# Deuteron NMR investigations of glass and phase transitions in $(KI)_{1-x}(ND_4I)_x$ mixed crystals

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Powdered potassium ammonium iodide mixed crystals with ammonium concentrations of 20% and 70% have been studied using deuteron NMR techniques. For the less doped sample the deuteron line starts to broaden and the spin-lattice relaxation time $T_1$ becomes nonexponential below about 20 K. These observations indicate the breakdown of ergodicity and the onset of orientational glass freezing. At the lowest temperatures $T_1$ reaches a plateau value. For the 70% sample a relatively abrupt onset of two-phase behavior at $T<35$ K is inferred from measurements of the spin-spin and spin-lattice relaxation times. These observations are taken to indicate an order-disorder transition to a crystalline phase which exhibits dynamically distinguishable lattice sites. [S0163-1829(98)05921-9]

## I. INTRODUCTION

Potassium ammonium iodide crystals $(KI)_{1-x}(NH_4I)_x$ form a series of solid solutions which show a complex $(x,T)$-phase diagram.[1] Ammonium-iodide-rich mixed crystals undergo a number of structural phase transitions for temperatures $T\leqslant 250$ K.[2,3] Upon sufficient dilution on the cation lattice, i.e., below the critical concentration $x_c\approx 0.45$, the cubic high-temperature crystal symmetry is preserved down to the lowest temperatures. For $x<x_c$ an orientational glass state is observed.[4] In this state the ammonium tetrahedra which constitute the orientational degrees of freedom are frozen into disordered configurations. This situation is similar to that in magnetic spin glasses and has stimulated numerous theoretical investigations.[5,6]

Surprisingly, the ammonium group exhibits a dipole moment when embedded in the cubic structure of $(KI)_{1-x}(NH_4I)_x$.[7] Therefore dielectric spectroscopy could be used to discern various glassy phases in this mixed system.[1,8] Below the percolation threshold at $x\approx 0.20$, indications for a single-particle slowdown have been reported. For $0.25<x<0.45$ collective freezing has been found to dominate,[7] which could be well described using a power law behavior as predicted by several models.[9,10] For concentrations closer to the critical one, the dielectric results suggested the existence of a short-range variant of a long-range-ordered structure, the so-called $\varepsilon$ phase,[3] which is stable slightly above $x_c$. Much less is known about the phase behavior of the deuterated mixed crystals; however, the absence of low-temperature phase transitions is documented for concentrations up to $x=0.5$.[11]

The focus of many previous studies has been on the temperature dependence of the order parameters above[3] and below the critical concentration. In the latter regime an Edwards-Anderson type of order parameter $q_{\mathrm{EA}}$ can be defined[12] and has been investigated using a number of experimental techniques. These include neutron,[13] x-ray,[14] and light scattering[15] as well as nuclear magnetic resonance (NMR) relaxometry and spectroscopy methods. The NMR experiments have been carried out using $^2$H,[16] $^{14}$N,[17] and $^{127}$I (Ref. 18) as probe nuclei. Generally, a relatively well-defined onset of the glass ordering has been reported, as, e.g., evidenced by the temperature dependence of the second moment [$\propto q_{\mathrm{EA}}$ (Ref. 19)] of the NMR line. Near the freezing temperature $T_f$ of ammonium iodide orientational glasses, the temperature dependence of the glass order parameter is not as abrupt as in most spin glasses.[20] Rather, in the vicinity of $T_f$ a smooth variation of $q_{\mathrm{EA}}$ is found, implying in particular that the order parameter is nonzero already above $T_f$. This latter effect is thought to arise from the coupling of the orientational degrees of freedom to the disorder on the center of mass lattice. This disorder obviously is due to local fluctuations of composition. These usually result in static lattice strains that are called random fields. It has been shown that these random fields can also have a pronounced effect on the decay of the longitudinal magnetization observed in NMR experiments.[17]

Previously, we have reported on the deuteron magnetization recovery in a powder sample of $(KI)_{0.5}(ND_4I)_{0.5}$.[16] The purpose of the present article is to present corresponding measurements on specimens with nominal compositions of $x=0.2$ and 0.7. In addition, we will show the NMR spectra of these samples, which have been recorded down to liquid helium temperatures.

