. The autocorrelation function for the As spin fluctuations can be approximated by

$$\langle S_z(0) S_z(t) \rangle = [S(S+1)/3] \exp(-t/T_{1\text{As}}) \tag{9}$$

so that

$$T_{1\text{HAs}}^{-1} = \tfrac{5}{4} M_2(\text{H-As}) T_{1\text{As}} / [1 + (\omega T_{1\text{As}})^2] . \tag{10}$$

Direct measurements of the As spin-lattice relaxation have shown that $T_{1\text{As}} \approx 200$–$300\ \mu$s. Since $\omega \approx 10^8 \text{ s}^{-1}$ and $\omega T_{1\text{As}} \gg 1$, one obtains

$$T_{1\text{HAs}}^{-1} = \tfrac{5}{4} M_2(\text{H-As}) / \omega^2 T_{1\text{As}} \approx 1.5 \times 10^{-4} \text{ s}^{-1} . \tag{11}$$

The contribution of the fast fluctuations of the As spins to the proton T_1 is thus negligible as well and cannot account for the experimental data.

C. Relaxation via H-As level crossing

The proton-As cross relaxation rate W_{HAs} is of the order of

$$W_{\text{HAs}} \approx [M_2(\text{H-As})]^{1/2} \sim 10^4 \text{ s}^{-1} , \tag{12}$$

when the proton and As transition frequencies coincide due to level crossing in partially polarized crystal regions. Since the proton-proton cross relaxation rate $W_{\text{HH}} \sim [M_2(\text{H-H})]^{1/2} \approx 3 \times 10^4 \text{ s}^{-1}$ is still faster and $T_{1\text{As}}^{-1} \approx 0.4 \times 10^4 \text{ s}^{-1}$, we have

$$W_{\text{HH}} > W_{\text{HAs}} > T_{1\text{As}}^{-1} , \tag{13}$$

so that a common spin temperature will be established in the proton—resonant-As Zeeman reservoir. The H-As cross-relaxation is effective only in those regions where the local polarization p is such that

$$\nu_{\text{As}}(p) \in (\nu_{\text{H}}, \nu_{\text{H}} + \Delta\nu_{\text{H}}) , \tag{14}$$

i.e., the As Zeeman perturbed quadrupole resonance frequency lies within the dipolar width of the proton Zeeman line $\Delta\nu_{\text{H}} \approx [M_2(\text{H-H})]^{1/2} + [M_2(\text{H-As})]^{1/2}$. Let us now assume that the crystal consists of several clusters with different p values or that the crystal contains clusters where the polarization continuously varies from 1 to 0. In this case, regions with different p values have different As resonance frequencies ν_{As}. Let us further denote, with $\Delta N(\nu)/N$, the fraction of As nuclei satisfying condition (14) at a given value of the proton resonance frequency ν_H. Since we have a common spin temperature in the proton—resonant-As Zeeman reservoir, one finds

$$\frac{d\beta}{dt} = -\frac{1}{T_1(\nu)}(\beta-\beta_L), \quad (15a)$$

where

$$\frac{1}{T_1(\nu)} = \frac{C_{As,res}}{C_{As,res}+C_H}\frac{1}{T_{1As}} + \frac{C_H}{C_{As,res}+C_H}\frac{1}{T_{1H}} \approx \frac{C_{As,res}}{C_H}\frac{1}{T_{1As}} + \frac{1}{T_{1H}}, \quad (15b)$$

with

$$C_{As,res} = \frac{\Delta N(\nu)}{N}C_{As} \ll C_H \quad (16)$$

standing for the heat capacity of the resonant part of the As Zeeman and quadrupolar energy reservoir. C_{As} and C_H are the total heat capacities of As and H nuclei, respectively. T_{1As}^{-1} represents the relaxation rate of the As nuclei in a cluster with the polarization p in the absence of cross relaxation to protons. Here, $T_1(\nu)$ represents the magnetic-field-dependent relaxation time of the combined proton—resonant-As Zeeman reservoir (which is most conveniently measured via the abundant species, i.e., via protons) and T_{1H} the relaxation time of the proton reservoir in the absence of cross relaxation to the As nuclei. It should be further noted that $C_H = 2C_{As}$.

Introducing the frequency distribution of the As resonance frequencies $f(\nu)$ in the various clusters as

$$f(\nu)\Delta\nu = \Delta N(\nu)/N, \quad (17)$$

one can rewrite expression (15b) as

$$\frac{1}{T_1(\nu)} = f(\nu)\Delta\nu_H \frac{1}{2}\frac{1}{T_{1As}(p)} + \frac{1}{T_{1H}}, \quad (18)$$

where $\Delta\nu_H$ is the dipolar width of the proton line.

A measurement of the frequency dependence of the proton Zeeman relaxation rates $T_1^{-1} = T_{1H}^{-1}(\nu)$ thus enables one to map out the frequency distribution of the As resonance frequencies $f(\nu)$ in the partially polarized clusters since T_{1As} and $\Delta\nu_H \approx 4.5\times10^4\ s^{-1}$ are known.

