^{87}Rb NMR study of the paraelectric-antiferroelectric phase transition in $Rb_{0.52}(ND_4)_{0.48}D_2AsO_4$

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^{87}Rb $\frac{1}{2}\rightarrow-\frac{1}{2}$ NMR line shape and spin-lattice relaxation time (T_1) data demonstrate the presence of a first-order transition from a paraelectric (PE) to an antiferroelectric (AFE) phase in substitutionally disordered $Rb_{0.52}(ND_4)_{0.48}D_2AsO_4$ where the PE and AFE lines overlap between 140 and 135 K. The ^{87}Rb site symmetry is compatible with the $I\bar{4}2d$ symmetry above T_c and with the $P2_12_12_1$ symmetry of pure $ND_4D_2AsO_4$ below T_c. Superimposed on the glassy order that produces an inhomogeneous broadening of the ^{87}Rb NMR lines is a dynamic disorder of the deuterons in the O—D $\cdots$ O bonds above T_c and an antiferroelectric long-range order below T_c. The O—D $\cdots$ O dynamics is driven by an antiferroelectric soft mode which freezes out at T_c and determines the ^{87}Rb T_1.

I. INTRODUCTION

It has been recently shown[1,2] that substitutionally disordered mixed crystals $Rb_{1-x}(ND_4)_xD_2AsO_4$—henceforth designated as RADA — of ferroelectric (FE) RbD_2AsO_4 and antiferroelectric (AFE) $ND_4D_2AsO_4$ represent a frustrated H-bonded system with randomly competing interactions.[3] For pure RbD_2AsO_4 the ferroelectric transition takes place at $T_c=178$ K whereas the antiferroelectric transition in pure $ND_4D_2AsO_4$ occurs at $T_c=304$ K. The system shows for small x a paraelectric-ferroelectric (PE-FE) and for large x a paraelectric-antiferroelectric (PE-AFE) transition. For intermediate x values no long-range ordering takes place and the system forms at low temperatures a "proton" or "deuteron" dipolar glass.[4,5] In contrast to isomorphous $Rb_{1-x}(ND_4)_xD_2PO_4$ (Refs. 4 and 5) the phase diagram is not symmetric[2] as the paraelectric-antiferroelectric transition temperature is much higher than the paraelectric-ferroelectric one.

In order to throw some light on the nature of these transitions and the local ordering at the antiferroelectric side of the phase diagram[1,2] we decided to perform a ^{87}Rb NMR study of $Rb_{0.52}(ND_4)_{0.48}D_2AsO_4$. We particularly hoped to determine the interplay between the incipient glassy order and the long-range antiferroelectric order. We wanted to see as well if the O—D $\cdots$ O dynamics is of the glassy type and exhibits a Bloembergen-Purcell-Pound– (BPP) like T_1 minimum[6] or is determined by an antiferroelectric soft mode as in pure $ND_4D_2AsO_4$.

The experiments were performed on a deuterated RADA crystal with an ammonium concentration of $x=0.48$ as determined by flame spectroscopy and a degree of deuteration of about 90% as determined by mass spectroscopy. The ^{87}Rb $\frac{1}{2}\rightarrow-\frac{1}{2}$ spectra were measured at 88.34 MHz. A Fourier transform $(90°)_x-(90°)_y$ solid-echo technique was used. The homogeneous linewidth was determined from the slope of the spin-echo amplitude versus pulse separation plot.

II. THEORY

The phase diagram of the $Rb_{1-x}(ND_4)_xD_2AsO_4$ system can be described by the random bond Ising model[3]

$$\mathcal{H}=-\tfrac{1}{2}\sum_{i,j}J_{ij}S_i^zS_j^z\ , \tag{1}$$

where the pseudospin variable $S^z=\pm1$ describes the two possible deuteron sites in the O—D $\cdots$ O bonds and the random interactions J_{ij} are distributed according to a Gaussian probability density

$$P(J_{ij})=\left[\frac{1}{2\pi J^2}\right]^{-1/2}\exp[-(J_{ij}-J_0)^2/(2J^2)]\ . \tag{2}$$