## II. EXPERIMENTAL DETAILS

Most NMR experiments were carried out at a Larmor frequency of $2\pi\times 40.2$ MHz using a home-built spectrometer. The length of the $\pi/2$ pulse typically was 4 $\mu$s. Spectra were recorded using the solid echo technique using appropriate phase cycling. The pulse spacing typically was 20 $\mu$s. The processing of the spectra incorporated minor first- and second-order phase corrections. Temperature stability of $\pm 0.1$ K was achieved using a cryostat from Oxford Instruments operated in the static mode. Some preliminary experiments extending down to 3 K were recorded using a another spectrometer at a Larmor frequency of $\omega_L=2\pi\times 52.7$ MHz. The samples were grown from aqueous ($D_2O$) solution, finely powdered under a dry atmosphere, and sealed in glass ampoules. The compositions $x$ given in the following refer to the nominal ones.

 

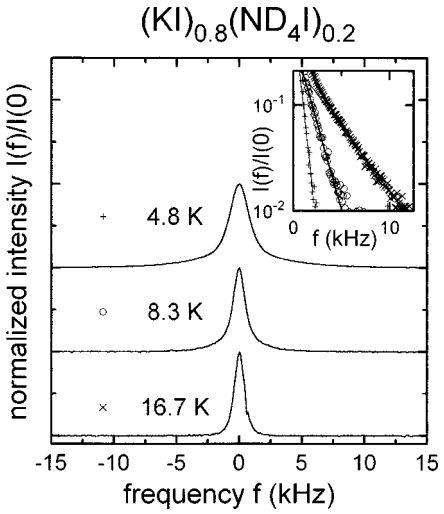


FIG. 1. Spectra of $(KI)_{0.8}(ND_4I)_{0.2}$ normalized to exhibit the same peak maximum. Note that the linewidth of the spectrum taken at 16.7 K is dominated by the field inhomogeneity of the superconducting magnet used for this study. For lower temperatures the NMR line broadens and develops a wing. The inset shows half of the symmetrized spectra in a semilogarithmic representation. From the straight lines in the inset, it is seen that the wings decay as $\log_{10}[I(f)/I(0)] = -f/\sigma$.

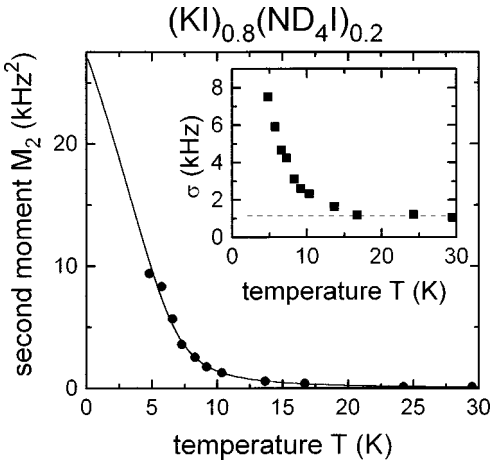


FIG. 2. Temperature dependence of the second moments of the deuteron spectra of $(KI)_{0.8}(ND_4I)_{0.2}$. The solid line is a fit using Eq. (3) and the parameters given in the text. The inset shows the parameter $\sigma$ characterizing the wings of the spectra. It exhibits a temperature dependence that is similar to that of $M_2$. The dashed line reflects the background contribution.

## III. RESULTS AND ANALYSES

### A. Orientational glass transition in $(KI)_{0.8}(ND_4I)_{0.2}$

In Fig. 1 we show the normalized deuteron resonance spectra $I(f)/I(f=0)$ of a powder sample with an ammonium concentration of $x=0.2$ for several temperatures. Here the frequency offset is denoted as $f=(\omega-\omega_L)/2\pi$. At higher temperatures (16.7 K and above) the line shape is dominated by the instrumental resolution, which is set to a width of about 1 kHz by the field inhomogeneity of our present magnet system. Upon cooling the lines develop a broad wing. At 4.8 K it shows a full width at half maximum of about 5 kHz. A close inspection of the data also reveals that at low temperature the central part of the lines exhibits some additional broadening. For all temperatures the shape of this central component can be well characterized by a Gaussian function. For the description of the wings, however, no simple line shape function was found to be fully satisfactory. In the inset of Fig. 1 we have replotted a part of the spectra using a logarithmic ordinate axis. It is seen that the wings of $I(f)$ exhibit an exponential law $\log_{10}[I(f)/I(f=0)] = -f/\sigma$, with a slope $\sigma^{-1}$ that decreases with temperature.

