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Cross-Relaxation Determination of Short Quadrupolar Spin-Lattice Relaxation Rates in Solids: Proton-Iodine Cross Relaxation in Antiferroelectric $Ag_2H_3IO_6$ and $(NH_4)_2H_3IO_6$

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The application of rotating- and dipolar-frame proton-relaxation measurements for the determination of fast quadrupolar relaxation rates of nonresonant spins S, the signals of which are too weak to be measured by the conventional NMR technique, is discussed. Both the case where the proton-S cross-relaxation rate is fast as compared to the S-spin-lattice relaxation rate and the case where it is slow are treated. The method is applied to $Ag_2H_3IO_6$ and $(NH_4)_2H_3IO_6$. The T dependence of the ^{127}I quadrupolar spin-lattice relaxation rates is extracted from the T dependence of the proton dipolar- and rotating-frame spin-lattice relaxation times. The iodine-spin-lattice relaxation times are found to be very short and seem to be controlled by electric-field-gradient (EFG) fluctuations due to the motion of protons between the two equilibrium sites in the O-H—O bonds. Using the known values of the static ^{127}I EFG tensor, the O-H—O proton intrabond jump time τ was found to be of the order of 10^{-10} sec at room temperature, i.e., of the same order as in KH_2PO_4-type ferroelectrics.

I. INTRODUCTION

The determination of the spin-lattice relaxation rates of nuclei with large quadrupole moments which are strongly coupled to the lattice via fluctuating electric-field-gradient (EFG) tensors is often nearly impossible because the resonance lines are very wide and hard to detect. In such a case the best way is the double-resonance detection—that is, cross relaxation to another spin species which has a strong signal and is weakly coupled to the lattice.[1,2] Since crossovers in the laboratory frame[3-5] are limited to certain directions and magnitudes of the external field, cross relaxation in the dipolar or rotating frame is a much simpler and better method.

The sensitivity of this double-resonance way of measuring short quadrupolar spin-lattice relaxation times can be shown to exceed the sensitivity of the direct nuclear-quadrupole-resonance (NQR) or quadrupole-pertrubed NMR measurements by several orders of magnitude.

In order to throw additional light on the dynamics of the phase changes in $Ag_2H_3IO_6$ and $(NH_4)_2H_3IO_6$ we decided to study the temperature dependences of the ^{127}I-spin–lattice relaxation times in both of these solids by measuring the proton-iodine cross-relaxation rates in the proton rotating and dipolar frame. Whereas in the laboratory frame the coupling to the iodines represents an effective relaxation mechanism for the protons only at the crossover crystal orientations—where $\omega(H)=\omega(^{127}I)$—this is not the case in the rotating and dipolar frame. In view of the fact that the separations between proton energy levels in the rotating or dipolar frame are comparable to that of the iodine dipolar system, the proton-iodine cross relaxation is expected to be fast and iodine-spin–lattice relaxation may dominate the rotating- and dipolar-frame proton-spin–lattice processes at all crystal orientations.

It is well known[6] that $Ag_2H_3IO_6$ and $(NH_4)_2H_3IO_6$ become antiferroelectric below 227 and 254 °K, respectively. The high-temperature structures of the two crystals are isomorphous[6]—space group $R\bar{3}$ with one formula unit per unit cell—and consist of almost regular IO_6 octahedra each of which is linked to its six nearest neighbors by O-H—O hydrogen bonds. The length of the O-H—O bonds is about the same ($R_{O-O}=2.5$–2.6 Å) as in the KH_2PO_4 family.[7] The rise of the Curie points on deuteration[6] demonstrates the role of the hydrogen atoms in the transition. By analogy with KH_2PO_4 one thus assumes[6] that each proton has two equilibrium positions in the O-H—O bonds and that the phase change is connected with an ordering of hydrogens. The low-temperature structures are not known but the appearance of a different superstructure–in $(NH_4)_2H_3IO_6$ the unit-cell dimensions are doubled along the a axis whereas in $Ag_2H_3IO_6$ they are doubled both along the c and the a axes—seems to show that the hydrogen-ordering schemes are different in these two compounds.[6]

Early proton-magnetic-resonance studies[8] using the continuous-wave technique detected only marginal changes in the proton linewidth on going through T_C. This can be easily understood as the distance between the two minima in the O-H—O bonds is small as compared to the interprotonic distances.[6] Accordingly a more sensitive way to study the dynamics of the proton motion is to observe the effect of this motion on the electric-field-gradient (EFG) tensor at the iodine sites. However, all attempts to observe spin-resonance signals of ^{127}I ($I=\frac{5}{2}$) in $(NH_4)_2H_3IO_6$ directly were unsuccessful in view of the large ^{127}I linewidths. Only recently Gränicher and Kind[4,5] succeeded in determining the time average values of the EFG tensor at the iodine sites in $(NH_4)_2H_3IO_6$ both above and below T_C using the iodine-proton crossover relaxation technique in the laboratory frame. They found that the spin-lattice relaxation time T_1 of the protons is appreciably shortened at certain crystal orientations where the iodine spin system has the same resonance frequency as the proton Zeeman system. From the angular dependence of these cross-relaxation frequencies they determined the ^{127}I quadrupole coupling constant e^2qQ/h and asymmetry parameter ($e^2qQ/h = 25.4$ MHz, $\eta = 0$ at room temperature, while $e^2qQ/h = 93.2$ MHz, $\eta = 0$ for one-quarter of the sites and $e^2qQ/h = 123.4$ MHz, $\eta = 0.33$ for the rest of the sites in the antiferroelectric phase). The drop in the proton T_1 at the cross-relaxation orientations has however not yet been related to the quadrupolar relaxation rates of the iodine spins.

A study is underway[16] to determine the ^{127}I EFG tensor in $Ag_2H_3IO_6$ using the same technique as in $(NH_4)_2H_3IO_6$.

In the following we shall (i) relate the iodine EFG tensor fluctuations—which determine the iodine-spin–lattice relaxation rate—to the dynamics of the protons in O-H—O bonds, (ii) study the effect of the proton-iodine spin coupling on the proton rotating- and dipolar-frame spin-lattice relaxation time in the limits of (a) fast cross relaxation when the proton-iodine coupling is of the same order or stronger than the iodine-spin–lattice coupling, and (b) slow cross relaxation when the iodine spin can be treated as a part of the lattice, and (iii) apply the theory to the Ag and NH_4 periodates.

II. EXPERIMENTAL PROCEDURE

The measurements of the rotating- and dipolar-frame spin-lattice relaxation times $T_{1\rho}$ and T_{1D} of protons in both single-crystal and polycrystalline samples of $(NH_4)_2H_3IO_6$ and in $Ag_2H_3IO_6$ were made using a 37-MHz coherent-pulsed spectrometer developed in this laboratory. A $\frac{1}{2}\pi$ pulse was followed immediately by a "spin-locking" pulse of variable length which was phase shifted by 90° with respect to the $\frac{1}{2}\pi$ pulse. The free-induction-decay signal following a "spin-locking pulse" of length τ is proportional to $e^{-\tau/T_{1\rho}}$. The dipolar spin-lattice relaxation time was measured both by Jeener 90°–45°–45° method and by the adiabatic demagnetization in the rotating frame (ADRF) method. Here the height of the spin-locking pulse is first adiabatically decreased to zero so that the proton system is allowed to relax in the local field for a time τ after which the system is remagnetized and the free-induction decay measured as a function of time τ. The pulse programs used for T_{1D} and $T_{1\rho}$ measurements are shown schematically in Fig. 1.

The single crystals of $Ag_2H_3IO_6$ and $(NH_4)_2H_3IO_6$ were kindly provided by Professor Gränicher and were grown in his laboratory at the ETH, Zürich. The polycrystalline samples were prepared in this laboratory.

III. EXPERIMENTAL RESULTS

The temperature dependence of the laboratory ($H_0 = 8900$ G) and dipolar-frame proton-spin–lattice relaxation times T_{1H} and T_{1DH} in $Ag_2H_3IO_6$ powder is presented in Fig. 2. The results agree with the ones obtained on the single-crystal sample.

In $Ag_2H_3IO_6$, T_{1H} depends on the purity of the sample and was in our case of the order of 10 sec. Except for a possible very small anomaly near T_C in pure samples it does not depend on temperature. The dominant relaxation mechanism for T_{1H} thus seems to be spin diffusion to paramagnetic impurities. The dipolar-frame proton relaxation time T_{1DH}, on the other hand, is strongly temperature dependent and is moreover nearly three orders of magnitude shorter than T_{1H}. In the paraelectric phase T_{1DH} first increases with decreasing temperature, reaches a maximum, and then sharply decreases as T_C is approached from above. On going through T_C into the antiferroelectric phase T_{1DH} sharply increases. Proton-iodine cross relaxation seems to be the only possible explanation for this behavior around and below T_C, whereas at higher temperatures a slow interbond proton motion seems to dominate the relaxation rate. The activation energy for this interbond motion is of the order of $E_a \simeq 0.3$ eV. To get the cross-relaxation contribution to the proton-spin–lattice relaxation rate in

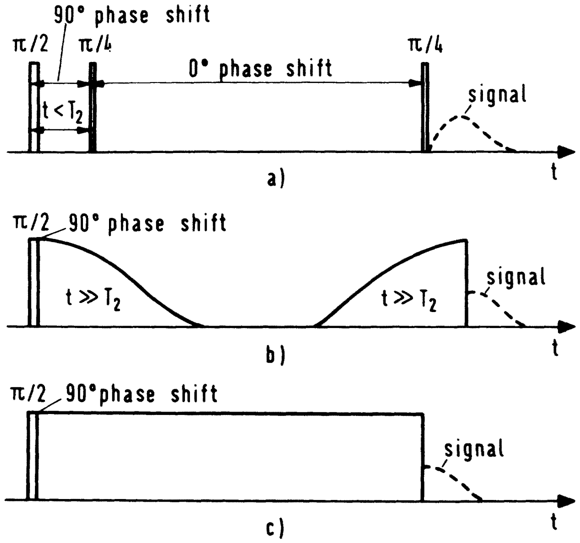

FIG. 1. Pulse programs used for measuring T_{1D} and $T_{1\rho}$: (a) Jeener-sequence (b) ADRF, and (c) rotating-frame method.