The J_{ij} are assumed[3] to be infinitely ranged with a mean $J_0=\tilde{J}_0/N$ and a variance $J=\tilde{J}/N^{1/2}$. Here N is the number of pseudospin sites. $\tilde{J}_0$ and $\tilde{J}$ are both concentration dependent,

$$\tilde{J}_0(x)=-\tilde{J}_0^{\mathrm{AFE}}x+\tilde{J}_0^{\mathrm{FE}}(1-x) \tag{3}$$

and

$$\tilde{J}(x)=2[x(1-x)]^{1/2}\tilde{J}_{0.5}\ . \tag{4}$$

Here $\tilde{J}_0^{AFE}>0$ and $\tilde{J}_0^{FE}>0$ are parameters appropriate for pure $ND_4D_2AsO_4$ and RbD_2AsO_4, whereas $\tilde{J}_{0.5}$ characterizes the 50% DRbDA-DADA mixture.

For $|\tilde{J}_0|>\tilde{J}$ a transition from a paraelectric into a ferroelectric ($\tilde{J}_0>0$) or antiferroelectric ($\tilde{J}_0<0$) phase appears, whereas for $\tilde{J}\geq|\tilde{J}_0|$ the transition is from a paraelectric into a pseudospin glass phase with zero long-range order $p=1/N\sum_i\langle S_i^z\rangle$, but nonzero Edwards-Anderson glassy order parameter $q=1/N\sum_i\langle S_i^z\rangle^2$.

If $|\tilde{J}_0|>\tilde{J}$ and $\tilde{J}_0<0$ as expected for $Rb_{0.52}(ND_4)_{0.48}D_2AsO_4$, we should have a paraelectric-antiferroelectric transition with nonzero long-range order (i.e., "staggered polarization" $p\neq 0$) below T_c. This should exist in addition to the pseudospin-glass order represented by q.

In analogy to $Rb_{1-x}(ND_4)_xD_2PO_4$ we now add to expression (1) a random field term $-\sum_i S_i^z f_i$. The random fields f_i are as well distributed according to a Gaussian probability density with a variance Δ and zero mean value.

The two order parameters p and q are determined by the coupled self-consistent equations

$$p=\int_{-\infty}^{+\infty}\frac{dz}{\sqrt{2\pi}}e^{-z^2/2}\tanh[\beta(\tilde{J}\sqrt{Q}z+|\tilde{J}_0|p)]\ , \tag{5a}$$

$$q=\int_{+\infty}^{+\infty}\frac{dz}{\sqrt{2\pi}}e^{-z^2/2}\tanh^2[\beta(\tilde{J}\sqrt{Q}z+|\tilde{J}_0|p)]\ . \tag{5b}$$

Here $\beta=1/(kT)$ and $Q=q+\Delta/\tilde{J}^2$. The temperature dependences of p and q expected on the basis of Eqs. (5a) and (5b) are schematically shown in Fig. 1. We see that q is—for $\Delta\neq 0$—different from zero at all temperatures whereas p is nonzero only below T_c. It should be noted that the temperature dependence of q is below T_c strongly affected by the temperature dependence of p.

The relation between the NMR frequency ν_i at a given Rb site and the local O—D $\cdots$ O bond polarization $p_i=\langle S_i^z\rangle$ can be written as

$$\nu_i=\nu_0+\sum_j C_{ij}\langle S_j^z\rangle\ . \tag{6}$$

The presence of glassy order will result in an inhomogeneous broadening of the Rb line. The second moment of the inhomogeneously broadened line is above T_c proportional to the Edwards-Anderson glassy order parameter q

$$M_2=\int f(\nu)(\nu-\nu_0)^2d\nu$$
$$=\frac{1}{N_{Rb}}\sum_i\sum_{jk}[C_{ij}C_{ik}\langle S_j^z\rangle\langle S_k^z\rangle]_{\rm av}=Cq,\quad T>T_c \tag{7}$$