Let us now try to find the relation between the As frequency distribution $f(\nu)$ and the local polarization distribution. We must first remember that $f(\nu)$ essentially corresponds to a distribution of pure nuclear quadrupole resonance (NQR) frequencies of the As nuclei. In magnetic fields where the proton Zeeman frequency lies between 6 and 40 MHz, the As Larmor frequency is between 1 and 6 MHz and is thus much smaller than the frequency measured by the H-As level-crossing experiment.

The electric-field-gradient (EFG) tensor at the As site is of covalent nature and its instantaneous value depends on the arrangement of the four hydrogens around a given AsO_4 group:

$$\underline{T} = \underline{T}(p_1,p_2,p_3,p_4)\ . \quad (19)$$

In the paraelectric phase far above T_c each H_2AsO_4 group rapidly fluctuates between six Slater H_2AsO_4 configurations[1-3] with ^{75}As EFG tensors[1] $\underline{T}^{(l)}$ where $l=1$–6. Replacing the time average by an ensemble average one finds

$$\langle \underline{T} \rangle = \sum_{l=1}^{6} \delta_l \underline{T}^{(l)}, \quad (20)$$

where[1]

$$\delta_{1,2} = \delta_0 \exp(\varepsilon/kT)/4(1-p) \quad (21)$$

and

$$\delta_0 = \delta_{3,4,5,6} = \left[1+\tfrac{1}{2}\exp\left[\frac{\varepsilon}{kT}\right]\frac{1+p^2}{1-p^2}\right]^{-1}, \quad (22)$$

with $\varepsilon = kT_c \ln 2$ and $\langle p_i\rangle = \langle p_j \rangle = p = 0$ for $T > T_c$ in the absence of local polarization. Since $\sum_{l=3}^{6}\underline{T}^{(l)} \approx 0$ we see that for $T > T_c$ the NQR frequency is determined by

$$\langle \underline{T} \rangle = \delta_1(\underline{T}^{(1)} + \underline{T}^{(2)}), \quad T > T_c\ . \quad (23)$$

The EFG tensor is axially symmetric and the largest principal axis is parallel to the crystal **z**||**c** axis. In the presence of a local polarization, the mean value of the As EFG tensor can be expressed as

$$\langle \underline{T}(t) \rangle = \underline{T}_0 + \underline{A}p + \underline{B}p^2 + \cdots, \quad (24)$$

since in the zero-field approximation, ν_Q does not depend on the sign of the local polarization. From now on, p stands for the absolute value of the reduced local polarization.

In the AsO_4 fixed x,y,z frame of KDA we get

$$\underline{T}_0 = t\begin{bmatrix}1&0&0\\0&1&0\\0&0&-2\end{bmatrix}, \quad \underline{B} = b\begin{bmatrix}1&0&0\\0&1&0\\0&0&-2\end{bmatrix}, \quad (25a)$$

and

$$\underline{A} = a\begin{bmatrix}-1&0&0\\0&1&0\\0&0&0\end{bmatrix}, \quad (25b)$$

where $a = 66$ MHz $\gg t+b = 3.4$ MHz in frequency units.

For $p\neq 0$, the cylindrical symmetry around the **z**(**c**) axis will be destroyed. The ^{75}As NQR frequency is

$$\nu_Q = \frac{e^2qQ}{2h}(1+\tfrac{1}{3}\eta^2)^{1/2}\ . \quad (26)$$

For weakly polarized regions, $p < 0.05$, the largest principal axis will still be parallel to the **z**||**c** axis and

$$q \approx 2t, \quad \eta \ll 1 \quad (27)$$

so that $\nu_Q \approx 3.4$ MHz. For more polarized regions ($p > 0.05$) the largest principal axes will be in the x-y plane and

$$q \approx t + ap + bp^2, \quad (28a)$$

$$\eta \approx \frac{3(t+bp^2)-ap}{t+bp^2+ap}\ . \quad (28b)$$

For $\nu_Q > 2\nu_{Q,\mathrm{parael}}$, the linear approximation can be used:

$$\nu_Q \approx \frac{e^2Q}{2h}(t+ap), \tag{29}$$

so that the As frequency distribution $f(\nu)$ is linearly related to the local polarization distribution $g(p)$

$$f(\nu)d\nu = g(p)dp \ . \tag{30}$$

We thus obtain

$$g(p) = f(\nu)\frac{d\nu}{dp} \cong \mathrm{const}\times f(\nu), \tag{31}$$

where we have from expression (29), $d\nu/dp \approx 30$ MHz.