In Fig. 2 we have plotted the second moments $M_2$ of the deuteron lines, with the instrumental contribution already subtracted. It is seen that $M_2$ strongly increases as the temperature is lowered. The inset shows that the inverse slopes $\sigma$ exhibit a very similar trend. This is to be expected since the second moment is dominated by the wings of the spectral lines.

It should be noticed that even at the lowest temperatures the powder line shapes remain practically unstructured and their breadth is only a tiny fraction of the width $\delta/2\pi = \frac{3}{4}eqQ/h = 136.5$ kHz of the rigid deuteron spectrum of $ND_4I$.[21] This indicates that the motion of the ammonium groups is fast on the time scale set by $\delta^{-1}$. This is true even at 4.8 K and of course should also be borne out by measurements of the spin-lattice relaxation time $T_1$.

We have recorded the magnetization recovery $M(t)$ following an inversion pulse augmented by a solid echo sequence over several orders of magnitude in time $t$. Similar to our previous study carried out for $(KI)_{0.5}(ND_4I)_{0.5}$,[16] we find also for the sample with $x=0.2$ that $M(t)$ can nicely be fitted to a Kohlrausch function $M(t) \propto \exp[-(t/T_1)^{1-\nu}]$. Using the exponent $\nu$, the average spin-lattice relaxation time $\langle T_1 \rangle = T_1\Gamma[1/(1-\nu)]/(1-\nu)$ can be determined where $\Gamma$ denotes Euler's gamma function. In Fig. 3 we show the mean relaxation times thus obtained as a function of inverse temperature. Starting from high temperature, the relaxation times decrease in an almost thermally activated fashion with

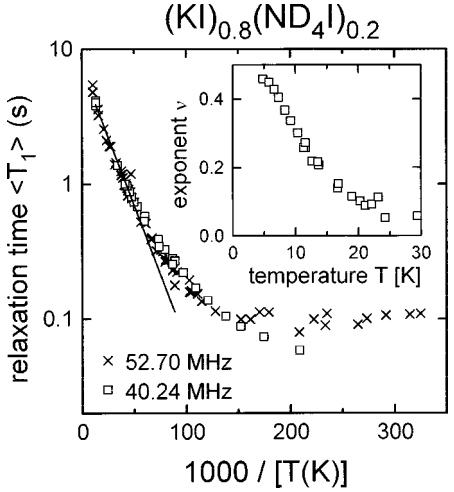


FIG. 3. Average spin-lattice relaxation times of $(KI)_{0.8}(ND_4I)_{0.2}$ plotted vs inverse temperature. The line corresponds to thermally activated behavior with an energy barrier of $E/k_B = 47$ K. The inset shows the temperature dependence of the stretching exponent $\nu$ for $T \leq 30$ K. At higher temperatures $\nu$ is zero within experimental error.

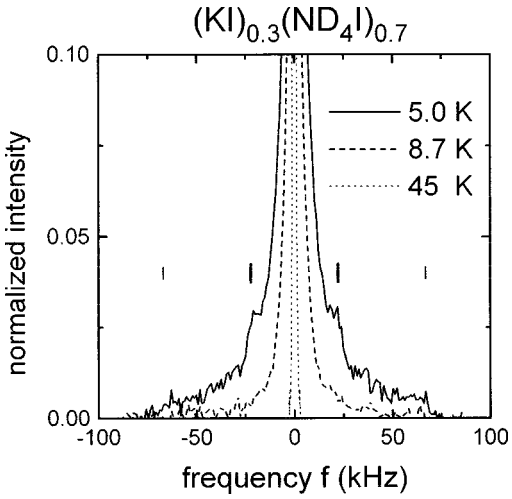


FIG. 4. Bottom part of representative deuteron spectra of $(KI)_{0.3}(ND_4I)_{0.7}$. At low temperatures there are indications for emerging edge singularities at the frequencies which are marked by bars. They correspond to frequency splittings of 44.6 kHz (thick bars) and 134 kHz (thin bars).