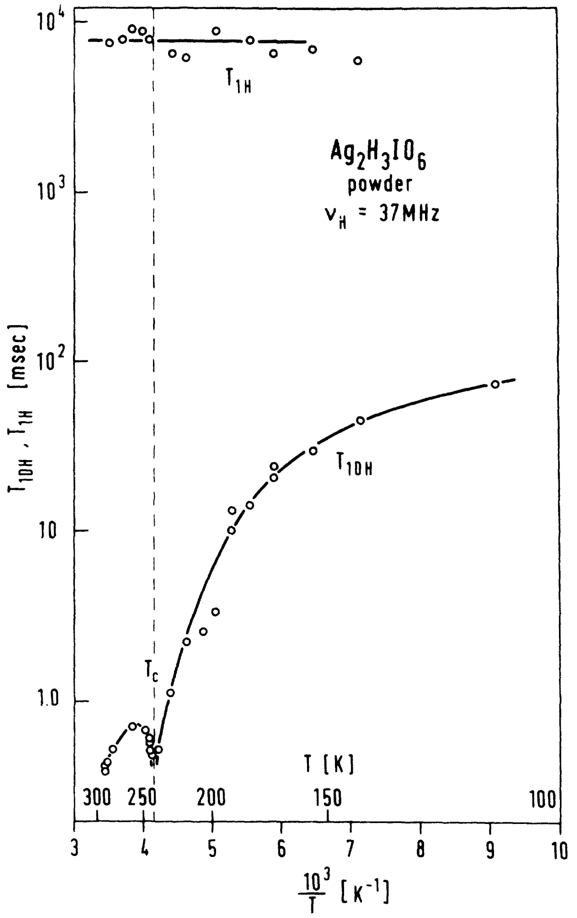

FIG. 2. Temperature dependence of the proton laboratory- and dipolar-frame spin-lattice relaxation time in $Ag_2H_3IO_6$.

the dipolar frame, the interbond contribution has to be subtracted.

The temperature dependence of T_{1H} and $T_{1\rho H}$ of $(NH_4)_2H_3IO_6$ is shown in Fig. 3. T_{1H} is here evidently determined by the modulation of the dipolar coupling due to hindered rotation of the NH_4 ions. The rotating-frame spin-lattice relaxation time $T_{1\rho H}$ shows a different temperature behavior than T_{1H}. Whereas T_{1H} *decreases* on approaching T_C from above, $T_{1\rho H}$ *increases*. On going to the antiferroelectric phase. $T_{1\rho H}$ very strongly decreases with decreasing temperature. The temperature behavior of $T_{1\rho H}$ in $(NH_4)_2H_3IO_6$ is thus just inverse to that found in $Ag_2H_3IO_6$.

Qualitatively, the same T dependence of $T_{1\rho H}$ is obtained in single crystal as in powdered samples of $(NH_4)_2H_3IO_6$. Whereas $T_{1\rho H}$ in $(NH_4)_2H_3IO_6$ is anisotropic, the angular dependence is relatively weak and no sharp dips—analogous to the ones seen in the laboratory frame T_{1H} at proton-iodine crossover orientations[4,5]—are observed.

There are two kinds of protons in $(NH_4)_2H_3IO_6$—the "ammonia" ones whose relaxation is mainly determined by hindered rotation of the NH_4 groups and the "hydrogen bond" ones whose relaxation is mainly determined by the proton-iodine coupling—the signals of which overlap. From the observed minimum in T_{1H} the T dependence of the rotational contributional to the relaxation rate of the ammonium protons in the rotating frame can be determined (Fig. 3). Using this result and assuming the existence of a common proton-spin temperature in the rotating frame, we can determine the proton-iodine cross-relaxation contribution $T^{-1}_{1\rho H}(I)$ (Fig. 4) to $T^{-1}_{1\rho H}$.

IV. THEORY

The two basic problems to solve in this study are:

(i) How to relate the temperature dependences of the protonic spin-lattice relaxation rate in the dipolar and rotating frame to the temperature dependence of the iodine-spin-lattice relaxation rate.

(ii) How to relate the temperature dependence of the iodine relaxation rate to the proton dynamics, which governs the dynamics of the antiferroelectric transition.

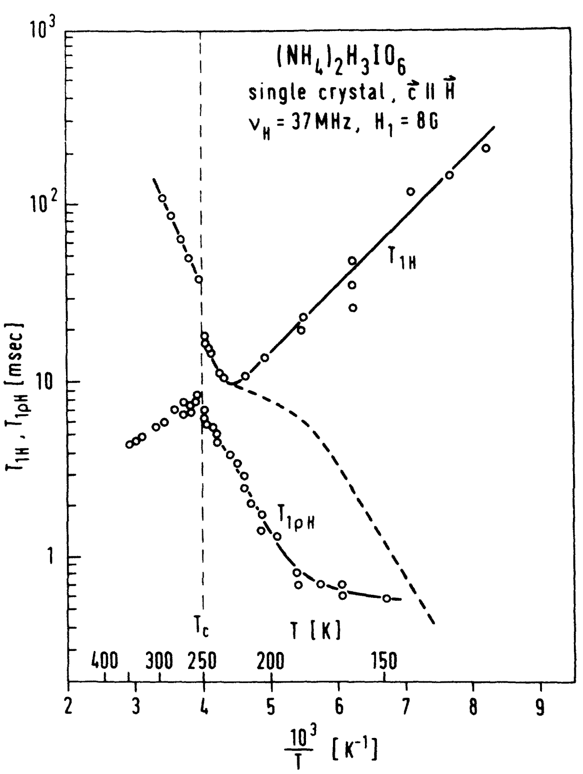

FIG. 3. Temperature dependences of the proton laboratory- and rotating-frame spin-lattice relaxation time in $(NH_4)_2H_3IO_6$. The dashed line represents the NH_4 group rotation contribution to $T_{1\rho H}$.

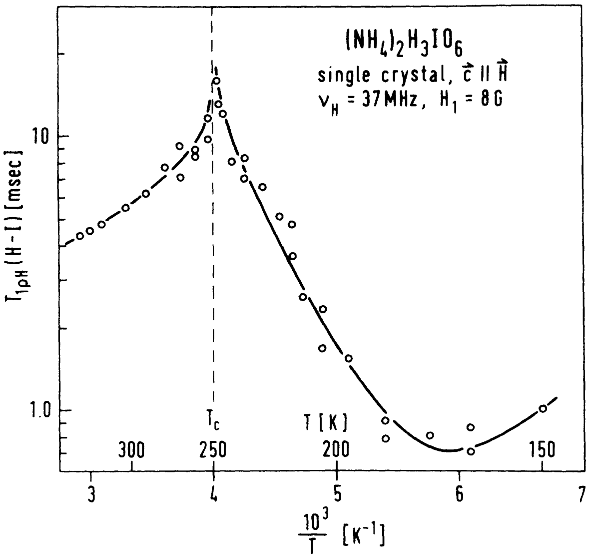

FIG. 4. Temperature dependence of the proton-iodine cross-relaxation contribution to the rotating-frame proton-spin–lattice relaxation rate in $(NH_4)_2H_3IO_6$.

These two problems can be easily solved on the basis of the following model: The fast motion of the protons between the two minima in the O-H—O bonds—which can be described as an overdamped "soft" quasispin wave or as critical-order-parameter fluctuations—modulates the electronic structure of the IO_6 octahedra. In view of the covalent nature of the iodine-oxygen bond, this modulation results in large and fast reorientations of the EFG tensor at the iodine sites, thus providing a strong relaxation mechanism for the iodine spins. Due to their fast relaxation rate, the ^{127}I spins are in good thermal contact with the lattice while the coupling to the proton system is significant only in the dipolar and rotating frame, or in the laboratory frame at certain orientations and magnitudes of the magnetic field at which proton and iodine levels cross. Thus in these three cases the proton-spin-lattice relaxation is mainly governed by the cross-relaxation to the iodine system.

A. EFG–Tensor Fluctuations at Iodine Sites

To solve the problem (ii) we suppose that the fluctuating EFG tensor $T_i(t)$ at the ith iodine site can be expanded in terms of quasispin variables $p_j(t)$ $(j=1_i\cdots 6_i)$ which describe the position of six protons surrounding a given IO_6 group in their H bonds[9]:

$$T_i(t)=T_{0i}+\sum_{j=1_i}^{6_i} p_j(t)\,V_i(i)+\sum_{l,m=1_i}^{6_i} p_l(t)\,p_m(t)\,U_i(l,m)+\cdots. \tag{4.1}$$

Since the fluctuations in $p_i(t)$ are generally much faster than the ^{127}I nuclear Larmor frequencies, the ^{127}I spectra are determined by the time-averaged EFG tensor $\langle T_i(t)\rangle$.

Replacing the time average by an ensemble average and using the molecular-field approximation for the sublattice polarization

$$\langle p_l(t)\rangle_{\mathrm{av}}=\langle p_j(t)\rangle_{\mathrm{av}}=p, \tag{4.2}$$

we get

$$\langle T_i(t)\rangle_{\mathrm{av}}=T_{0i}+p\,V_i+p^2U_i$$

$$+\sum_{l,m} U_i(l,m)\,\langle\Delta p_l\,\Delta p_m\rangle_{\mathrm{av}}+\cdots, \tag{4.3}$$

where

$$V_i=\sum_{j=1_i}^{6_i} V_i(j)\,, \tag{4.4a}$$

$$U_i=\sum_{l,m=1_i}^{6_i} U_i(l,m), \tag{4.4b}$$

and

$$\Delta p_l=p_l-p. \tag{4.4c}$$

Above T_C, the sublattice polarization is zero, $p=0$, so that the temperature dependence of $\langle T_i(t)\rangle_{\mathrm{av}}$ is determined by the fluctuation term $\Sigma_{l,m}U_i(l,m)$ $\langle\Delta p_l\,\Delta p_m\rangle_{\mathrm{av}}$. Below T_C, on the other hand, the term linear in p, V_ip, is expected to dominate the temperature dependence of the ^{127}I NQR frequencies.

