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Anomalous rotational dynamics of NH₄ ions in the paraelectric phase of $K_{1-x}(NH_4)_xH_2PO_4$ mixed crystals

A V Belushkin†§, C J Carlile† and L A Shuvalov‡

† Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, UK
‡ Institute of Crystallography, 117333 Moscow, Russia

Abstract. A study of the rotational dynamics of NH₄ ions in the paraelectric phase of mixed crystals of $K_{1-x}(NH_4)_xH_2PO_4$ by quasielectric neutron scattering is reported. For high NH₄ concentrations ($x = 0.9$) no anomalous behaviour was found and the model of NH₄ ion jumps between equivalent orientations in the crystal gave a good description of the experimental data. In contrast the crystal with $x = 0.6$, which forms a protonic dipolar glass state at low temperatures, revealed an unusual temperature dependence of the elastic incoherent structure factor far above the glass formation boundary. This temperature dependence is analysed in the framework of the model of dynamical cluster formation in the paraelectric phase. The order parameter for the gradually condensing NH₄ groups is obtained. The results are compared with data obtained by other methods on related compounds.

1. Introduction

Mixtures of certain ferroelectric and antiferroelectric crystals over a particular composition range are known to form a proton glass state at low temperatures (see [1] for a review). The properties of this state resemble the properties of magnetic spin glasses. There are however some important differences between spin glasses and proton glasses. In proton glasses the freezing into a glass state occurs over a large temperature interval and the corresponding Edwards–Anderson order parameter is non-zero for all temperatures [2]. The inclusion of both random bonds and random electric fields to describe the physical properties of such systems is necessary. This fact makes the theoretical analysis of these materials rather difficult. While the static properties of the protonic glass state have been extensively studied, the dynamical aspects of the glass transition are much less well understood and the nature of the transition is still not completely clear.

The most commonly studied system that reveals a transition into the protonic glass state is the mixed crystal $Rb_{1-x}(NH_4)_xH_2PO_4$ (RADP). For this system a non-zero Edwards–Anderson order parameter was found far above the transition temperature to the static glass phase. The low-temperature properties of mixed crystals are characterized by a dramatic slowing down of the proton motion associated with the hydrogen bonds and a subsequent random freezing into a frustrated hydrogen-bond network [3]. However, at temperatures above the transition into the static glass regime, the dynamics of the ammonium ions start to play an important role [4, 5]. Electron paramagnetic resonance experiments have shown the existence of fluctuations between different local ordered configurations in the paraelectric phase of the sample. Neutron and x-ray diffuse-scattering experiments also

§ On leave from the Frank Laboratory of Neutron Physics, 141980 Dubna, Russia.

confirm the coexistence of dynamically active clusters with frozen regions [6–9]. In an earlier quasielastic incoherent neutron scattering study the unusual temperature behaviour of the elastic incoherent structure factor (EISF) for the NH_4 ion reorientations was observed and assigned to a partial freezing of the NH_4 reorientations at high temperatures [10]. Unfortunately no quantitative analysis of the results has been performed.

Proton glass properties similar to those of RADP were also found in a related compound, the mixed crystal $K_{1-x}(NH_4)_xH_2PO_4$ (KADP) [11]. However because of the difficulties in preparing high-quality samples over the whole composition range the properties of this system are less well studied. The temperature–composition phase diagram of KADP has been established by dielectric, pyroelectric, elastic-compliance and x-ray diffraction measurements [11, 12]. The previous study [13] of the NH_4 ion reorientations in this KADP system revealed qualitatively similar temperature anomalies for the glass-composition sample in its paraelectric phase to those observed in RADP.

In the present paper new results on NH_4 ion dynamics in the paraelectric phase of KADP and their quantitative analysis for the NH_4 concentrations of $x = 0.9$ and $x = 0.6$ are reported. The $x = 0.9$ sample undergoes an antiferroelectric phase transition at 120 K, which is strongly first order in character [12]. The $x = 0.6$ sample at temperatures below 70 K shows anomalous properties characteristic of a proton glass [11, 12]. A quantitative analysis of the quasielastic neutron scattering data allowed us to compare the reorientational dynamics of the NH_4 ions for the two samples. The temperature dependence of the order parameter for the NH_4 ions in the glass-composition sample, far above the glass-transition temperature, has been evaluated.