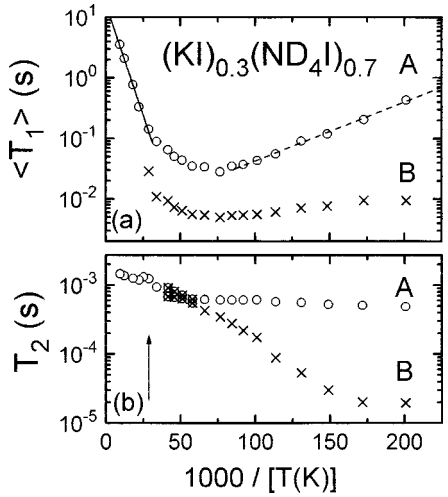


FIG. 5. Spin-lattice and spin-spin-relaxation times from bimodal fits to the longitudinal and transverse magnetization curves of $(KI)_{0.3}(ND_4I)_{0.7}$ are shown in parts (a) and (b), respectively; cf. Eqs. (1) and (2). Above $T_C = 35$ K, marked by the arrow, only component $A$ (circles) is present. Deuterons performing threefold jumps give rise to component $B$ (crosses). For several intermediate temperatures no unambiguous assignment is possible on the basis of the $T_2$ data. Note that due to the finite dead time of our spectrometer the relaxation times for component $B$ at $T < 6$ K are somewhat uncertain. The solid and dashed lines correspond to effective energy barriers of 170 and 22 K, respectively.

$\langle T_1 \rangle \propto \exp(-E/k_B T)$. The line in the figure corresponds to an energy barrier $E/k_B$ of 47 K. At low temperatures no minimum in the spin-lattice relaxation time could be observed. Rather, within experimental error, a plateau value is reached for the measurements carried out using a Larmor frequency of 52.7 MHz. The measurements performed at a lower frequency (40.24 MHz) show that a shorter plateau value will most likely be reached if the experiments are extended to lower temperatures. In order to check whether the observed temperature independence of $T_1$ is due to reduction effects[22] (see also the discussion below), we have measured spin-spin relaxation times. Since $T_2$ was always found to be longer than 200 $\mu$s and thus much larger than the solid echo refocusing time, the $T_1$ experiments are not deteriorated by this effect.

Constant low-temperature spin-lattice relaxation times were also observed in crystals such as $CH_4$ (methane) (Ref. 23) and $Rb_{1-x}(NH_4)_xH_2PO_4$ (a proton glass) (Ref. 24). In these solids the $T_1$ plateau was interpreted to indicate that tunneling processes become dominant at low temperature.

In the inset of Fig. 3 the temperature dependence of the exponent $\nu$ is presented. It is seen that it is significantly nonzero below temperatures of about 20 K. Like in supercooled liquids and polymers[25] the onset of nonexponentiality of the intrinsically exponential deuteron relaxation[26] signals the occurrence of a distribution of molecular correlation times and hence the breakdown of ergodicity on the time scale set by $T_1$. Remarkably, the ergodicity breaking occurs at a temperature which coincides with the one at which the line shape starts to broaden. Also, it should be noted that the plateau in $T_1$ is reached only much below the freezing temperature.

### B. Two-phase behavior in $(KI)_{0.3}(ND_4I)_{0.7}$

We have also recorded solid echo spectra for $(KI)_{0.3}(ND_4I)_{0.7}$. The lower parts of some of the spectra are presented in Fig. 4. In addition to the central component below $T \approx 10$ K, a wing becomes apparent that broadens upon further cooling. At the lowest temperature the precursors of edge singularities usually known from solid state spectra can be recognized. The thick vertical bars in Fig. 4 mark their frequency positions at $\pm 22.7$ kHz. It is remarkable that these coincide with the edge singularities expected for a $ND_4$ group that performs rapid 120° jumps around one of its $C_3$ axes.[27] Rapid means that the jump rate is larger than given by the spectral width $\delta$. Upon close inspection indications for singularities at $\pm 67$ kHz (thin vertical lines in Fig. 4) due to the presence of more rigid ammonium groups can be detected. The central component then obviously corresponds either to a motional process which is much faster than that around the $C_3$ axes or to a quasi-isotropic type of motion. Most likely seems to be that the molecules giving rise to the central component perform tetrahedral jumps.