The ^{127}I-spin–lattice relaxation, on the other hand, is determined by the fluctuating part of the EFG tensor

$$\Delta T_i(t)=T_i(t)-\langle T_i(t)\rangle_{\mathrm{av}}\approx\sum_{j=1_i}^{6_i} V_i(j)\,\Delta p_j(t). \tag{4.5}$$

The autocorrelation function of its component $\Delta T_{\alpha\beta i}(t)$ is

$$\langle\Delta T_{\alpha\beta i}(0)\,\Delta T_{\alpha\beta i}(t)\rangle_{\mathrm{av}}$$

$$=\sum_{k,j=1_i}^{6_i} V_{\alpha\beta i}(j)\,V_{\alpha\beta i}(k)\,\langle\Delta p_k(0)\,\Delta p_j(t)\rangle_{\mathrm{av}}. \tag{4.6}$$

Introducing $\Delta p_{\vec{q}}(t)$—the Fourier transform of the $\Delta p_j(t)$—and taking the RPA yields

$$\langle\Delta T_{\alpha\beta i}(0)\,\Delta T_{\alpha\beta i}(t)\rangle_{\mathrm{av}}=\frac{1}{N_H}$$

$$\times\sum_{\vec{q}}\left|V_{\alpha\beta i}(\vec{q})\right|^2\langle\Delta \mathrm{p}_{\vec{q}}(0)\,\Delta p_{-\vec{q}}(t)\rangle_{\mathrm{av}}\,, \tag{4.7}$$

where N_H is the number of protons in the sample and

$$V_{\alpha\beta i}(\vec{q})=\sum_{j=1_i}^{6_i} e^{i\vec{q}\cdot(\vec{r}_j-\vec{r}_i)}\,V_{\alpha\beta i}(j). \tag{4.8}$$

The iodine relaxation rates will be later expressed as linear combinations of the following spectral densities:

$$J_i^{(\alpha\beta)}(\omega)=\frac{1}{N_H}\sum_{\vec{q}}|V_{\alpha\beta i}(\vec{q})|^2 j_{\vec{q}}(\omega), \tag{4.9}$$

with

$$j_{\vec{q}}(\omega)=\int_{-\infty}^{\infty} e^{i\omega t}\langle \Delta p_{\vec{q}}(0)\,\Delta p_{-\vec{q}}(t)\rangle_{\text{av}}\,dt, \tag{4.10}$$

whose form depends on the model of the proton dynamics. In our case we shall use the Ising model[9] which gives in the RPA approximation

$$j_{\vec{q}}(\omega)=\frac{(1-p^2)T}{T-T_C(\vec{q})(1-p^2)}\;\frac{2\tau_{\vec{q}}}{1+(\omega\tau_q)^2}, \tag{4.11}$$

with

$$\tau_{\vec{q}}=\tau\frac{T}{T-T_C(\vec{q})(1-p^2)}, \tag{4.12}$$

where τ is the proton intrabond jump time and $T_C(\vec{q})$ depends on the proton—proton interactions.[9] As $\omega\tau$ will be always much less than 1 all spectral densities can be taken at zero frequency.

In the above treatment we assume the existence of two sublattices, where all hydrogen bonds are ordered below T_C and disordered above T_C. This model can be easily extended to the case of more than two sublattices.

B. Proton-Spin-Lattice Relaxation in the Dipolar and Rotating Frames

The Hamiltonian of the proton-iodine system and the lattice is

$$\mathcal{H}=\mathcal{H}_{ZH}+\mathcal{H}_{DH}+\mathcal{H}_{ZI}+\mathcal{H}_{DI}+\mathcal{H}_{DHI}+\mathcal{H}_{QI}+\mathcal{H}_{\text{rf}}+\mathcal{H}_L, \tag{4.13}$$

where $\mathcal{H}_{ZH}$ is the H Zeeman, $\mathcal{H}_{DH}$ is the H dipolar, $\mathcal{H}_{ZI}$ is the I Zeeman, $\mathcal{H}_{DI}$ is the I dipolar, $\mathcal{H}_{DIH}$ is the HI dipolar, $\mathcal{H}_{QI}$ is the I quadrupolar, $\mathcal{H}_{\text{rf}}$ is the rf, and $\mathcal{H}_L$ is the lattice-part of the Hamiltonian. In the frame rotating with the proton resonance frequency we have in a very good approximation[10a] an effective Hamiltonian (omitting weakly coupled and rotating parts)

$$\mathcal{H}_{\text{eff}}=\mathcal{H}'_{DH}+\mathcal{H}_{XH}+\mathcal{H}'_{DI}+\mathcal{H}'_{DHI}+\Delta\mathcal{H}_{QI}(t)+\mathcal{H}_L, \tag{4.14}$$

where

$$\mathcal{H}_{XH}=\sum_i \hbar\omega_1 I_{xi}, \tag{4.15}$$

$$\mathcal{H}'_{DH}=\sum_{i<j} f_{ij}^{(0)}A_{ij}^{(0)}, \tag{4.16}$$

with

$$f_{ij}^{(0)}=\hbar\gamma_H^2(1-3\cos^2\theta_{Hij})/r_{Hij}^3 \tag{4.17}$$

and

$$A_{ij}^{(0)}=I_{zi}I_{zj}-\tfrac{1}{4}(I_{+i}I_{-j}+I_{-i}I_{+j}), \tag{4.18}$$

$$\mathcal{H}'_{DI}=\sum_{i<j} h_{ij}^{(0)}B_{ij}^{(0)}, \tag{4.19}$$

with

$$h_{ij}^{(0)}=\hbar\gamma_I^2(1-3\cos^2\theta_{Iij})/r_{Iij}^3 \tag{4.20}$$

and

$$B_{ij}^{(0)}=S_{zi}S_{zj}-\tfrac{1}{4}(S_{+i}S_{-j}+S_{-i}S_{+j}), \tag{4.21}$$

$$\mathcal{H}'_{DHI}=\sum_{i,j}F_{ij}^{(0)}C_{ij}^{(0)}, \tag{4.22}$$

with

$$F_{ij}^{(0)}=\hbar\gamma_H\gamma_I(1-3\cos^2\theta_{IHij})/r_{IHij}^3 \tag{4.23}$$

and

$$C_{ij}^{(0)}=S_{zi}I_{zj}-\tfrac{1}{4}(S_{+i}I_{-j}+S_{-i}I_{+j}), \tag{4.24}$$

and at last

$$\Delta\mathcal{H}_{QI}(t)=E\sum_i\sum_{\mu=0}^{\pm 2}\Delta T_i^{(\mu)}(t)D_i^{(-\mu)}e^{i\omega\mu t}, \tag{4.25}$$

with

$$\begin{gathered} D_i^{(0)}=3S_{zi}^2-S_i^2,\quad D_i^{(\pm 1)}=S_{zi}S_{\pm i}+S_{\pm i}S_{zi},\\ D_i^{(\pm 2)}=S_{\pm i}^2, \end{gathered} \tag{4.26}$$

and

$$\begin{gathered} \Delta T_i^{(0)}(t)=\Delta T_{zzi}(t),\quad \Delta T_i^{(\pm 1)}(t)=\Delta T_{xzi}(t)\pm\Delta T_{yzi}(t),\\ \Delta T_i^{(\pm 2)}(t)=\tfrac{1}{2}[\Delta T_{xxi}(t)-\Delta T_{yyi}(t)]\pm i\Delta T_{xyi}(t), \end{gathered} \tag{4.27}$$

where $\Delta T_i(t)$ is the fluctuating part of the EFG tensor at iodine site [expression (4.5)] and

$$E=e^2Q/4S(2S-1). \tag{4.28}$$

In all these expressions conventional symbols are used.

From the structure of the Hamiltonian one can see that there are three commuting parts

$$\mathcal{H}'_H=\mathcal{H}_{XH}+\mathcal{H}'_{DH}, \tag{4.29a}$$

$$\mathcal{H}_I=\mathcal{H}'_{DI}, \tag{4.29b}$$

and

$$\mathcal{H}_L, \tag{4.29c}$$

which are in pairs coupled by the interaction

$$\mathcal{V}(t)=\mathcal{H}'_{DHI}+\Delta\mathcal{H}_{QI}(t). \tag{4.30}$$

To solve the problem (i) we will study the energy transfer between three energy reservoirs corresponding to $\mathcal{H}_H$, $\mathcal{H}_I$, and $\mathcal{H}_L$ caused by the coupling $\mathcal{V}(t)$. To simplify the treatment we will discuss only two limiting cases: (a) fast cross relaxation—the coupling of the iodine spin system to the proton spin system is of the same order or stronger than that to the lattice, and (b) slow cross relaxation—the iodine-lattice coupling is much stronger than the iodine-proton one (Table I).

TABLE I. Various limiting cases of proton-iodine cross relaxation in the dipolar or rotating frame treated in this paper. Here $\omega_1 = \gamma H_1$ is a measure of the strength of the rf field, ω_D measures the strength of the dipolar field, and W_{IH} stands for the iodine proton cross-relaxation rate. T_{1DI} is the iodine-spin–lattice relaxation time.

	$W_{1H}T_{1DI} \gtrsim 1$	$W_{1H}T_{1DI} \ll 1$
$\omega_1 \lesssim \omega_D$	fast cross-relaxation strong mixing	slow cross-relaxation strong mixing
$\omega_1 \gg \omega_D$	fast cross-relaxation weak mixing	slow cross-relaxation weak mixing

1. Fast-Cross-Relaxation Limit

In this case the proton-iodine coupling is of the same order or stronger than the iodine coupling to the lattice. Consequently, we must treat each energy reservoir $\mathcal{H}_H$, $\mathcal{H}_I$, and $\mathcal{H}_L$ separately. While the lattice and proton (for $\langle \mathcal{H}_{XH}\rangle \lesseqgtr \langle \mathcal{H}'_{DH}\rangle$) energy reservoirs can be well described by temperatures, that is not true for the iodine energy reservoir. Its elements are more strongly coupled to the lattice and to the protons than among themselves. This fact prevents us from treating the whole relaxation process with the help of the Provotorov[11] spin-temperature formalism.