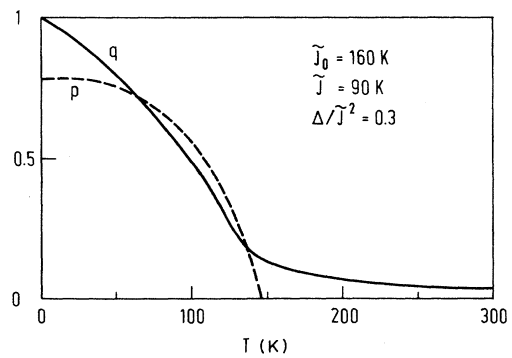

FIG. 1. Temperature dependences of the glassy order parameter q and the long-range order parameter p according to Eqs. (5a) and (5b) for $\tilde{J}_0=160$ K, $\tilde{J}=90$ K, and $\Delta/\tilde{J}^2=0.3$.

where $C=1/N_{\rm Rb}\sum_i\sum_j C_{ij}^2$. Here $[\cdots]_{\rm av}$ denotes the disorder average, i.e., the simultaneous average over random bonds and random fields.

The center of gravity $\bar{\nu}=\int f(\nu)\nu\,d\nu$ of the NMR lines is in this case proportional to the long-range order parameter p,

$$\bar{\nu}=\nu_0,\quad T>T_c\ (p=0) \tag{8a}$$

$$\bar{\nu}=\nu_0+\nu_1 p,\quad T<T_c\ (p\neq 0)\ . \tag{8b}$$

If higher-order terms are added to the expansion (6), one sees that above T_c the center of gravity of the NMR line $\bar{\nu}$ is proportional to q and is thus not really T-independent as predicted by Eq. (8a).

III. RESULTS AND DISCUSSION

The effect of substitutional disorder and the incipient glass ordering lead to a large inhomogeneous broadening of the ^{87}Rb $\frac{1}{2}\rightarrow-\frac{1}{2}$ NMR line even at room temperature. The inhomogeneous broadening is strongly anisotropic, increases with decreasing temperature, and becomes as high as 20 kHz at some orientations (Fig. 2). The homogeneous linewidth on the other hand is only $\simeq$ 300 Hz. In agreement with the average site symmetry of the paraelectric phase $\bar{4}2m$ there is just a single ^{87}Rb $\frac{1}{2}\rightarrow-\frac{1}{2}$ NMR line at room temperature in the rotation spectrum. The average ^{87}Rb electric field gradient (EFG) tensor is axially symmetric ($\eta=0$) and the principle axes (X,Y,Z) are parallel to the crystal axes x,y,z. The largest principle axis Z is parallel to the crystal z$\|$c axis.

On lowering the temperature, the NMR line continuously broadens down to 140 K where a new broad line starts to grow out of the noise (Fig. 3). The new line coexists with the paraelectric line down to 132 K where the paraelectric line disappears. The new line thus belongs to the low-temperature phase. This behavior is quite analogous to the one observed in $Rb_{0.22}(ND_4)_{0.78}D_2PO_4$ (Ref. 8) where a paraelectric-antiferroelectric phase transition takes place as well.

The relative intensities of the two lines—i.e., the volume fractions of the paraelectric and antiferroelectric phases—are plotted versus temperature in Fig. 4. The coexistence of the two phases over a range of nearly 8 K demonstrates that we deal in $Rb_{0.52}(ND_4)_{0.48}D_2AsO_4$ with a first-order phase transition from the PE to the AFE phase.

The normalized frequency shift $(\bar{\nu}-\nu_0)/\nu_1$ of the ^{87}Rb $\frac{1}{2}\rightarrow-\frac{1}{2}$ transition is plotted versus temperature in Fig. 5. Here ν_1 is the limiting value of the shift $\bar{\nu}-\nu_0$ for $T\rightarrow 0$. Above $T_c\approx 140$ K $(\bar{\nu}-\nu_0)/\nu_1$ varies only slightly with temperature. At T_c $(\bar{\nu}-\nu_0)/\nu_1$ jumps from about 0.02 to about 0.85 demonstrating the sudden onset of the long-range order characteristic for a phase transition of first order. Below T_c $(\bar{\nu}-\nu_0)/\nu_1$ continues to increase with decreasing temperature as expected for a situation where the long-range order parameter p (i.e., the "staggered" polarization) is not yet saturated.