Also for $(KI)_{0.3}(ND_4I)_{0.7}$ spin-lattice relaxation measurements were carried out. The magnetization recovery curves were found to be single exponential at high temperatures. Again, they could be described as thermally activated (see the solid line in Fig. 5). The activation energy $E/k_B$ is of the order of 170 K. Below $T_C \approx 35$ K the magnetization curves abruptly turn nonexponential, but attempts to describe them with a single stretched exponential function failed. A good parametrization could, however, be achieved with a superposition of a Kohlrausch function and a single exponential,

$$M(t) = A \exp[-(t/T_{1A})] + B \exp[-(t/T_{1B})^{1-\upsilon}], \quad (1)$$

incorporating two components for convenience denoted as $A$ and $B$.[28] The fitting parameters thus obtained are presented in Figs. 5 and 6. The coefficients $\langle T_{1A} \rangle (= T_{1A})$ and $\langle T_{1B} \rangle$ are shown in Fig. 5(a). The latter are obtained from least-squares fits to the magnetization recovery curves at $T < T_C$. It is seen that the relaxation times of component $A$ pass

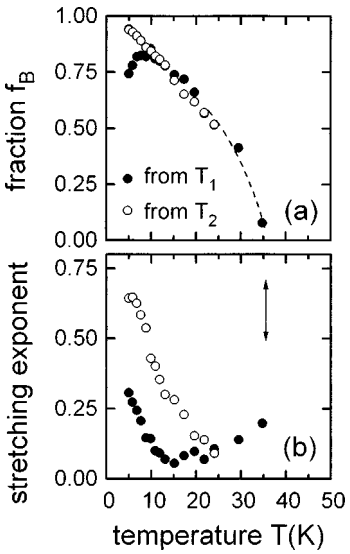


FIG. 6. Temperature dependence of parameters characterizing the decay of the longitudinal and the transverse magnetization of component $B$ of $(KI)_{0.3}(ND_4I)_{0.7}$. In frame (a) the fraction $f_B = B/(A+B)$ is shown. The dashed line is to guide the eye, only. In frame (b) we show the exponents $\nu$ (solid symbols) and $\lambda$ (open symbols) as defined in Eqs. (1) and (2), respectively. Above $T_C = 35$ K, marked by the arrow, the longitudinal magnetization decays exponentially and the transverse magnetization dephases in a Gaussian fashion.

smoothly through $T_C$ and reach a shallow minimum near 13 K. On the low-temperature side the magnitude of the slope $s = |d\langle T_{1A}\rangle/d(1/T)|$ is about a factor of 8 smaller than on the high-temperature side. Such a behavior usually is indicative for a very asymmetric distribution of correlation times.[29] For component $B$ the average spin-lattice relaxation times in the range of the $T_1$ minimum are about a factor of 8 shorter than for component $A$.

The stretching exponent of component $B$ is shown in Fig. 6(b). Immediately below $T_C$ it exhibits values of 0.2 passes through a minimum near where the minimum in $T_1$ shows up and towards low temperatures increases again. The apparent narrowing of the deuteron magnetization recovery in the vicinity of the $T_1$ minimum (for which $s \rightarrow 0$) is well known.[16] A squeezed mapping of the distribution of correlation times onto the distribution of spin-lattice relaxation times is, however, also to be expected in the slow motion regime where the coefficient $s$ is relatively small. This may explain why for $x = 0.7$ the exponent $\nu$ observed at low temperatures [Fig. 6(b)] is smaller than the corresponding values found for the mixed crystals with $x = 0.2$ (Fig. 3) and 0.5.[16]

From the weighting factors appearing in Eq. (1), we can define the fraction of deuterons $f_B = B/(A+B)$ that exhibit the shorter spin-lattice relaxation time. As documented in Fig. 6(a), $f_B$ rapidly increases below $T_C$. The temperature dependence of this quantity resembles that of an order parameter associated with a second-order phase transition. Curiously, however, $f_B$ seems to decrease at the lowest temperatures.