Instead of using the spin-temperature description, the energy reservoirs must be now characterized by the energy which they contain, i.e., by the expectation values of $\mathcal{H}_i$. The time dependence of these quantities will be obtained from the corresponding kinetic equations. As the operators $\mathcal{H}_i$ are orthogonal in the following sense:

$$\operatorname{Tr}\{\mathcal{H}_i\mathcal{H}_j\} = 0 \quad \text{for } i \neq j, \tag{4.31}$$

the formalism developed by Shimizu[12] can be applied to obtain the rate equations for our system (see Appendix A). Assuming that $\langle \mathcal{H}_L\rangle \gg \langle \mathcal{H}_i\rangle$ $(i = I, H)$ and using

$$[\mathcal{H}_i, \mathcal{H}_j] = 0, \tag{4.32}$$

we get

$$\frac{d}{dt}\langle \mathcal{H}_i(t)\rangle = -\sum_{j=I,H} R_{ij}[\langle \mathcal{H}_j(t)\rangle - \langle \mathcal{H}_j(\infty)\rangle], \tag{4.33}$$

where

$$\langle \mathcal{H}_i(t)\rangle = \operatorname{Tr}[\rho(t)\mathcal{H}_i], \tag{4.34}$$

$\rho(t)$ is the density matrix of the system and R_{ij} is given in (A7). Defining an inverse quasispin temperature as

$$\alpha_i(t) = \langle \mathcal{H}_i(t)\rangle / C_i, \tag{4.35}$$

where

$$C_i = \operatorname{Tr}(\mathcal{H}_i^2), \tag{4.36}$$

the system (4.33) reduces to

$$\frac{d}{dt}\alpha_H(t) = -W_{HI}[\alpha_H(t) - \alpha_I(t)], \tag{4.37a}$$

$$\frac{d}{dt}\alpha_I(t) = W_{IH}[\alpha_H(t) - \alpha_I(t)] - \frac{1}{T_{1DI}}[\alpha_I(t) - \alpha_L], \tag{4.37b}$$

where

$$W_{IH} = \frac{C_H}{C_I} W_{HI} = \frac{1}{\hbar^2 \operatorname{Tr}(\mathcal{H}_I^2)} \int_0^\infty \operatorname{Tr}([\mathcal{H}_I, \mathcal{H}'_{DHI}]$$

$$\times e^{i\mathcal{H}_0 t/\hbar}[\mathcal{H}'_{DHI}, \mathcal{H}_H] e^{-i\mathcal{H}_0 t/\hbar})\, dt \tag{4.38}$$

and

$$\frac{1}{T_{1DI}} = \frac{1}{\hbar^2 \operatorname{Tr}(\mathcal{H}_I^2)}$$

$$\times \int_0^\infty \langle \operatorname{Tr}\{[\mathcal{H}_I, \Delta\mathcal{H}_Q(0)][\Delta\mathcal{H}_Q(t), \mathcal{H}_I]\}\rangle_{\text{av}}\, dt, \tag{4.39}$$

with

$$\mathcal{H}_0 = \mathcal{H}_H + \mathcal{H}_I, \tag{4.40}$$

and where the symbol $\langle\ \rangle_{\text{av}}$ means the ensemble average.

The above system is formally analogous to the Provotorov equations though the meaning of the coefficients is different. Accordingly, the spin-temperature formalism is justified even in this case where the inverse temperature is just a formal quantity.

Let us first examine the relaxation in the dipolar frame $(\mathcal{H}_{XH} = 0)$. Solving the equations (4.37) with the assumption

$$C_I \ll C_H,$$

we find that the energy of the proton dipolar energy reservoir changes with the following characteristic rates:

$$(1 + T_{1DI}W_{1H})T_{1DI}^{-1}$$

and

$$\frac{C_I}{C_H}(W_{IH}^{-1} + T_{1DI})^{-1},$$

so that we have for the proton system two characteristic relaxation times. As the first relaxation rate is much faster, the relaxation process of the protons in the dipolar frame is in the present limit well described with the following single relaxation time

$$T_{1DH} = (W_{IH}^{-1} + T_{1DI})\frac{C_H}{C_I}. \tag{4.41}$$

Expression (4.38) for the cross-relaxation rate be evaluated only approximately, assuming a Gaussian line shape. As shown in Appendix A we get

$$W_{IH}=\frac{C_H}{C_I}W_{HI}=\left(\frac{3\pi}{2}\right)^{1/2}\frac{M_2^*(HI)}{[M_2(HH)]^{1/2}}\frac{C_H}{C_I}, \tag{4.42}$$

where

$$M_2^*(HI)=\frac{S(S+1)}{3\hbar^2 n_H M_2(HH)}\sum_{j=1}^{n_H}\sum_{i\neq j}\sum_{l}F_{li}^{(0)^2}f_{ij}^{(0)^2} \tag{4.43}$$

and

$$M_2(HH)=\frac{3I(I+1)}{4\hbar^2 n_H}\sum_{j=1}^{n_H}\sum_{i\neq j}f_{ij}^{(0)^2}, \tag{4.44}$$

where n_H is the number of the nonequivalent protons. The iodine-dipolar-frame spin–lattice relaxation time (4.39) can be, using (4.25), expressed as

$$\frac{1}{T_{1DI}}=\frac{E^2}{\hbar^2\,\mathrm{Tr}(\mathcal{H}_{DI}'^2)}\sum_i\sum_{\mu=0}\int_0^\infty e^{i\omega_\mu t}\times\langle\Delta T_i^{(\mu)}(0)\,\Delta T_i^{(-\mu)}(t)\rangle_{\mathrm{av}}\,\mathrm{Tr}([\mathcal{H}_{DI}',D_i^{(\mu)}]\times[D_i^{(-\mu)},\mathcal{H}_{DI}'])\,dt. \tag{4.45}$$

Evaluating the traces, (4.45) reduces to

$$\frac{1}{T_{1DI}}=\frac{3}{160}\frac{e^4Q^2}{S^2\hbar^2}\frac{2S+3}{2S-1}\times[J^{(0)}(0)+4J^{(1)}(\omega)+8J^{(2)}(2\omega)], \tag{4.46}$$

where

$$J^{(\mu)}(\omega_\mu)=\frac{1}{n_I}\sum_{i=1}^{n_I}\int_{-\infty}^{\infty}\langle\Delta T_i^{(\mu)}(0)\,\Delta T_i^{(-\mu)}(t)\rangle_{\mathrm{av}}e^{i\omega_\mu t}\,dt \tag{4.47}$$

and n_I is the number of the nonequivalent iodine sites.

In the rotating frame where ω_1 is not much bigger than ω_D the two-proton spin energy reservoirs have a common spin temperature (strong mixing case) and the relaxation time is approximately given (see Appendix A) by

$$T_{1\rho H}\cong T_{1DH}[1+3(\omega_1/\omega_D)^2], \tag{4.48}$$

where

$$\omega_D=[M_2(HH)]^{1/2}\ . \tag{4.49}$$

For higher ω_1, W_{IH} decreases as $\exp[-\frac{3}{2}(\omega_1/\omega_D)^2]$ and the condition for the validity of the fast cross-relaxation limit could be broken. The second difficulty for $\omega_1\gg\omega_D$ is that the two proton energy reservoirs corresponding to $\mathcal{H}_{DH}'$ and $\mathcal{H}_{XH}$ must be treated separately (weak mixing case). The whole derivation of the kinetic equations must be slightly changed as $\mathcal{H}_{DH}'$ and $\mathcal{H}_{XH}$ do not commute.

2. Slow Cross-Relaxation Limit

In this case the iodine coupling to the lattice is assumed to be much stronger than to the protons. The iodine spin reservoir is thus always in thermal equilibrium with the lattice and can be treated as a part of it [see Fig. 5(b)]. This means that the characteristic flipping time of the iodine spin fluctuations which modulate the *HI* coupling is just the iodine-spin–lattice relaxation time itself. The relaxation of the proton energy reservoir can be treated similarly to the relaxation due to the paramagnetic impurities.[13] The corresponding effective Hamiltonian in the rotating frame is

$$\mathcal{H}_{\mathrm{eff}}=\mathcal{H}_{XH}+\mathcal{H}_{DH}'+\mathcal{H}_{DHI}'[S(t)]\,. \tag{4.50}$$

In the rotating frame the proton system can be described by a single spin temperature only if its rotating-frame spin-lattice relaxation time is much longer than the "mixing time[10c]"

$$T_m\propto e^{(\omega_1/\omega_D)^2/2} \tag{4.51}$$

between rf and dipolar reservoirs. If this condition is not fulfilled there are two different spin temperatures corresponding to the proton dipolar and rf part of the Hamiltonian. So we must treat two different cases of (*a*) strong and (*b*) weak mixing.

a. Strong mixing. Following Goldman,[10a] the rotating-frame spin-lattice relaxation of the proton system is in the case of the exact resonance given by

$$\frac{1}{T_{1\rho H}}=\left(\frac{\mathrm{Tr}(\mathcal{H}_{XH}^2)}{T_{1XH}}+\frac{\mathrm{Tr}(\mathcal{H}_{DH}'^2)}{T_{1DH}}\right)\frac{1}{\mathrm{Tr}(\mathcal{H}_{XH}^2+\mathcal{H}_{DH}'^2)}, \tag{4.52}$$

with

$$\frac{1}{T_{1XH}}=\frac{1}{\hbar^2\,\mathrm{Tr}(\mathcal{H}_{XH}^2)}\times\int_0^\infty\langle\mathrm{Tr}\{[\mathcal{H}_{XH},\mathfrak{V}(0)][\mathfrak{V}^*(t),\mathcal{H}_{XH}]\}\rangle_{\mathrm{av}}\,dt \tag{4.53}$$

and

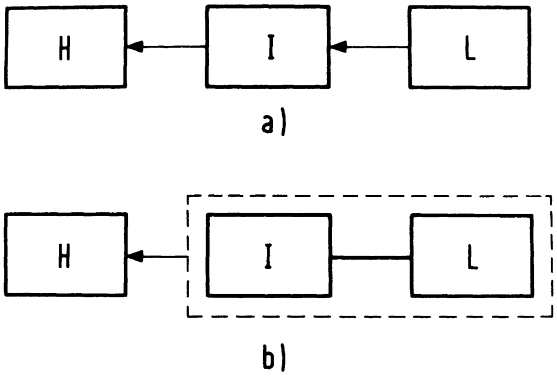

FIG. 5. Schematic representation of the proton, iodine, and lattice energy reservoirs and their connections in the periodates for (a) fast cross relaxation and (b) slow cross relaxation.

$$\frac{1}{T_{1DH}}=\frac{1}{\hbar^2\,\mathrm{Tr}(\mathcal{H}_{DH}'^{2})}\times\int_0^{\infty}\langle\mathrm{Tr}\{[\mathcal{H}_{DH}',\mathcal{V}(0)][\mathcal{V}^*(t),\mathcal{H}_{DH}']\}\rangle_{\mathrm{av}}\,dt, \tag{4.54}$$

where

$$\mathcal{V}(t)=\mathcal{H}_{DHI}'(S(t)) \tag{4.55}$$

and the asterisk means

$$\mathcal{V}(t)^*=\exp[i(\mathcal{H}_{XH}+\mathcal{H}_{DH}')t/\hbar]\mathcal{V}(t)\times\exp[-i(\mathcal{H}_{XH}+\mathcal{H}_{DH}')t/\hbar]. \tag{4.56}$$

In the case that the average quadrupole part $\langle\mathcal{H}_{QI}(t)\rangle_{\mathrm{av}}$ of the Hamiltonian of the S spins is comparable or greater than their Zeeman part $\mathcal{H}_{ZI}$ the axis of quantization of the S spins is no longer parallel to H_0. In the limit that $\langle\mathcal{H}_{QI}(t)\rangle_{\mathrm{av}}\gg\mathcal{H}_{ZI}$, the S spins are quantized along the largest principal axis of the S-site EFG tensor. In this new frame marked with a prime we have

$$S_z(t)=S_z'(t)\cos\theta+S_x'(t)\sin\theta, \tag{4.57a}$$

$$S_x(t)=-S_z'(t)\sin\theta+S_x'(t)\cos\theta, \tag{4.57b}$$

where θ is the angle between H_0 and the quantization axis. It should be mentioned that in the fast cross-relaxation limit this transformation is not necessary as the traces are invariant under the coordinate transformation.