It should be noted that if the relation between ν_i and $p_i=\langle S_i^z\rangle$ would be strictly linear—as given by Eq. (6)—

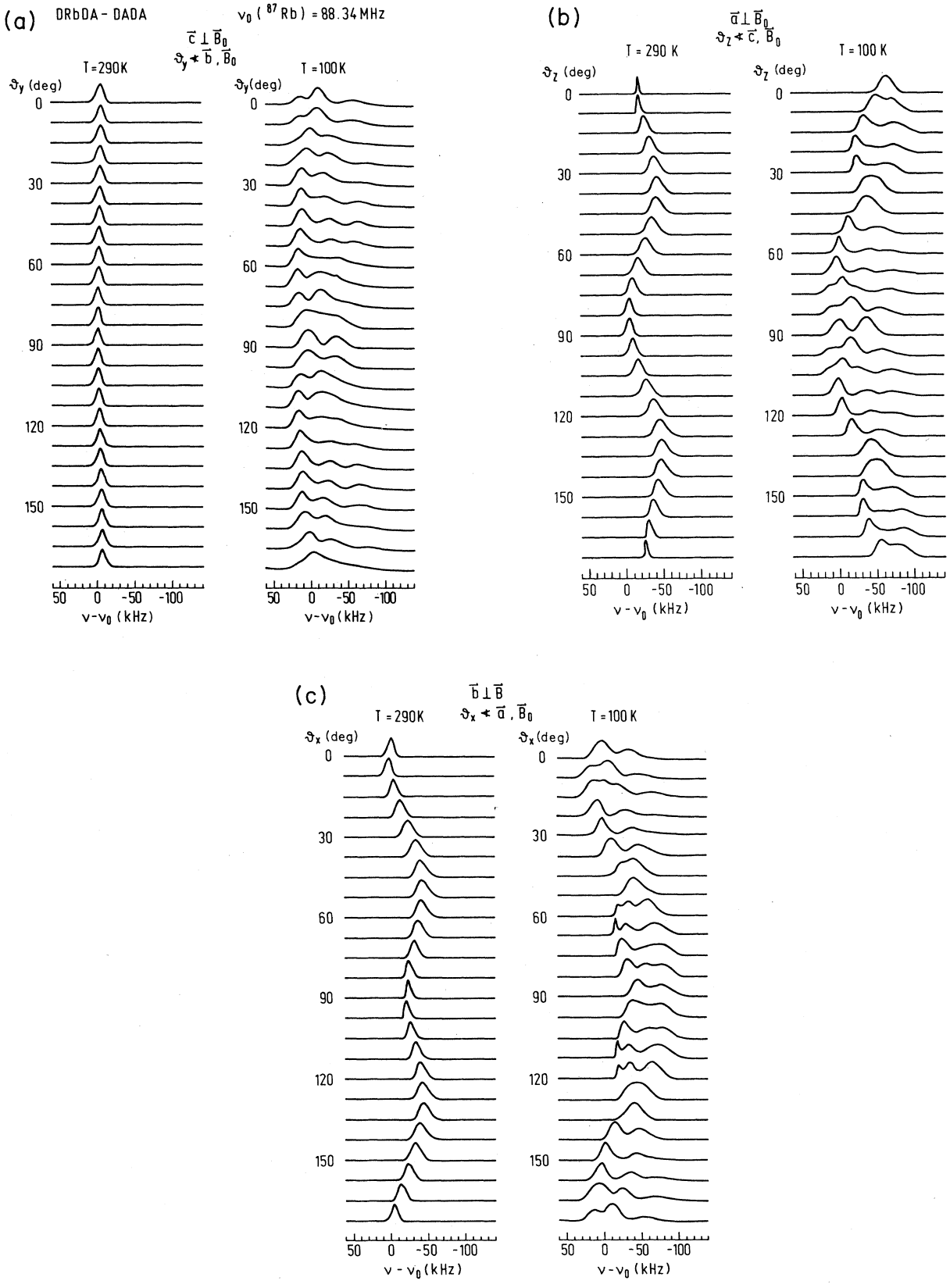

FIG. 2. Angular dependence of the ^{87}Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$ NMR line shapes at 290 and 100 K.