2. Experimental details

The quasielastic neutron scattering experiments were performed on the IRIS spectrometer [14] at the ISIS pulsed spallation neutron source, at Rutherford Appleton Laboratory UK. IRIS is a white-beam time-of-flight crystal analyser spectrometer. The final neutron energy, after scattering from the sample, was selected by Bragg reflection of neutrons from pyrolytic-graphite (PG) analysers cooled to 30 K in near backscattering geometry. The PG(004) reflection from the analyser was used in this study, which provides an energy resolution of ~ 50 μeV. 51 scintillation detectors cover a neutron momentum transfer range Q from 0.85 to 3.7 Å^{-1}.

The same powder samples as before [13] were used. They were placed in thin Al foil sachets, which produce negligible background. The sample transmission of 92% was sufficiently high to reduce the effect of multiple scattering, which had been a significant contribution in the previous experiments and especially so for the high-NH_4-concentration sample [13] when the sample transmission was less than 85%. The neutron scattering experiments were performed at several sample temperatures in the range from 260 K to 350 K. The stability of the temperature control was better than ±0.5 K.

A vanadium standard, replacing the sample under the same experimental conditions, was used to obtain the detector efficiencies and to define the spectrometer resolution.

The time-of-flight data were normalized to the incident neutron spectrum and detector efficiencies and then transformed into the scattering law $S(Q, \omega)$. To improve the statistics the individual detectors were grouped in blocks of four after the experiment. Detectors affected by diffraction from the sample were excluded from the analysis.

3. Data analysis

To analyse the data the experimental spectra were approximated by the following formula:

$$I_{inc}(Q, \omega) = S(Q, \omega) \otimes R(Q, \omega) + B(Q, \omega)$$

$$= e^{-2W}[I^{el}(Q)\delta(\omega) + \sum_{n=1}^{m} I_n^{qel}(Q)L_n(\omega; \Gamma_n)] \otimes R(Q, \omega) + B(Q, \omega). \qquad (1)$$

Here I^{el} and I^{qel} denote the intensities of the elastic and quasielastic contributions respectively to the measured intensity; $L_n(\omega; \Gamma_n)$ are the normalized Lorentzian components with half widths at half maximum (HWHM) equal to Γ_n; $R(Q, \omega)$ is the spectrometer resolution function and $B(Q, \omega)$ is the background. ω represents the energy transfer. The experimental data for each temperature and each detector group were modelled by this formula on the basis of a Bayesian approach [15]. This method not only allows an estimate of the values for the fitted parameters in (1) but also a posterior probability of how many quasielastic components there is most evidence for in the data. The energy spectrum from the vanadium standard was used as the resolution function $R(Q, \omega)$. The vanadium data were grouped in the same way as the spectra from the samples were. The background was approximated by a linear function. The earlier data [13] for the $x = 0.6$ sample were also reanalysed in the same manner.

Such an analysis revealed that the highest probability is for the situation when only one quasielastic line is present in the spectra. Increasing the number of Lorentzians in the fitting procedure does not lead to a significant improvement of the fit and the posterior probability decreases. This is true for both samples studied over the whole temperature range and for all the detector groups, in a consistent manner. The experimental elastic incoherent structure factor (EISF), defined as the ratio

$$EISF_{exp} = I^{el}/(I^{el} + I_1^{qel}) \qquad (2)$$

was then extracted from the data as a function of neutron momentum transfer Q and temperature.
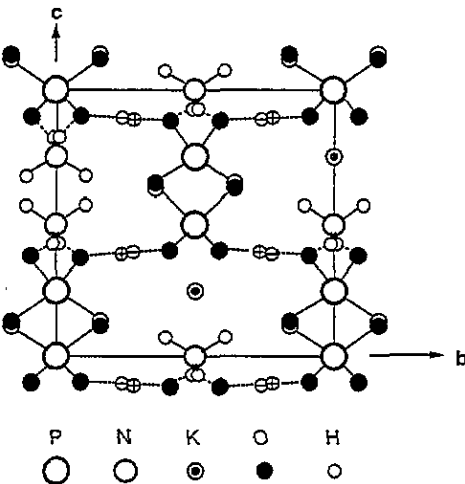
Figure 1. The b–c projection of the $K_{1-x}(NH_4)_xH_2PO_4$ crystal structure. The structure is the same as for the paraelectric phases of the pure parent compounds KH_2PO_4 [16] and $NH_4H_2PO_4$ [17] but in the mixed crystal the K ions are randomly substituted for the NH_4 ions. The protons in the hydrogen bonds are disordered (dynamically in the paraelectric phase and statically in the proton-glass state) between two potential minima marked + and − in the figure.