The relaxation of the proton system is caused by the iodine–spin fluctuations which can be described by

$$\langle S_z'(0)S_z'(t)\rangle_{\mathrm{av}}=\tfrac{1}{3}S(S+1)g_{s_z}(t), \tag{4.58a}$$

$$\langle S_+'(0)S_-'(t)\rangle_{\mathrm{av}}=\tfrac{1}{3}S(S+1)g_{s_\pm}(t)e^{i(\omega_I-\omega_S)t}, \tag{4.58b}$$

where $g_{s_z}(t)$ and $g_{s\pm}(t)$ in general need not be exponential (see Appendix B). As $\omega_I-\omega_S\gg\omega_1$ the terms with S_+' or S_-' do not contribute to the relaxation rate in the rotating frame and will be omitted. Thus, $\mathcal{V}(t)$ is reduced to

$$\mathcal{V}(t)=\sum_{ij}F_{ij}^{(0)}(I_{zi}\cos\theta+\tfrac{1}{2}I_{xi}\sin\theta)S_{zj}'(t). \tag{4.59}$$

Using the fact that the transverse spin–spin relaxation time of the proton system is much longer than the characteristic flipping time of the iodines T_{1I} we may take

$$I_{zi}^*(t)=I_{zi}\cos\omega_1 t-I_{yi}\sin\omega_1 t, \tag{4.60a}$$

$$I_{xi}^*(t)=I_{xi}\,. \tag{4.60b}$$

Thus, expressions (4.53) and (4.54) can be written

$$1/T_{1XH}=\tfrac{1}{2}M_2(HI)\cos^2\theta\,K(\omega_1) \tag{4.61}$$

and

$$1/T_{1DH}=\tfrac{1}{3}\{\tfrac{1}{2}\sin^2\theta[\tfrac{5}{4}M_2^*(HI)+M_2^{**}(HI)]K(0)+\cos^2\theta[M_2^*(HI)-M_2^{**}(HI)]K(\omega_1)\}, \tag{4.62}$$

where according to Eq. (B12),

$$K(\omega_1)=\int_{-\infty}^{\infty}e^{i\omega_1 t}g_{s_z}(t)\,dt=\sum_{k=1}^{3}a_k\frac{2\tau_k}{1+(\omega_1\tau_k)^2}, \tag{4.63}$$

$$M_2(HI)=\frac{S(S+1)}{3\hbar^2 n_H}\sum_{i=1}^{n_H}\sum_j F_{ij}^{(0)2}, \tag{4.64}$$

and

$$M^{**}(HI)=\frac{S(S+1)}{3\hbar^2 n_H M_2(HH)}\sum_{i=1}^{n_H}\sum_{j\neq i}\sum_l f_{ij}^{(0)2}F_{il}^{(0)}F_{jl}^{(0)}. \tag{4.65}$$

b. Weak mixing. In this case the rf part $\mathcal{H}_{XH}$ and the dipolar part $\mathcal{H}_{DH}'$ of the Hamiltonian (4.50) are nearly uncoupled so that each system can be described by a separate spin temperature. The corresponding relaxation rates are again given by (4.53) and (4.54) where now in (4.53),

$$\mathcal{V}^*(t)=e^{i\mathcal{H}_{XH}t/\hbar}\,\mathcal{V}(t)\,e^{-i\mathcal{H}_{XH}t/\hbar} \tag{4.66}$$

and in (4.54),

$$\mathcal{V}^*(t)=\mathcal{V}(t). \tag{4.67}$$

So the rotating-frame spin-lattice rate in the weak-mixing limit is

$$\frac{1}{T_{1\rho H}}=M_2(HI)\cos^2\theta\sum_{k=1}^{3}\frac{a_k\tau_k}{1+(\omega_1\tau_k)^2}\,. \tag{4.68}$$

V. APPLICATION TO $Ag_2H_3IO_6$ AND $(NH_4)_2H_3IO_6$

In both $Ag_2H_3IO_6$ and $(NH_4)_2H_3IO_6$ the quadrupole coupling of iodines was in our case of the same order (or weaker) as the Zeeman coupling above T_C and much stronger than the Zeeman coupling below T_C. Above T_C the iodine spins are thus approximately quantized along the external magnetic field and below T_C along the largest principal axis of the EFG tensor.

In the case of $Ag_2H_3IO_6$ the fast cross-relaxation limit seems to be a good approximation for the dipolar and low-rf-field rotating-frame relaxation measurements below T_C, while above T_C the conditions for the validity of this limit are not quite fulfilled. The iodine-dipolar-frame relaxation time (Fig. 6) has been extracted from the measured T_{1DH} of the powdered sample (Fig. 2) on the basis of the approximate powder average of the expression (4.41)

$$T_{1DH}=(\overline{W}_{1H}^{-1}+T_{1DI})\frac{\overline{C}_H}{\overline{C}_I}, \tag{5.1}$$

where for sake of simplicity each element (as C_H, C_I, etc.) is averaged separately instead of taking the average of the expression as a whole. The bar here means the powder average.

A rough calculation gives for $\overline{C}_H/\overline{C}_I\cong 190$ and for

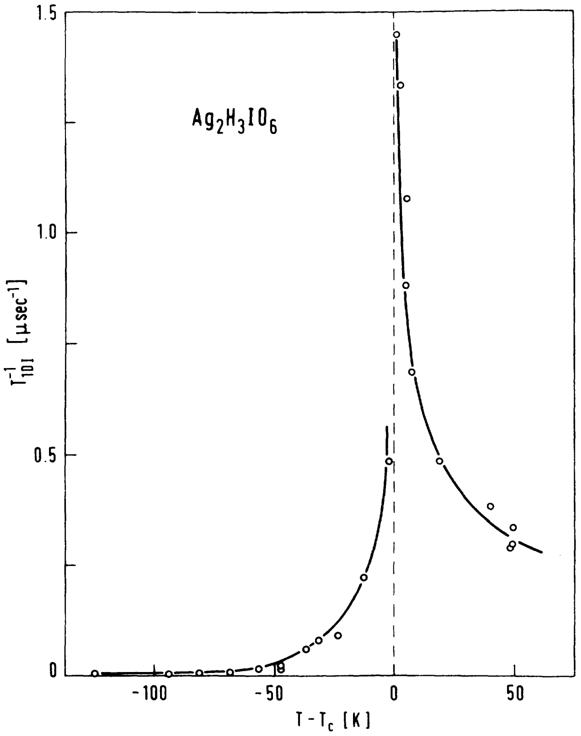

FIG. 6. Temperature dependence of the iodine dipolar-frame spin-lattice relaxation time in $Ag_2H_3IO_6$ as obtained from proton-relaxation measurements.

$\overline{W}_{IH}^{-1} \cong 0.4$ µsec. The T dependence of the ^{127}I-spin-lattice relaxation time in $Ag_2H_3IO_6$ (Fig. 6) as obtained from Eq. (5.1) shows a similar anomalous behavior on approaching T_C as the deuteron,[9] Cs,[14] and As[15] relaxation times measured in KH_2PO_4-type hydrogen-bonded ferroelectrics. The anomaly seems to be of a logarithmic type, $T_1 \propto \ln(T - T_C)$ + const as expected in an Ising model with anisotropic interactions.[14,15]

The increase in T_{1DH} by a factor of 100 on cooling through T_C demonstrates that all hydrogen bonds are ordered in the low-temperature phase of $Ag_2H_3IO_6$. If for instance half of the H bonds would be still disordered as this was suggested[5] for $(NH_4)_2H_3IO_6$ one would expect [see Eq. (4.46)] an increase in T_{1DH} by only a factor of 4 and not a factor of 100. It is our opinion that both the static and the dynamic ^{127}I resonance and relaxation results can be explained by a model, in which all hydrogen bonds are ordered below T_C but the different deformations of the IO_6 octahedra result in different ^{127}I EFG tensors below T_C.

To get a rough idea about the proton-intrabond dynamics we should know the proportionality factor relating T_{1DI} to the proton intrabond correlation time τ. As already mentioned, the static EFG tensors in the ordered and disordered phases of $(NH_4)_2H_3IO_6$ have been measured by Kind and Gränicher[4] and the tensors in $Ag_2H_3IO_6$ are being determined by the same group.[16] Though these results show different behavior of different nonequivalent IO_6 groups in the unit cell and in addition some important differences between silver and ammonium salts, we shall, for an order-of-magnitude estimate of the proton-intrabond correlation time τ, use the same EFG-tensor-fluctuation values in both crystals. We further assume that the magnitude of the EFG-tensor fluctuations are given by the difference in the static EFG tensor above and below T_C which allows us to substitute the expression (4.8) by an approximate one,

$$V_{\alpha\beta i}(\vec{q}) = \tfrac{1}{6} V_{\alpha\beta i} \sum_{j=1_i}^{6_i} e^{-i\vec{q}\cdot(\vec{r}_i-\vec{r}_j)}, \qquad (5.2)$$

where $2V_{\alpha\beta i}$ is the difference between the ordered- and disordered-phase EFG tensor at the iodine site. So according to (4.7), (4.10), (4.27), and the assumption $\omega\tau \ll 1$, the spectral densities (4.47) can be written

$$J^{(\mu)}(\omega) = J^{(\mu)}(0) = \frac{1}{n_I} \sum_{i=1}^{n_I} |V_i^{(\mu)}|^2 I(T)\, \tau(1-p^2), \qquad (5.3)$$

where

$$I(T) = \frac{1}{\tau(1-p^2)} \sum_{\vec{q}} \sum_{l,j=1_i}^{6_i} e^{i\vec{q}\cdot(\vec{r}_l-\vec{r}_j)} j_{\vec{q}}(0). \qquad (5.4)$$

Using the data of Ref. 4 to determine the tensors $V_i(\vec{q})$ according to (5.2) and inserting the components transformed to the magnetic field fixed frame in (5.3) we get, after performing the powder average,

$$T_{1DI}^{-1} \simeq 4.8\times 10^{15}(\mathrm{sec}^{-2})\, \tau I(T)\, (1-p^2) \qquad (5.5)$$

for the effective iodine quadrupolar-dipolar-frame spin–lattice relaxation rate as seen by the protons. From this expression a value of $\tau = 0.5\times 10^{-10}$ sec is obtained at $T = 290$ K in the paraelectric phase. This is of the same order of magnitude as the value of the deuteron- and proton-intrabond jump times in KH_2PO_4-type ferroelectrics.[9b,14,15,17,18]

The T dependence of T_{1DI} below T_C is mainly determined by the temperature variations of the sublattice polarization p. Assuming that $I(T)$ is nearly constant when p is near 1 we get from T_{1DI} (Fig. 6) the temperature dependence of the sublattice polarization presented in Fig. 8.

