

Coherent inelastic neutron scattering in $K_{1-x}(ND_4)_xI$ mixed crystals

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys.: Condens. Matter 4 9235

(<http://iopscience.iop.org/0953-8984/4/47/005>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 12:32

Please note that [terms and conditions apply](#).

Coherent inelastic neutron scattering in $K_{1-x}(ND_4)_xI$ mixed crystals

J-F Berret†, J-L Sauvajol† and B Hennion‡

† Groupe de Dynamique des Phases Condensées, Unité associée au CNRS 233, Université de Montpellier II, F-34095 Montpellier, France

‡ Laboratoire Léon Brillouin, F-91190 Gif-sur-Yvette, France

Received 2 March 1992, in final form 5 August 1992

Abstract. The lattice and rotational dynamics of $K_{1-x}(ND_4)_xI$ mixed crystals have been investigated by means of coherent inelastic neutron scattering as a function of the ammonium concentration and temperature. As the temperature is lowered, anomalies in the behaviour of transverse acoustic phonons propagating along the fourfold axis have been found. These are, firstly, a relaxational behaviour in the phonon energy and acoustic damping for $x = 0.42$ and $x = 0.62$ and, secondly, the existence of a dynamical central peak in the mixed and pure systems. For the three compounds investigated, the neutron data are interpreted in terms of coupling between dipolar orientational fluctuations and transverse acoustic phonons propagating along the fourfold axis. This rotation–translation coupling is efficient for wavevectors $q^* \geq 0.5$, but its strength is largest at the Brillouin zone boundary (the X point). Finally the overall dynamical response measured by neutron scattering suggests a collective slowing down of the ND_4^+ dynamics on lowering the temperature.

1. Introduction

Substitutional disorder in ammonium iodide crystals is responsible for a large variety of structural behaviour. In the past few years, much attention has been paid to $K_{1-x}(ND_4)_xI$ mixed crystals since this system was discovered to exhibit a dipolar glass state at intermediate concentrations ($x \simeq 0.50$) and low temperatures ($T < 50$ K) [1–3]. The orientational degrees of freedom have been related to induced dipolar moments associated with the ND_4^+ ions. At ambient temperature, $K_{1-x}(NH_4)_xI$ mixed crystals are in a face-centred cubic (FCC) structure (phase I). Here, the tetrahedrally shaped molecules reorient between equivalent directions determined by the octahedral crystal field. Reorientations take place in typical times τ_r of about 5 ps [4].

The low-temperature situation is much more complicated. A tentative (x, T) phase diagram has been proposed recently for the low-temperature phases of $K_{1-x}(NH_4)_xI$ [5]. Three compositional ranges have been identified. Above a critical mixing ratio $x_c \simeq 0.75$, the mixed system undergoes a structural phase transition from NaCl to CsCl structures at x -dependent temperatures. For $0.3 < x < x_c$, an orientational glassy state develops below a characteristic freezing temperature T_F and is dominated by dipolar short-range order of an antiferroelectric type. At still lower concentrations $x < 0.3$, the orientational freezing becomes a single-ion process.

In the present paper we focus on the dynamical aspect of the orientationally disordered phases of $K_{1-x}(ND_4)_xI$ mixed crystals. Deuterated samples at $x = 0.42$,

$x = 0.62$ and $x = 1$ have been investigated by means of coherent inelastic neutron scattering (CINS) as a function of temperature between $T = 300$ K and $T = 9$ K. Deuteration is required to obtain coherent scattering results. However, it should be pointed out that deuteration of $K_{1-x}(NH_4)_xI$ affects neither the crystal structure (T_c -values for NH_4I and ND_4I are close to each other [6]) nor the dynamics of the reorienting dipoles. In a previous communication [3], the slowing down of the dipolar dynamics was probed on an $x = 0.42$ sample by the CINS technique. As the dramatic results of this preliminary study showed, there was the first evidence of coupling between dipolar fluctuations and acoustic modes for a neutron wavevector at the boundary of the Brillouin zone [3]. We give here a comprehensive account of the CINS experiments. Neutron data for $x = 0.62$ and $x = 1$ have been included and a qualitative analysis is finally provided in terms of coupled relaxation motions of atomic displacements and molecular reorientations.

2. Experimental details

$K_{1-x}(ND_4)_xI$ single crystals were obtained from S Haussühl at the Universität zu Köln. The samples were grown from aqueous solutions with nominal concentrations $x = 0.50$, $x = 0.75$ and $x = 1$. The true ammonium contents $x = 0.42$, $x = 0.62$ and $x = 1$ were determined by measuring the mass fraction of nitrogen atoms from small pieces (within an absolute uncertainty of about 2%). Their typical sizes were less than about 0.5 cm³.