4. Theoretical model

In figure 1 a schematic view of the b–c projection of the $K_{1-x}(NH_4)_xH_2PO_4$ structure is shown. The mixed crystals have the same tetragonal symmetry (space group $I\bar{4}2d$) as their parent compounds, KH_2PO_4 (KPD) and $NH_4H_2PO_4$ (ADP), in the paraelectric phase [16, 17]. Over the temperature range studied both the $x = 0.9$ and $x = 0.6$ samples retain this symmetry, as was confirmed by checking the diffraction patterns recorded simultaneously with the quasielastic scattering data. One can see from the figure that the most probable model of NH_4 ion reorientation, from the crystal-symmetry point of view, is the model of instantaneous jumps between equivalent NH_4 orientations in the lattice. For this model the theoretical scattering law has the following form [10]:

$$S(Q, \omega) = e^{-2W}[\text{EISF}_t\delta(\omega) + (1 - \text{EISF}_t)L(\omega; \Gamma)] \tag{3}$$

where EISF_t is the theoretical elastic incoherent structure factor given by

$$\text{EISF}_t(Q) = 1 - \frac{1}{4}\sum_{j=1}^{6}\sin^2\left(\frac{Q \cdot d_j}{2}\right). \tag{4}$$

The d_j vectors connect the four protons at the apexes of a tetrahedron. Because the protons in the hydrogen bonds do not participate in the reorientation of the tetrahedron a weighting factor $w = 1/(1 + 2x)$ has to be introduced, which is the ratio of the hydrogen bonded to the total number of protons. Performing a powder averaging one obtains the following formula for the theoretical EISF_t:

$$\text{EISF}_t(Q) = w + (1 - w)\tfrac{1}{4}(1 + 3(\sin Qd)/Qd). \tag{5}$$

Other theoretical approaches commonly used for the description of NH_4 ion reorientations in different environments seem to be unlikely in the present case when one considers the crystal structure of the system. However, for the sake of completeness, the EISF calculations for the $x = 0.9$ sample have been performed for several other models including 120° reorientations around *fixed* threefold axes of the tetrahedron, 90° jumps at random around the twofold tetrahedron axes [18], and 90° jumps around twofold axes combined with 120° jumps around any threefold axes of the tetrahedron [19]. In all cases the weighting factor w was introduced and a proper powder averaging was performed.

5. Discussion

The analysis of the data as described in section 3 allowed the following physical parameters to be obtained: the intensities of the elastic I^{el} and quasielastic I_1^{qel} components and their dependence on sample temperature and neutron momentum transfer Q, and the temperature dependence of the Lorentzian HWHM. From the temperature variation of the HWHM the activation energy for the NH_4 ion reorientations was evaluated. The present experiments confirmed the values obtained earlier [13]. For the $x = 0.9$ sample the relaxation time for NH_4 ion reorientations changes from $(2.3 \pm 0.5) \times 10^{-10}$ s at $T = 260$ K to $(0.64 \pm 0.04) \times 10^{-10}$ s at $T = 330$ K, giving an activation energy $E_a = 130 \pm 1$ meV. This value is substantially higher than the value $E_a = 74 \pm 3$ meV for the $x = 0.6$ sample in which the relaxation times change from $(1.3 \pm 0.3) \times 10^{-10}$ s at 260 K to $(0.60 \pm 0.04) \times 10^{-10}$ s at 330 K. This observation is an indication that the correlations between reorienting NH_4 groups decrease as their concentration becomes smaller due to dilution with K ions.

5.1. A comparison of the theoretical model with the experimental EISF for the $x = 0.9$ sample

The comparison of different theoretical models with the experimentally obtained EISF calculated using formula (2) has been made for the $x = 0.9$ sample. This sample shows no temperature dependence of the EISF, in agreement with previous experiments [13]. This observation, coupled with the equivalence of all NH_4 groups from a crystallographic point of view, indicates that all these groups are involved in the reorientation process down to the temperature of the first-order antiferroelectric phase transition. This idea finds additional support in the 'fixed-window' scan experiment [13] where a change in slope of the temperature dependence of the 'fixed-window' intensity was only observed close to the phase-transition temperature.
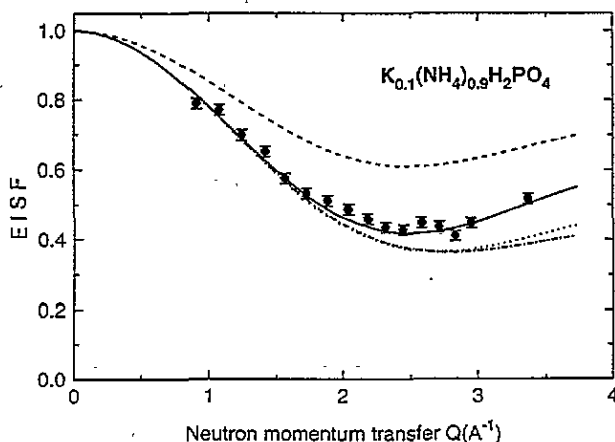
Figure 2. The comparison of the experimentally obtained EISF for the $K_{0.1}(NH_4)_{0.9}H_2PO_4$ sample with the calculations based on different models for the NH_4 ion reorientations. Solid line, the model of instantaneous jumps between equivalent NH_4 ion reorientations in the crystal; dashed line, the model of reorientations around a *fixed* threefold axis of the tetrahedron; dotted line, the model of jumps by 90° at random around the twofold axes of the NH_4 ion; dashed–dotted line, the model of simultaneous reorientations by 90° around any of the twofold axes and by 120° around any of the threefold axes of the tetrahedron.