As, above T_C, T_{1DI} is quite short, the transition from the fast to the slow cross-relaxation limit occurs already when $\omega_1 \simeq \omega_D$. This is reflected in the sharp change of the slope in the $T_{1\rho H}$-vs-ω_1^2 plot [Fig. 7(b)]. At low fields we have for $T_{1\rho H}$ expression (4.48) which, at higher fields when the weak-mixing slow-cross-relaxation limit is valid, transforms to (4.68). As this last expression contains three characteristic relaxation times we approximate it for practical purposes with

$$T_{1\rho H}=\frac{1}{M_2(HI)}\;\frac{1+(\omega_1 T_{1I})^2}{a\,T_{1I}}\,, \tag{5.6}$$

which is characterized by only one effective iodine-spin–lattice relaxation time T_{1I} and a constant a (see Appendix B). This effective relaxation time is of the same order of magnitude as T_{1DI} and will be now explicitly related to it.

Using similar approximations as when deriving the expression for T_{1DI} we get the effective iodine relaxation time T_{1I} (Appendix B) as

$$T_{1I}^{-1}=0.94\times10^{15}(\mathrm{sec}^{-2})\,\tau I(T)\simeq 0.20\,T_{1DI}^{-1}, \quad T>T_C \tag{5.7}$$

$$T_{1I}^{-1}=0.85\times10^{15}(\mathrm{sec}^{-2})\,\tau I(T)\,(1-p^2)\simeq 0.18\,T^{-1}_{1DI}, \quad T<T_C. \tag{5.8}$$

T_{1I} obtained from the frequency dependence of $T_{1\rho H}$ at 250 K agrees with the one obtained from the T_{1DH} measurements.

As, below T_C, T_{1I} becomes much longer, the transition from the fast to the slow cross-relaxation limit occurs at higher rf fields (see Fig. 7(a)], but nevertheless the $T_{1\rho H}$-vs-ω_1^2 plot is well described by (4.48) only for low-rf fields because at higher ones ($\omega_1>\omega_D$) the rf energy reservoir separates from the dipolar one.

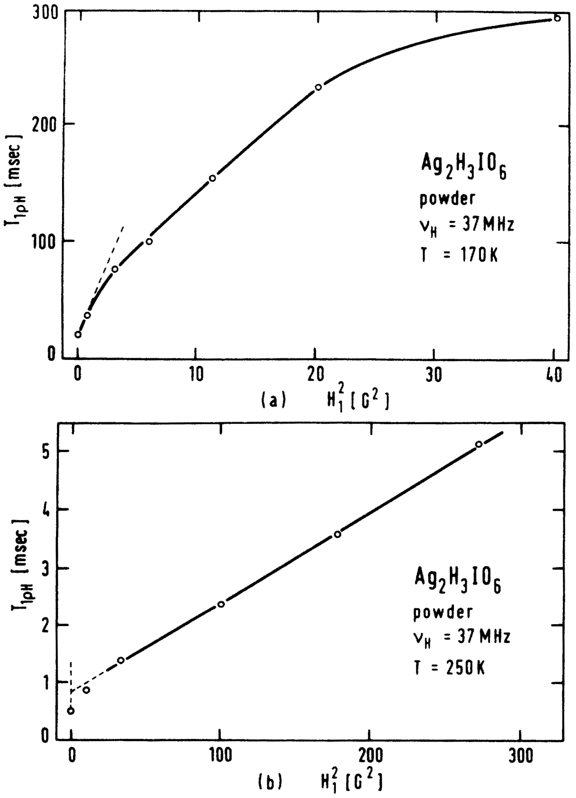

FIG. 7. Frequency dependence of the proton rotating-frame spin-lattice relaxation in $Ag_2H_2IO_6$ (a) at 170 and (b) 250 K. In (a) the dashed line indicates the theoretical predictions of the fast cross-relaxation limit, whereas in (b) the vertical dashed line indicates the predictions of the fast and the tilted of the slow-cross-relaxation limit.

In the case of the $(NH_4)_2H_3IO_6$ crystal, the proton relaxation rate is a combination of the relaxation rate due to the rotations of the NH_4 groups and the cross-relaxation rate to the iodines. The relaxation rate in the laboratory frame is completely determined by the first process (see Fig. 3) and can be written according to the spin-temperature approximation, as a superposition of the "ammonium" and "hydrogen-bond" proton-spin–lattice relaxation rates

$$\frac{1}{T_{1H}}=\frac{8}{11}\,\frac{1}{T_{1H}^{a}}+\frac{3}{11}\,\frac{1}{T_{1H}^{h}}\,. \tag{5.9}$$

As the distances between the "hydrogen-bond" protons are much larger than between the "ammonium" ones only the first part of (5.9) is important and can be described by a well-known formula

$$\frac{1}{T_{1H}^{a}}=\frac{9}{10}\,\frac{\gamma_n^4\hbar^2}{r^6}\left(\frac{\tau_r}{1+(\omega\tau_r)^2}+\frac{4\tau_r}{1+(2\omega\tau_r)^2}\right), \tag{5.10}$$

where ω is the proton Larmor frequency in the applied external magnetic field, $r\cong 1.58$ Å is the distance between protons in the ammonium group, and τ_r is the correlation time for the hindered rotations. The measured values can be well described in the high-temperature region by $\tau_r=\tau_0\exp(E_a/kT)$, with $E_a\simeq 0.17$ eV and $\tau_0\cong 2.6\times10^{-13}$ sec. At T_C there is a discontinuous change in τ_r by a factor of 2.

In the rotating frame the dominant process is the relaxation via iodines especially at higher temperatures. The relaxation rate is given by the following sum:

$$\frac{1}{T_{1\rho H}}=\frac{8}{11}\left(\frac{1}{T_{1\rho H}^{a}}\,(H-H)+\frac{1}{T_{1\rho H}^{a}}\,(I-H)\right)+\frac{3}{11}\left(\frac{1}{T_{1\rho H}^{h}}\,(H-H)+\frac{1}{T_{1\rho H}^{h}}\,(I-H)\right). \tag{5.11}$$

The "rotational" contribution of the "hydrogen-bond" protons due to NH_4-H coupling is negligible while that of the "ammonium" ones is well described by (see Fig. 3, dashed line)

$$\frac{1}{T_{1\rho H}^{h}}\,(H-H)=\frac{9}{10}\,\frac{\gamma_H^4\hbar^2}{r^6}\left(\frac{3}{2}\,\frac{\tau_r}{1+(2\omega_1\tau_r)^2}+\frac{5}{2}\,\frac{\tau_r}{1+(\omega\tau_r)^2}+\frac{\tau_r}{1+(2\omega\tau_r)^2}\right). \tag{5.12}$$

Subtracting the rotational contribution from $T_{1\rho H}^{-1}$, we obtain the cross-relaxation contribution $T_{1\rho H}^{-1}(I\text{-}H)$ (see Fig. 4) which can be in the slow-cross-relaxation limit for high ω_1 (weak mixing)

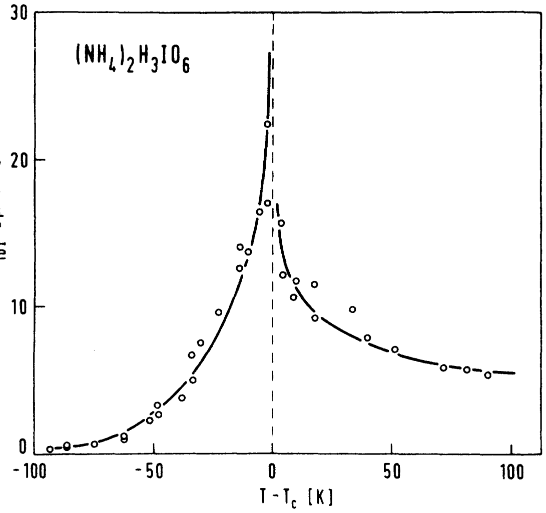

FIG. 8. Temperature dependence of the iodine dipolar-frame spin-lattice relaxation time in $(NH_4)_2H_3IO_6$ as obtained from proton-relaxation measurements.

written

$$\frac{1}{T_{1\rho H}}(I\text{-}H)=\left[\tfrac{8}{11}M_2(H^a\text{-}I)+\tfrac{3}{11}M_2(H^h\text{-}I)\right]\times\frac{2aT_{1I}}{1+(\omega_1 T_{1I})^2}\,,\qquad(5.14)$$

where T_{1I} is an effective iodine-spin–lattice relaxation time, $M_2(H^a\text{-}I)$ is the second moment of the "ammonium" proton-iodine dipolar interactions, and $M_2(H^h\text{-}I)$ of "hydrogen-bond" proton-iodine dipolar interactions. The T_{1I} obtained in this way is now—according to the relations (5.7) and (5.8)—transformed into T_{1DI} and shown in Fig. 8. Its temperature dependence is very similar to that of T_{1DI} of Ag periodate but its value is a factor of about 20 smaller. This explains why the proton relaxation process in the rotating frame of the NH_4 periodate can be described by the slow cross-relaxation limit, while that in the Ag periodate can be better described by the fast-cross-relaxation limit especially for low- or zero-rf fields.

The proton-intrabond jump time τ of $(NH_4)_2H_3IO_6$ is found to be a factor 20 shorter than for $Ag_2H_3IO_6$. On the other hand the sublattice polarization p has similar temperature dependences in both crystals (see Fig. 9).

It should be pointed out that due to the presence of the NH_4 contribution the iodine-spin–lattice relaxation rate in $(NH_4)_2H_3IO_6$ is obtained in a more indirect way than in $Ag_2H_3IO_6$ and the results are therefore much less reliable.