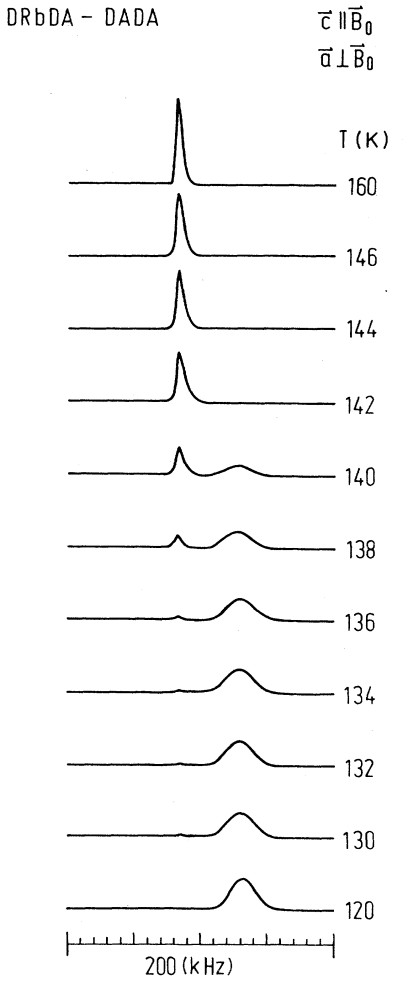

FIG. 3. Temperature dependence of the ^{87}Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$ NMR spectra at $\mathbf{c} \parallel \mathbf{B}_0$, $\mathbf{a} \perp \mathbf{B}_0$ in the region of the paraelectric-antiferroelectric phase transition.

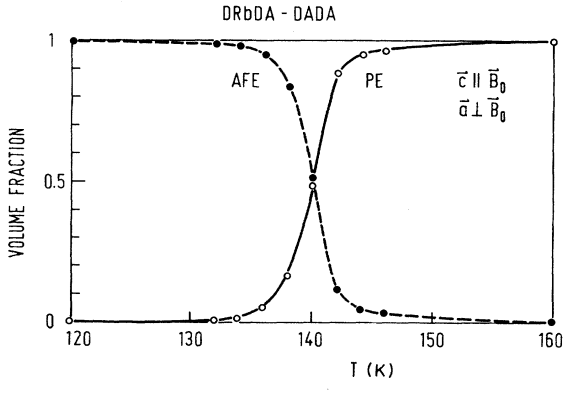

FIG. 4. Temperature dependence of the volume fractions of the paraelectric (solid line) and antiferroelectric (dashed line) phases in the region of the paraelectric-antiferroelectric phase transition.

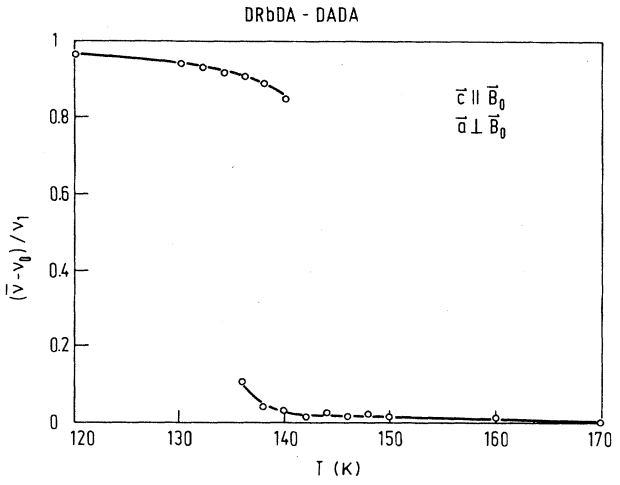

FIG. 5. Normalized frequency shift $(\bar{\nu}-\nu_0)/\nu_1$ of the ^{87}Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition vs temperature for $\mathbf{c} \parallel \mathbf{B}_0$, $\mathbf{a} \perp \mathbf{B}_0$.

the temperature dependence of $(\bar{\nu}-\nu_0)/\nu_1$ would be identical to the temperature dependence of p.