In figure 2 the experimental EISF is shown by points with error bars and the lines show the results of calculations based on the models discussed in section 4. Experimental data correspond to a sample temperature of 330 K, for which the best statistics were obtained in the experiment. Results for other temperatures are the same within experimental error. There was no need to perform any multiple-scattering corrections because the thickness of the sample was such as to make them negligible. This fact increases the reliability of the comparison of experimental data with the model calculations. As one can see, the best agreement between the experiment and the calculations is obtained for the model of NH_4 ion jumps between equivalent orientations in the crystal. Other models do not give satisfactory agreement with the experiment. An additional argument against the models of 90° jumps and combined 90° and 120° jumps is based on the fact that these two models predict more than one Lorentzian component in the scattering law. As discussed in section 3 the data analysis gives the highest probability for just one Lorentzian component. Therefore one can conclude that only the model of NH_4 instantaneous jumps between equivalent orientations discussed in detail in section 4 gives an adequate description of the experiment.

5.2. The model description of the experimental EISF in the x = 0.6 sample

At the beginning of this section it is worthwhile to emphasize the following. It is well known that in the glass state of RADP and KADP there exists a broad distribution of relaxation times [1, 12]. However, in the paraelectric phase, far above the glass-transition temperature, all experimental results obtained so far reveal only a single relaxation time that characterizes the dynamics of the system [4, 5]. The Bayesian analysis described in section 3 predicted the existence of only one Lorentzian component in our spectra from the $x = 0.6$ sample at all temperatures, in agreement with the existence of a single relaxation time for the dynamics of the NH$_4$ groups. Therefore the anomalous temperature behaviour of the EISF observed in previous experiments [13] cannot be ascribed to the presence of the relaxation-time distribution in the sample.

To explain this unusual temperature dependence, the temperature range in the present study has been extended up to 350 K. The results confirm the previous finding that there is a progressive increase in the experimental EISF when the sample temperature decreases. For a quantitative description of this temperature dependence of the EISF the same model as for the $x = 0.9$ sample has been applied. However in the present case the number of NH$_4$ groups involved in the reorientation process was assumed to vary depending on the temperature and therefore the relative number of mobile protons w (see (5)) was treated as an adjustable parameter. Good quality fits to the experimental data using (5) have been obtained over the whole temperature range from 240 to 350 K. The results of the fits are shown in figure 3. One can define an order parameter $n(T)$ for the NH$_4$ groups as being the ratio of 'frozen' to the total number of NH$_4$ ions in the sample.

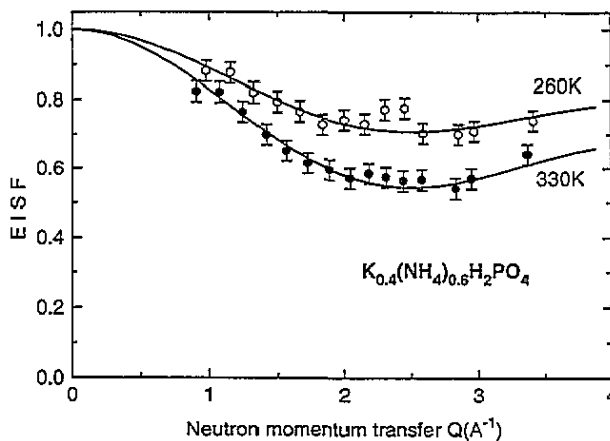**Figure 3.** The comparison of the experimental EISF for the K$_{0.4}$(NH$_4$)$_{0.6}$H$_2$PO$_4$ sample with the model of NH$_4$ ion reorientations between equivalent positions in the crystal. The number of reorienting NH$_4$ groups was treated as an adjustable parameter. For clarity only data obtained at 330 K and 260 K are shown.