In analyzing the experimental data we have to remember that the sharp dips in the experimental $T_1(\nu)$ below 10 MHz correspond to "multiple quantum transitions" in weakly or nonpolarized clusters (i.e., mainly double quantum transitions). Their width (0.1—0.3 MHz) indicates the width of the As frequency distribution $f(\nu)$ in the vicinity of $\nu_{Q,\mathrm{parael}}$. In calculating $g(p)$, these effects should be excluded. Similarly, we should exclude the effect of paramagnetic impurities influencing the relaxation behavior at higher frequencies. We thus evaluate $g(p)$ in the 6—40 MHz range from

$$\tilde{T}_1^{-1}(\nu) = T^{-1}_{1\mathrm{H,expt}} - T^{-1}_{1\mathrm{H}}(\nu > 40 \ \mathrm{MHz}), \tag{32}$$

using

$$g(p) = \frac{2T_{1\mathrm{As}}(p)(\partial\nu/\partial p)}{\tilde{T}_1(\nu)\Delta\nu_{\mathrm{H}}} \tag{33}$$

where we have taken into account the fact that

$$T^{-1}_{1\mathrm{As}}(p) \approx T^{-1}_{1\mathrm{As}}(p=0)(1-p^2) \approx (1-p^2)/(250\times 10^{-6}) \ \mathrm{s}^{-1},$$

at $T = 130$ K.

The results are presented in Fig. 3. They show that (i) the short-range local polarization distribution is continuous within the resolution of this experiment. The present experiment does not distinguish between a continuous distribution of clusters with different polarizations or a continuous polarization distribution within a short-range-ordered cluster which may be induced by defects. (ii) $g(p)$ is very small at large p values and increases sharply as p approaches the value 0.1. The values of $g(p)$ above 0.05 are not too reliable because of the necessity of making corrections for multiple quantum transitions. The volume fraction occupied by regions with $p > 0.1$,

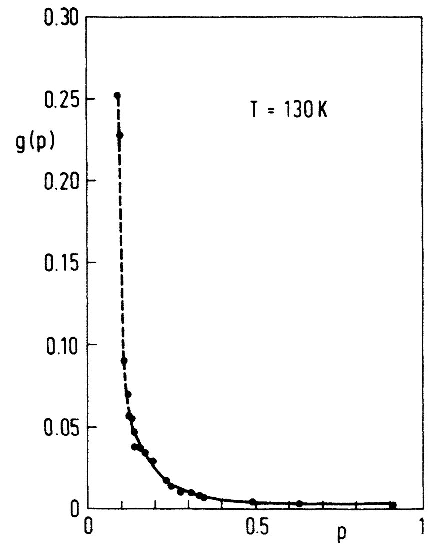

FIG. 3. Local polarization distribution at $T = 130$ K. The contributions of the multiple quantum transitions have been subtracted. Nevertheless, the obtained values of $g(p)$ above $g(p) = 0.05$ are not too reliable.

$$\left.\frac{\Delta N}{N}\right|_{p>0.1} = \int_{0.1}^{1} g(p)dp, \tag{34}$$

amounts to 1% at $T = 130$ K. Thus, the large majority of the crystal at $T - T_c = 33$ K is only weakly polarized. There are, however, regions where the polarization is nearly complete, $p \approx 1$.

It should be stressed that in the present cross-relaxation experiment, only strongly polarized regions ($p > 0.1$) where the pure As NQR frequency exceeds 6 MHz have been detected. In view of their small volume fraction ($< 1\%$), these highly polarized regions are hard to study by other, more direct techniques. An extension of the cross-relaxation technique to lower frequencies—where the proton T_1 becomes rather short—could, in principle, map out the complete local polarization distribution function $g(p)$ between $-1 \le p \le 1$. Other more direct methods are, however, easier for low-p values.

[1]For a review see, for instance, R. Blinc and B. Žekš, *Soft Modes in Ferroelectrics and Antiferroelectrics* (North-Holland, Amsterdam, 1974).

[2]J. C. Slater, J. Chem. Phys. **9**, 16 (1941).

[3]H. B. Silsbee, E. A. Uehling, and V. H. Schmidt, Phys. Rev. 133, A165 (1964); R. Blinc and S. Svetina, Phys. Rev. **147**, 423 (1966).

[4]P. G. de Gennes, Solid State Commun. **1**, 132 (1963).

[5]M. Tokunaga and T. Matsubara, Prog. Theor. Phys. **35**, 581 (1966); **36**, 857 (1966).

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

[7]J. L. Bjorkstam, Adv. Magn. Res. **7**, 1 (1974).

[8]M. Mali, J. Roos, E. Courtens, and K. A. Müller, *Proceedings of the 22nd Congress Ampere, Zurich, 1984*, edited by K. A. Müeller, R. Kind, and J. Roos (University of Zurich, Zurich, 1984).

[9]E. Courtens, Phys. Rev. Lett. **39**, 561 (1977); **41**, 1171 (1978).

[10]A. S. Chaves and R. Blinc, Phys. Rev. Lett. **43**, 1037 (1979).

[11]R. Blinc, M. Mali, J. Pirš, and S. Žumer, J. Chem. Phys. **58**, 2262 (1973).

[12]R. Blinc, J. Slak, F. C. Sa Barreto, A. S. T. Pires, Phys. Rev. Lett. **42**, 1000 (1979).

[13]G. L. Paul, W. Cochran, W. J. L. Buyers, and R. A. Cowley, Phys. Rev. B **2**, 4603 (1970).