The temperature dependences of the second moment M_2 of the ^{87}Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$ NMR line is presented in Fig. 6. Whereas above T_c $(\bar{\nu}-\nu_0)/\nu_1$ is only weakly temperature dependent, M_2 strongly increases with decreasing temperature over most of the paraelectric phase, similarly as the Edwards-Anderson order parameter q in the presence of random fields. At T_c there is a discontinuous increase in M_2 which reflects the increase in q due to the discontinuous increase in p as well as the splitting in the ^{87}Rb spectrum.

In view of the first-order nature of the PE-AFE phase transition the experimental T dependence of $(\bar{\nu}-\nu_0)/\nu_1$ and M_2 cannot be quantitatively compared with the theoretical T dependences of p and q (Fig. 1) as described

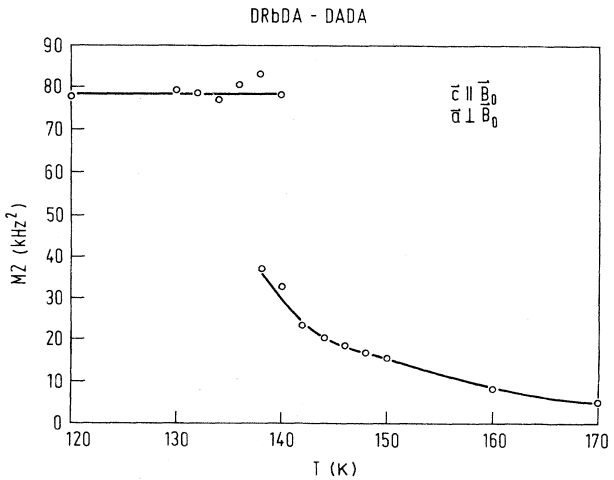

FIG. 6. Second moment of the ^{87}Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$ NMR line vs temperature.

by Eqs. (5a) and (5b). These equations are appropriate for the case of a transition of second order and not for a transition of first order. The first-order nature of the transition in $Rb_{1-x}(ND_4)_xD_2AsO_4$ is the result of four spin interaction terms[7] which are not contained in the random bond–random field Ising model Hamiltonian[3] leading to expressions (5a) and (5b).

In the low-temperature phase below T_c up to four ^{87}Rb lines can be resolved at some orientations. The maxima of these lines give rise to a rotation pattern from which four different ^{87}Rb EFG tensors can be calculated. The EFG tensors have the same eigenvalues but different orientations with respect to the crystal axes. In all four tensors the largest principal axis Z is no longer parallel to the crystal $\mathbf{z}\|\mathbf{c}$ axis. The average tilt angle of the principal Z axis with respect to the $\mathbf{c}$ axis of the crystal is about 20°. The distribution of the tilt angles around the mean value—which can be approximated by a Gaussian with a root-mean-square deviation of $\approx 5°$—is, as in $Rb_{1-x}(ND_4)_xD_2PO_4$,[8] the main source of the glassy type inhomogeneous broadening of the ^{87}Rb lines. The general orientation of the four EFG tensors with respect to the crystal axes and the fact that the asymmetry parameter $\eta=(V_{XX}-V_{YY})/V_{ZZ}$ is now different from zero ($\eta\simeq 0.2$) shows that the site symmetry $\bar{4}$ and the two glide mirror planes d_a and d_b of the paraelectric phase are lost at the Rb sites. This is compatible with the $P2_12_12_1$ space group of the antiferroelectric phase of pure $ND_4D_2AsO_4$.[7]

It should be mentioned that whereas the four low-temperature EFG tensors clearly reflect the local symmetry of the antiferroelectric phase the relation between them is still given by the symmetry operation $\bar{4}2m$, i.e., by the full symmetry of the paraelectric phase. This higher apparent symmetry of the rotation pattern thus reflects the existence of 90° domains which are related by the symmetry elements lost at T_c.