VI. CONCLUSION

The above results seem to show that the cross relaxation in the rotating and dipolar frames is a powerful method for the determination of short NQR relaxation times of nuclei which because of their low natural abundance or large NMR linewidth cannot be measured directly.

Though the iodine-spin–lattice relaxation results for $Ag_2H_3IO_6$ and $(NH_4)_2H_3IO_6$ are relatively crude, they seem to show that the dynamics of the protons in the O-H—O bonds in the periodates is not very different from the dynamics in KDP-type ferroelectrics.

APPENDIX A: EVALUATION OF KINETIC EQUATIONS AND PROTON-IODINE RELAXATION RATES

Let us take a Hamiltonian of the form

$$\mathcal{H}(t)=\sum_{i=1}^{n}\mathcal{H}_i+\mathcal{V}(t),\qquad(\mathrm{A1})$$

where the parts $\mathcal{H}_i$ are orthogonal in the sense that the trace of the product is zero [Eq. (4.31)] and are coupled in pairs by the interaction $\mathcal{V}(t)$ which need not be small. Our task is to get the time dependence of the expectation values $\langle\mathcal{H}_i(t)\rangle$ defined by (4.34). The set of n exact equations for such a Hamiltonian has been developed by Shimizu.[12] When the various $\mathcal{H}_i$ commute (which is true in our case for low-rf fields), the Shimizu equations reduce to

$$\frac{d}{dt}\langle\mathcal{H}_k(t)\rangle=-\frac{1}{\hbar^2}\int_0^t dt'\Big(\langle\mathrm{Tr}\{[\mathcal{H}_k,\mathcal{V}(t)]S(t',0)[\mathcal{V}(t'),(1-P)\rho(0)]S^*(t',0)\}\rangle_{\mathrm{av}}+\sum_{j=1}^{n}\langle\mathrm{Tr}\{[\mathcal{H}_k,\mathcal{V}(t)]S(t,t')[\mathcal{V}(t'),\mathcal{H}_j]S^*(t,t')\}\rangle_{\mathrm{av}}\frac{\langle\mathcal{H}_j(t)\rangle}{\mathrm{Tr}(\mathcal{H}_j^2)}\Big),\qquad(\mathrm{A2})$$

where $\rho(0)$ is the initial density matrix of the system,

$$P=\sum_{k=1}^{n}\frac{\mathcal{H}_k}{\mathrm{Tr}(\mathcal{H}_k^2)}\mathrm{Tr}(\mathcal{H}_k\cdots)\qquad(\mathrm{A3})$$

is the projector on the spcae of the operators $\mathcal{H}_k$, and

$$S(t,t')=\exp(i/\hbar)\int_{t'}^{t}(1-P)\mathcal{H}(\tau)\,d\tau,\qquad(\mathrm{A4})$$

$$S^*(t,t')\ \exp(i/\hbar)\int_{t'}^{t}\mathcal{H}(\tau)(1-P)\,d\tau.\qquad(\mathrm{A5})$$

The symbol $\langle\ \rangle_{\mathrm{av}}$ means an ensemble average. Assuming that the initial density matrix has a high-temperature canonical form,

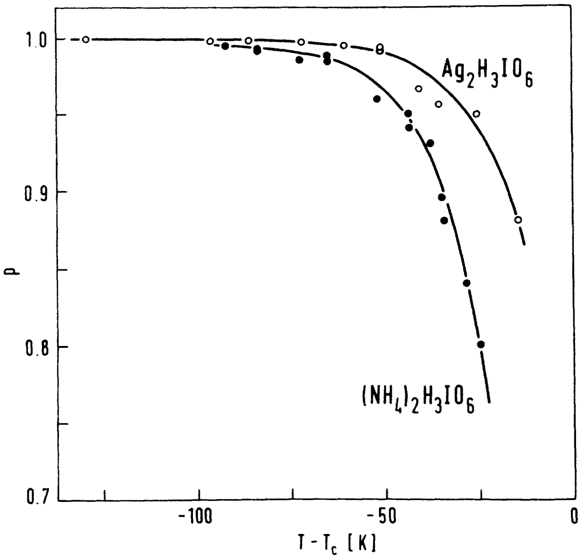

FIG. 9. Temperature dependence of the sublattice polarizations in $Ag_2H_3IO_6$ and $(NH_4)_2H_3IO_6$ as obtained from the temperature dependences of the iodine-spin-lattice relaxation rates.

$$\rho(0)=1-\sum_{i=1}^{n}\alpha_i(0)\mathcal{H}_i\,, \tag{A6}$$

the first term of (A2) vanishes. As we are interested only in the time development of $\langle\mathcal{H}_i(t)\rangle$ for times much larger than the characteristic correlation times of $S(t,t')$ and $\mathcal{V}(t)$, we extend the limit of integration to infinity and change the variable $t-t'$ to t', so that (A2) becomes

$$\frac{d}{dt}\langle\mathcal{H}_k(t)\rangle=-\frac{1}{\hbar^2}\sum_{j=1}^{n}\int_0^\infty dt'\,\langle\mathrm{Tr}\{[\mathcal{H}_k,\mathcal{V}(0)]S(t',0)$$

$$\times[\mathcal{V}(t'),\mathcal{H}_j]\,S^*(t',0)\}\rangle_{\mathrm{av}}\,\frac{\langle\mathcal{H}_j(t)\rangle}{\mathrm{Tr}(\mathcal{H}_j^2)}\,, \tag{A7}$$

or in matrix form

$$\frac{d}{dt}\langle\mathcal{H}_k(t)\rangle=-\sum_{j=1}^{n}R_{kj}\,\langle\mathcal{H}_j(t)\rangle\,. \tag{A8}$$

Since for $t\to\infty$ the set (A8) reduces to

$$0=-\sum_{j=1}^{n}R_{kj}\,\langle\mathcal{H}_j(\infty)\rangle, \tag{A9}$$

it can be rewritten

$$\frac{d}{dt}\langle\mathcal{H}_k(t)\rangle=-\sum_{j=1}^{n}R_{kj}\,[\langle\mathcal{H}_j(t)\rangle-\langle\mathcal{H}_j(\infty)\rangle]\,. \tag{A10}$$

Taking into account that the heat capacity of the lattice is much larger than the heat capacities of other terms, we have

$$\langle\mathcal{H}_L(t)\rangle\simeq\langle\mathcal{H}_L(\infty)\rangle=\mathrm{const} \tag{A11}$$

and the set of equations (A10) is reduced. Introducing formally a subsystem spin temperature with (4.35), the reduced set (4.33) becomes

$$\frac{d}{dt}\,a_k(t)=-W_{kj}\,[a_j(t)-a_j(\infty)]\,, \tag{A12}$$

where

$$W_{kj}=\frac{1}{\hbar^2\,\mathrm{Tr}\{\mathcal{H}_k^2\}}\int_0^\infty dt'\,\Big\langle\mathrm{Tr}\Big[\{[\mathcal{H}_k,\mathcal{V}(0)]\exp\frac{i}{\hbar}\,(1-P)\big(\mathcal{H}_0t'+\textstyle\int_0^{t'}\mathcal{V}(t'')dt''\big)$$

$$\times[\mathcal{V}(t'),\mathcal{H}_j]\exp\frac{i}{\hbar}\,\big(-\mathcal{H}_0t'-\textstyle\int_0^{t'}\mathcal{V}(t'')dt''\big)\,(1-P)\Big]\Big\rangle_{\mathrm{av}} \tag{A13}$$

and

$$\mathcal{H}_0=\sum_{i=1}^{n}\mathcal{H}_i\,. \tag{A14}$$

If we limit ourselves to the case

$$\mathcal{H}_0\gg\frac{1}{t}\int_0^t\mathcal{V}(t'')dt'',$$

expression (A13) reduces to

$$W_{kj}=\frac{1}{\hbar^2\,\mathrm{Tr}(\mathcal{H}_k^2)}\int_{0'}^\infty dt'\,\langle\mathrm{Tr}\{[\mathcal{H}_k,\mathcal{V}(0)]$$

$$\times e^{(i/\hbar)\mathcal{H}_0t'}[\mathcal{V}(t'),\,\mathcal{H}_j]\,e^{-(i/\hbar)\mathcal{H}_0t'}\}\rangle_{\mathrm{av}}\,. \tag{A15}$$

In our case where $\mathcal{V}(t)$ is given by (4.30) and $\mathcal{H}_0$ by (4.40), the matrix (A15) is characterized with cross-relaxation rates W_{HI} and W_{II}. The rate

$$W_{HH}=\frac{1}{\hbar^2\,\mathrm{Tr}(\mathcal{H}_{DH}'^2)}\int_0^\infty dt\,\mathrm{Tr}([\mathcal{H}_{DH}',\mathcal{H}_{DHI}']$$

$$\times e^{(i/\hbar)\mathcal{H}_0t}[\mathcal{H}_{DHI}',\mathcal{H}_{DH}']\,e^{-(i/\hbar)\mathcal{H}_0t}) \tag{A16}$$

becomes, using

$$e^{(i/\hbar)\mathcal{H}_0t}[\mathcal{H}_{DH}'+\mathcal{H}_{DHI}']e^{-(i/\hbar)\mathcal{H}_0t}$$

$$=\frac{d}{dt}\,(e^{(i/\hbar)\mathcal{H}_0t}\mathcal{H}_{DHI}'e^{(-i/\hbar)\mathcal{H}_0t}), \tag{A17}$$

equal to

$$W_{HH}=-W_{HI}\,, \tag{A18}$$

where W_{HI} is given by (4.38). W_{II} can similarly be written

$$W_{II}=\frac{C_H}{C_I}\,W_{HI}+\frac{1}{T_{1DI}}\,, \qquad \text{(A19)}$$

where C_H and C_I are given by (4. 36) and T_{1DI} by (4. 39). The correlation time of $\Delta\mathcal{H}_Q(t)$ has been assumed to be much shorter than the transverse relaxation time of the protons.

Assuming a Gaussian line shape

$$\mathrm{Tr}\,([\mathcal{H}'_{DH},\mathcal{H}'_{DHI}]\,e^{(i/\hbar)\mathcal{H}_0 t}[\mathcal{H}'_{DHI},\mathcal{H}_{DH}]\,e^{-(i/\hbar)\mathcal{H}_0 t})$$

$$\cong\mathrm{Tr}\,([\mathcal{H}'_{DH},\mathcal{H}'_{DHI}][\mathcal{H}'_{DHI},\mathcal{H}'_{DH}])$$

$$\times\exp\{-\tfrac{1}{2}[M_2(HH)+M_2(II)]\,t^2\}, \qquad \text{(A20)}$$

we get expression (4. 42).