In order to investigate this latter effect, we have studied the transversal dephasing $S(\tau)$; i.e., we have measured spin-spin relaxation times. Again, below $T_C$, we find it necessary to use a two-component description

$$S(\tau) = A\ \exp[-(2\tau/T_{2A})^2] + B\ \exp[-(2\tau/T_{2B})^{1-\lambda}]. \tag{2}$$

We expect that the ratio of the weighting factors $A$ and $B$ appearing in this equation and those deduced from the spin-lattice relaxation measurements [cf. Eq. (1)] follow the same temperature dependence. Thus $f_B$ should not depend on whether it was determined from $T_1$ or from $T_2$ measurements. Within experimental error this conjecture is indeed confirmed, at least for $T > 10$ K; cf. Fig. 6(a). Component $A$ dephases in a Gaussian manner and thus seems to behave as expected. The other exponent, $\lambda$, associated with component $B$, steadily increases with decreasing temperature [Fig. 6(b)].

The temperature dependences of $T_{2A}$ and particularly of $T_{2B}$ as shown in Fig. 5(b) are quite interesting. While $T_{2A}$ below $T_C$ is almost constant, $T_{2B}$ continuously decreases with temperature. Below about 8 K, the fitted $T_{2B}$ values are comparable to the dead time of our spectrometer. The small values of $T_{2B}$ suggest that we are closely approaching the deuteron $T_2$ minimum, indicative for motion taking place on the time scale given by the inverse width of the rigid lattice spectrum. It is reassuring that this is also to be inferred from the low-temperature spectra shown in Fig. 4. It is well known that in this regime of intermediate narrowing, a part of the magnetization (viz., that characterized by the shortest $T_2$) is usually not refocused using a solid echo sequence. This phenomenon gives rise to a so-called reduction factor[22] of the very fast dephasing components. Since $T_1$ was measured using a solid echo technique, this naturally explains the apparent ''reduction'' of $f_B$ as determined from spin-lattice relaxation times at low temperatures [cf. Fig. 6(a)]. Obviously, in this temperature range it is more reliable to evaluate $f_B$ from measurements of spin-spin relaxation times.

## IV. DISCUSSION

We will first discuss the results for the sample with $x = 0.2$. As shown in previous investigations, e.g., Ref. 17, the second moment of the deuteron NMR line is proportional to the Edwards-Anderson order parameter $q_{\mathrm{EA}}$. There are several theoretical approaches that allow one to determine $q_{\mathrm{EA}}$.[5,6] From a simple mean field model which takes into account random bonds as well as random fields, $q_{\mathrm{EA}}$ can be calculated self-consistently via[19]

$$q_{\mathrm{EA}} = \frac{1}{\sqrt{2\pi}} \int dz\ e^{-z^2/2} \tanh^2[z\sqrt{q_{\mathrm{EA}}(T_g/T)^2 + (T_\Delta/T)^2}]. \tag{3}$$

Here $T_g$ and $T_\Delta$ are measures of the contributions due to random bonds and random fields, respectively. From the fit of Eq. (3) to the experimental data, as represented by the solid line in Fig. 2, we find $T_g = 6.9$ K and $T_\Delta = 1.8$ K. In a first approximation $T_g$ should scale with the concentration of the orientational degrees of freedom. Therefore it is not surprising to find that here $T_g$ is about a factor of 2 smaller than for samples with $x \approx 0.4-0.5$.[17,18] The relative importance of the random field contributions as quantified by the ratio $T_\Delta/T_g$, due to entropy reasons, should be largest for $x = 0.5$. In fact, for the $x = 0.2$ crystal $T_\Delta/T_g$ is considerably smaller than for the previously investigated, more heavily doped samples.[17,18]

Next, we turn to the $(KI)_{0.3}(ND_4I)_{0.7}$ crystal. As noted above, the minimum values of $T_{1A}$ and $T_{1B}$ differ by a factor of about 8; see also Fig. 5(a). This compares well with what is expected from the assumption of two differently rotating ammonium species. For isotropically reorienting $ND_4$ groups a coupling constant of 136.5 kHz determines the $T_1$ minimum. The more complex motion of deuterons, carrying out rapid threefold jumps with an additional (slower) reorientation of the $C_3$ axis, leads to a reduced coupling constant of about 45.5 kHz. Since spin-lattice relaxation times depend quadratically on the coupling constant, a factor of 9 is expected under the circumstances just described. Note, however, that according to the assignment given in Fig. 5(b), $T_{1B}$ should be longer than $T_{1A}$. Let us reiterate that this assignment is based on the coincidence of the temperature dependences of $f_B$ as determined from $T_1$ as well as from $T_2$ [cf. Fig. 6(a)]. At present, we are unable to resolve why $T_{1B} < T_{1A}$ [cf. Fig. 5(a)]. We note, however, that still another assignment of two species $A$ and $B$ (which would predict that $T_{1A}$ is 9 times longer than $T_{1B}$) is obtained by assuming that $A$ corresponds to a deuteron parallel to the $C_3$ axis and $B$ to the three deuterons involved in the $C_3$ rotation. This would give $f_B = \frac{3}{4}$, independent of temperature. Since this is not observed experimentally [cf. Fig. 6(a)], we think that the two-site model is favored by our data.