The temperature dependence of the ^{87}Rb $\frac{1}{2}\rightarrow-\frac{1}{2}$ spin-lattice relaxation time T_1 is shown in Fig. 7 for $\mathbf{c}\|\mathbf{B}_0$, $\mathbf{a}\perp\mathbf{B}_0$. On cooling down from room temperature T_1 first increases, reaches a maximum of about 30 ms at 260 K and then decreases down to about 2 ms in the 140–130 K range. At T_c, T_1 discontinuously increases by a factor of ≈ 15 and then continues to increase gradually with decreasing temperature.

It should be stressed that in the range where the paraelectric and ferroelectric lines coexist the T_1 of the paraelectric line is short and the T_1 of the antiferroelectric line is long. The shape of the T_1 versus $10^3/T$ plot is again similar to the one observed in $Rb_{0.22}(ND_4)_{0.78}D_2PO_4$,[8] but very different from the one observed in the deuteron glass $Rb_{0.5}(ND_4)_{0.5}D_2PO_4$.[6] The absence of a broad asymmetric minimum in the T_1 versus $10^3/T$ plot, in particular, proves that we do not deal here with a glassy freeze out of the motion of the deuterons between the two potential minima in the O—D · · · O bond but rather with a condensing antiferroelectric soft mode as in $ND_4D_2PO_4$.[7]

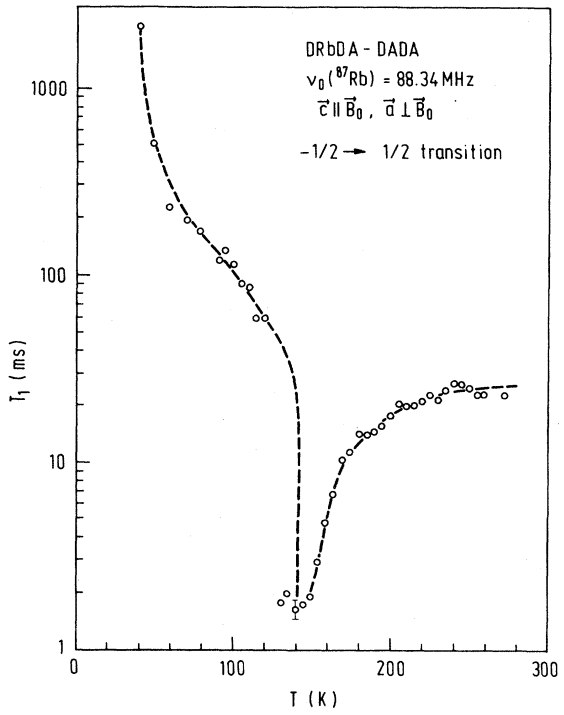

FIG. 7. Temperature dependence of the ^{87}Rb $\frac{1}{2}\rightarrow-\frac{1}{2}$ spin-lattice relaxation time T_1 in the region T_c.

The temperature dependence of the ^{87}Rb T_1 around T_c can be explained by the same condensing soft-mode model as in other KD_2PO_4 and $ND_4D_2PO_4$ crystals.[7] We thus see that superimposed on the glassy order,[3] which produces the inhomogeneous broadening of the NMR lines, there is a dynamic disorder of the deuterons in the O—D · · · O bonds. The dynamic disorder is driven by the antiferroelectric soft mode which determines the Rb T_1 and freezes out at T_c. The freeze out of the soft mode results in long-range antiferroelectric ordering of the O—D · · · O deuterons and the formation of 90° domains as predicted by the Slater-Takagi model[7] of KH_2PO_4 and $NH_4H_2PO_4$ type crystals.

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