When the rf field is not zero but still small enough that $\mathcal{H}'_{DH}$ and $\mathcal{H}_{XH}$ represent a common proton energy reservoir, W_{HH} is again given by (A16), but $\mathcal{H}_H$ is now

$$\mathcal{H}_H=\mathcal{H}'_{DH}+\mathcal{H}_{XH}\,. \qquad \text{(A21)}$$

After a similar approximation as before,

$$\mathrm{Tr}\,([\mathcal{H}_H,\mathcal{H}'_{DHI}]\,e^{(i/\hbar)\mathcal{H}_0 t}[\mathcal{H}'_{DHI},\mathcal{H}_H]\,e^{-(i/\hbar)\mathcal{H}_0 t})$$

$$=\mathrm{Tr}\,([\mathcal{H}_H,\mathcal{H}'_{DHI}][\mathcal{H}'_{DHI},\mathcal{H}_H])$$

$$\times\exp\{-\tfrac{1}{2}[M_2(HH)+M_2(II)[\,t^2\}\,e^{i\omega_1 t}, \qquad \text{(A22)}$$

we obtain

$$W_{HH}(\omega_1)\cong W_{HH}(0)\,\frac{1+u(\omega_1^2/\omega_D^2)}{1+3(\omega_1^2/\omega_D^2)}\,\exp\left(-\frac{3}{2}\,\frac{\omega_1^2}{\omega_D^2}\right), \qquad \text{(A23)}$$

where

$$u=\tfrac{5}{4}\,M_2(HI)/M_2^*(HI). \qquad \text{(A24)}$$

As u is in our case not far from $\frac{3}{2}$, expression (A24) reduces to

$$W_{HH}(\omega_1)\cong W_{HH}(0)\,[1+3\,(\omega_1^2/\omega_D^2)]^{-1}. \qquad \text{(A25)}$$

Using this relation and

$$C_H(\omega_1)=C_H(0)\,[1+3\,(\omega_1^2/\omega_D^2)], \qquad \text{(A26)}$$

we get for the proton-spin–lattice relaxation time in the rotating frame expression (4. 48).

APPENDIX B: EVALUATION OF CORRELATION FUNCTION $\langle S_z(0)S_z(t)\rangle_{\mathrm{av}}$ AND ITS SPECTRAL DENSITY FOR $S=\frac{5}{2}$

We wish to evaluate the spectral density of $\langle S_z(0)\,S_z(t)\rangle_{\mathrm{av}}$ for iodine ($S=\frac{5}{2}$) in the presence of Zeeman as well as quadrupole interactions. We neglect the dipolar interactions and divide the total Hamiltonian

$$\mathcal{H}=\mathcal{H}_Z+\mathcal{H}_Q(t)+\mathcal{H}_D \qquad \text{(B1)}$$

into a time-independent average part

$$\mathcal{H}_0=\mathcal{H}_Z+\langle\mathcal{H}_Q(t)\rangle_{\mathrm{av}}\,, \qquad \text{(B2)}$$

which determines the eigenstates of the system, and into a time-dependent fluctuating part

$$\Delta\mathcal{H}_{QI}(t)=\mathcal{H}_Q(t)-\langle\mathcal{H}_Q(t)\rangle_{\mathrm{av}}\,, \qquad \text{(B3)}$$

which is responsible for the transitions between the eigenstates $|\pm\frac{1}{2}\rangle$, $|\pm\frac{3}{2}\rangle$, and $|\pm\frac{5}{2}\rangle$ of $\mathcal{H}_0$. In view of the fact that in the presence of quadrupole interactions adjacent energy levels are nonequidistant, the system can not be described by a spin temperature and the approach of the magnetization towards equilibrium is nonexponential, so that a single spin-lattice relaxation time T_{1I} cannot be defined for the general case.

Introducing the departures $n-n^0$ of the populations of the various energy levels from their thermal equilibrium values n^0 and

$$n'_1=(n_{1/2}-n^0_{1/2})-(n_{-1/2}-n^0_{-1/2}), \qquad \text{(B4)}$$

$$n'_2=(n_{3/2}-n^0_{3/2})-(n_{-3/2}-n^0_{-3/2}), \qquad \text{(B5)}$$

$$n'_3=(n_{5/2}-n^0_{5/2})-(n_{-5/2}-n^0_{-5/2}), \qquad \text{(B6)}$$

as well as using the relation $W_{nm}=W_{mn}$ for the transition probabilities, we can write the kinetic equations as

$$\frac{dn'_3}{dt}=W_{5/2,1/2}n'_1+W_{5/2,3/2}n'_2-(W_{5/2,3/2}+W_{5/2,1/2})n'_3\,, \qquad \text{(B7)}$$

$$\frac{dn'_2}{dt}=(W_{3/2,1/2}-W_{3/2,-1/2})n'_1$$

$$-(W_{5/2,3/2}+W_{3/2,\,1/2}+W_{3/2,\,1/2})n'_2$$

$$+W_{5/2,1/2}n'_3\,. \qquad \text{(B8)}$$

$$\frac{dn'_1}{dt}=-(W_{5/2,1/2}+W_{3/2,1/2}+W_{3/2,-1/2}+2W_{1/2,-1/2})\,n'_1$$

$$+(W_{3/2,1/2}-W_{3/2,-1/2})n'_2+W_{5/2,\,1/2}n'_3\,. \qquad \text{(B9)}$$

We are looking for solutions of the form

$$n'_i=\alpha_i A\exp(-t/\tau_1)+\beta_i B\exp(-t/\tau_2)$$

$$+\gamma_i C\exp(-t/\tau_3), \qquad \text{(B10)}$$

where τ_1^{-1}, τ_2^{-1}, and τ_3^{-1} are eigenvalues of the secular determinant which corresponds to the above system [(B3), (B10)], α_i, β_i, γ_i ($i=1$, 2, 3) are known functions of the transition probabilities W_{mn}, and A, B, C are constants which have to be determined from the initial conditions.

Expressing $S_z(t)$ in terms of n'_i,

$$S_z(t)=\langle\tfrac{1}{2}|S_z|\tfrac{1}{2}\rangle n'_1(t)+\langle\tfrac{3}{2}|S_z|\tfrac{3}{2}\rangle n'_2(t)+\langle\tfrac{5}{2}|S_z|\tfrac{5}{2}\rangle n'_3(t), \qquad \text{(B11)}$$

and averaging over all possible initial states, we obtain

$$\langle S_z(0)\,S_z(t)\rangle_{\mathrm{av}}=\tfrac{1}{3}S(S+1)\sum_{i=1}^{3}a_i e^{-t/\tau_i}\,, \qquad \text{(B12)}$$

where a_1, a_2, and a_3 are determined from the six conditions: $\langle (n_i')^2\rangle = \frac{1}{3}$, $\langle n_i' n_j'\rangle = 0$.

The transition probabilities W_{mn} can be obtained by standard first-order perturbation theory as long as $W_{mn}\tau \ll 1$, where τ is the correlation time for the fluctuations in $\Delta\mathcal{H}_{QI}(t)$. We have

$$W_{mn} = \frac{1}{\hbar^2}\int_{-\infty}^{\infty} e^{i\omega_{mn}t}\,\langle\langle n|\Delta\mathcal{H}_{QI}(0)|m\rangle\langle m|\Delta\mathcal{H}_{QI}(t)|n\rangle\rangle_{\text{av}}\,dt, \tag{B13}$$

where $\Delta\mathcal{H}_{QI}(t)$ is given by (4.25) and

$$\hbar\omega_k = \langle m|\mathcal{H}_0|m\rangle - \langle m+k|\mathcal{H}_0|m+k\rangle. \tag{B14}$$

For the case

$$\langle\mathcal{H}_Q\rangle_{\text{av}} \gg \mathcal{H}_Z,$$

which seems to be realized both in $Ag_2H_3IO_6$ and in $(NH_4)_2H_3IO_6$ in the ordered phase, the evaluation of $\langle S_z(0)S_z(t)\rangle_{\text{av}}$ is particularly simple as spins are quantized along the Z principal axis of the EFG tensor. From the nature of the EFG-tensor fluctuations in $(NH_4)_2H_3IO_6$ in the first approximation, as the eigenframe of the EFG tensor for three-quarters of the iodine sites is only slightly rotated towards the crystal frame, it follows that the only nonvanishing transition probabilities are

$$W_{5/2,\,1/2} = 2\sqrt{10}\,(E^2/\hbar^2)\,J^{(2)}(\omega_2) \tag{B15}$$

and

$$W_{3/2,-1/2} = 6\sqrt{2}\,(E^2/\hbar^2)\,J^{(2)}(\omega_2), \tag{B16}$$

where $J^{(2)}(\omega)$ is given by (5.3).

For this case we obtain for the quantities occurring in expression (B12) the following values:

$$a_1 = 1.91,\quad a_2 = -0.91,\quad a_3 = 0; \tag{B17}$$

$$\begin{aligned}\tau_1^{-1} &= 7.2\,(E^2/\hbar^2)\,J^{(2)}(0),\\ \tau_2^{-1} &= 22.5\,(E^2/\hbar^2)\,J^{(2)}(0),\quad \tau_3^{-1} = 0,\end{aligned} \tag{B18}$$

so that to a very good approximation the spectral density of $\langle S_z(0)S_z(t)\rangle_{\text{av}}$ can be described by an effective iodine-spin-lattice relaxation time T_{1I}

$$\int_{-\infty}^{\infty} e^{i\omega t}\langle S_z(0)S_z(t)\rangle_{\text{av}}\,dt = \frac{S(S+1)}{3}\,a\,\frac{2T_{1I}}{1+(\omega T_{1I})^2}, \tag{B19}$$

where for $\omega T_{1I} \lesssim 1$,

$$a = 1.5, \tag{B20}$$

$$T_{1I} = 1.07\,\tau_1. \tag{B21}$$

For the case

$$\langle\mathcal{H}_Q\rangle_{\text{av}} \ll \mathcal{H}_Z,$$

which for both crystals seems to be a rough approximation to the true situation above T_C, the tensor $V(t)$ has to be transformed to the magnetic field fixed frame of reference as the spins are quantized along H_0. All transition probabilities thus depend on the angle between H_0 and the principal-axes system of the EFG tensor. For a polycrystalline sample one can nevertheless approximate the spectral density of the autocorrelation function of S_z by expression (B19) where $a \simeq 1.2$ and T_{1I} [given by (5.7)] have been determined using a computer.

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