5.3. The temperature dependence of the order parameter

In figure 4 the temperature dependence of the order parameter $n(T)$ for the NH$_4$ groups in the $x = 0.6$ sample is shown by points with error bars. For the analytic description of this temperature behaviour an empirical formula has been chosen of the form

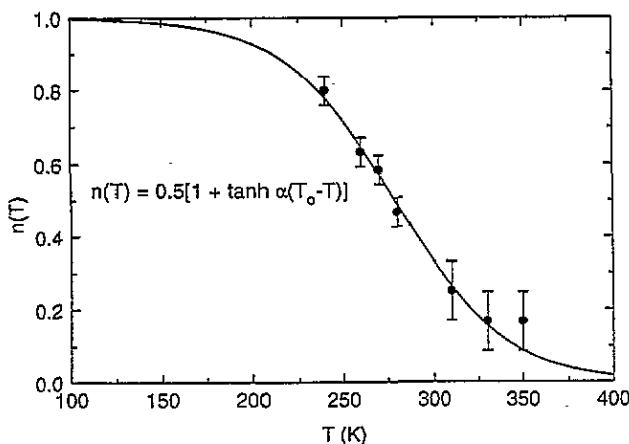$$n(T) = \tfrac{1}{2}[1 + \tanh \alpha (T_0 - T)]. \tag{6}$$

Figure 4. The temperature dependence of the order parameter $n(T)$ for the NH_4 groups in the $K_{0.4}(NH_4)_{0.6}H_2PO_4$ sample. The solid line is the best fit using the empirical formula $n(T) = 0.5(1 + \tanh \alpha(T_0 - T))$.

This formula gives a very good fit to the experimental data and predicts that at ~ 100 K all NH_4 groups would be frozen in the lattice. This prediction agrees very well with the results of the 'fixed-window' scan [13]. As the temperature increases the number of 'frozen' NH_4 groups (or in other words the range of spatial correlations) decreases. However, at any temperature this number is non-zero.

A formula similar to (6) has been used in the analysis of dielectric [20] and NMR experiments [4] on the related compound $Rb_{1-x}(NH_4)_xH_2PO_4$ (RADP) to describe the temperature-independent distribution of activation energies related to the relaxation times by the Vogel–Fulcher law. Moreover the derived parameters of (6), $\alpha = 0.0164 \pm 0.001$ K^{-1} and $T_0 = 278 \pm 2$ K, are very close to those obtained in dielectric and NMR experiments on RADP. It is not yet clear whether this fact is a simple coincidence or whether it has some physical meaning. However it is known [4] that randomly frozen NH_4 ion configurations form a frustrated network, which affects the fluctuating paraelectric units at lower temperatures. Therefore the observed effect of a gradual freezing of NH_4 groups in the paraelectric phase must definitely be connected with rather universal properties of this type of glass.

6. Summary and conclusions

The rotational dynamics of NH_4 groups in $K_{1-x}(NH_4)_xH_2PO_2$ (KADP) has been studied by quasielastic neutron scattering. It was shown that the dynamics can be successfully described by the model of instantaneous NH_4 jumps between equivalent orientations in the lattice. For high ammonium concentrations ($x = 0.9$) the EISF, which reflects the main geometric characteristics of the reorientation process, is temperature independent. All NH_4 groups are mobile with an activation energy of $E_a = 130 \pm 1$ meV down to the temperature of the strongly first-order antiferroelectric phase transition. In contrast the sample with $x = 0.6$ shows a much lower activation energy for the NH_4 ion reorientations, $E_a = 74 \pm 3$ meV, and the EISF is strongly dependent on temperature. The latter effect is connected with the gradual condensation of NH_4 groups into clusters whose lifetime (10^{-8} s) [21] is much longer than the characteristic frequency of our method (10^{11} Hz). The dynamics of the NH_4

groups inside these clusters is much slower than the characteristic frequency probed by our method and therefore could not be studied. The process of NH_4 group freezing saturates at ~ 100 K in agreement with the results of diffuse neutron scattering experiments [6], which show that around this temperature the spatial correlations no longer increase. An analysis of the temperature dependence of the EISF has allowed an evaluation of the order parameter for NH_4 groups in the sample. The fit to the temperature dependence of this order parameter with an empirical formula, similar to those used in the analysis of dielectric [20] and NMR [4] results, gives good agreement with the experiment. The parameters of the fit also agree well with those obtained by dielectric and NMR methods. The possible consequences of this finding are awaiting theoretical investigation but obviously reflect some universal aspect of the process of proton-glass formation.

Acknowledgments

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