For the crystal with $x = 0.7$ the most striking feature is the observation of a phase transition at a very low temperature of $T_C = 35$ K [cf. Fig. 6(a)], below which we find evidence for the existence of two different deuteron sites. It is interesting to mention that in a related protonated compound $(KI)_{0.27}(NH_4I)_{0.73}$, a structural phase transition was discovered to take place at $T_C = 63$ K using neutron diffraction techniques.[3] Upon cooling, this sample transforms from a NaCl-type symmetry into a trigonal one. The latter is characterized by a distortion angle of 89.9° and therefore can be considered pseudocubic for most purposes. At 5 K this compound exhibited an interesting structure which contains four ammonium sublattices with two inequivalent ammonium sites in the unit cell. On three of these sublattices the molecules were found to exhibit $C_{3v}$ symmetry (site $B$ in the assignment of Fig. 5), while on the other site the $NH_4$ ions turned out to be almost perfectly tetrahedral.[3] With this assignment of sites at 5 K, in the simplest case the fraction $f_B$ should be $\frac{3}{4}$ according to the diffraction study.

Thus there is a large degree of similarity between the results from neutron scattering and from the present NMR investigation. The difference in the phase transition temperatures, apart from the fact that we compare protonated and deuterated compounds, is probably due to differences in the ammonium concentration. Another slight difference is that at 5 K the fraction $f_B$ determined from NMR is larger than 0.75. In order to estimate the low-temperature limit of $f_B$ more reliably, it is obvious that deuteron spin-lattice relaxation times and spectra should be determined at much lower temperatures.

## V. CONCLUSIONS

In the present work we have used static and dynamic deuteron NMR measurements to study the freezing of the ammonium groups in the mixed crystals $(KI)_{1-x}(ND_4I)_x$ for $x = 0.2$ and 0.7. For the less doped sample we find a continuous broadening of the NMR absorption line. The analysis of the data using Eq. (3) indicates that the onset of the freezing process is only slightly affected by static random fields, stemming from local composition fluctuations. At low temperatures the spin-lattice relaxation times become temperature independent, in analogy to measurements on several quantum solids.[23,24] This is a possible hint of the existence of tunneling excitations. For the crystal with $x = 0.7$ the behavior of the spin-spin and spin-lattice relaxation times indicates that a second-order phase transition takes place near 35 K. It is associated with the occurrence of ammonium molecules that perform anisotropic reorientations on a subset of lattice sites which steadily grows in number upon cooling. This type of behavior is compatible with results from neutron diffraction in which evidence for a partially ordered low-temperature phase was obtained.[3] From the deuteron spectra of $(KI)_{03}(ND_4I)_{0.7}$ direct evidence for the $C_3$ motion of the ammonium groups is becoming detectable at low temperature ($T = 5$ K). Further insight into the slowing down of the dynamics in these crystals is to be expected from investigations carried out at lower temperatures.

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[27] Using the quadrupole coupling for $ND_4I$ ($eqQ/h = 182$ kHz) as given in Ref. 21, the singularities are expected to be $eqQ/(4h) = 45.5$ kHz apart.
[28] At high temperatures the exponentiality of component *A* is well established. At the lowest temperatures, where by analogy to the $x = 0.2$ sample the magnetization recovery is expected to be the most nonexponential, component *B* prevails. This hampers a precise determination of the shape parameter for component *A* at low temperatures.
[29] Another possibility is that the slope of the low-temperature wing of the $T_1$ curve corresponds to a librational energy of the ammonium group.