Inelastic neutron scattering measurements of acoustic phonons were performed at the Laboratoire Léon Brillouin on triple-axis spectrometers installed on the cold and thermal sources of the Orphée reactor. The orientations of the crystals at room temperature were taken in order to study the phonon modes along the high-symmetry directions of cubic reciprocal space. Depending on the energy used to probe, frequency resolutions of 280 GHz, 110 GHz and 60 GHz full width at half-maximum (FWHM) were used, corresponding to incident wavevectors for the (graphite-filtered) neutrons of 2.66 Å⁻¹, 1.97 Å⁻¹ and 1.64 Å⁻¹, respectively. In its standard configuration, the neutron spectrometer is mounted with a double (PG002) monochromator, with a PG002 analyser and with horizontal collimations fixed at $- / - / - / 60/60$, equivalent to a simple monochromator with $- / 23/60/60$. Owing to the relative small sample size, the use of the cold spectrometers (operating with good resolutions) was limited to the largest single crystal at our disposal, namely to the $x = 0.42$ specimen.

3. Results

3.1. Dispersion curves at room temperature

The lattice dynamics of ND_4I in phase I have been studied experimentally by Vagelatos *et al* [7]. These workers have shown that, despite the orientational disorder, well defined acoustic and optic modes could be obtained in the plastic phase of ND_4I . The accuracy of the present experiment was tested by comparing our data with those reported previously. For the transverse acoustic (TA) phonon at wavevector $q = [0, 0, 2\pi/a]$, a phonon energy $\hbar\omega_{TA} = 666 \pm 8$ GHz was obtained, a value in good agreement with the results of Vagelatos *et al*, 640 ± 22 GHz.

Figure 1 displays the dispersion curves of longitudinal acoustic (LA) and TA modes propagating along the three directions of highest symmetry in $K_{1-x}(ND_4)_xI$. Data for ammonium iodide have been included for comparison and shown as full curves [7]. The most interesting result in figure 1 is the decrease in the phonon energies at reduced wavevector $q^* = qa/2\pi = 1$ (X point) when substituting K^+ ions by ND_4^+ ions (a denotes the lattice parameter). As x passes from 0 to 1, this decrease is nearly linear. Note that the relatively small scattering volume prevented us from determining the [001] LA modes and more generally the optical phonons.

In the following sections, we focus essentially on the TA branch along the [001] crystalline axis, as a function of temperature, composition and energy transfer. This interest was motivated at the beginning of this study by the hope to observe pre-transitional effects at the martensitic NaCl-to-CsCl transition of ND_4I [8].

3.2. Temperature dependence

3.2.1. Lattice parameter. As we looked at the temperature evolution of the lattice dynamics of $K_{1-x}(ND_4)_xI$, the lattice parameter $a(x, T)$ of the FCC phase had to be determined. Although the accuracy of the present measurements ($\Delta q_{res} = 0.02 \text{ \AA}^{-1}$) is not as good as in usual diffraction experiments, the overall $a(T)$ -behaviour could be obtained. As shown in figure 2, for the two lowest-ammonium-concentration systems, $a(x, T)$ decreases continuously down to 10 K. Here, no phase transition occurs and it can be concluded that the potassium sublattice has stabilized the structure of the plastic phase.

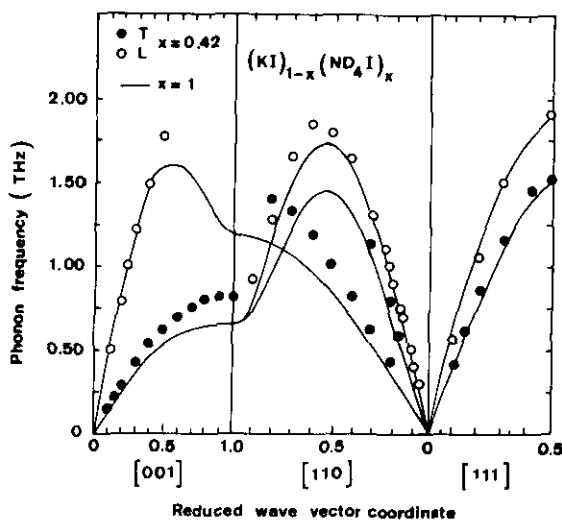


Figure 1. Dispersion curves for LA (○) and TA (●) phonons in $K_{1-x}(ND_4)_xI$ at ambient temperature (phase I). Measurements were performed on a thermal source at incident wavevector $k_i = 2.66 \text{ \AA}^{-1}$ and using a 280 GHz energy resolution. Data for ND_4I (—) are from [7].

ND_4I on the contrary exhibits a phase transition at $T_c = 235 \text{ K}$, i.e. at about 20 K below the value reported in the literature (according to [6], $T_c = 254 \text{ K}$).

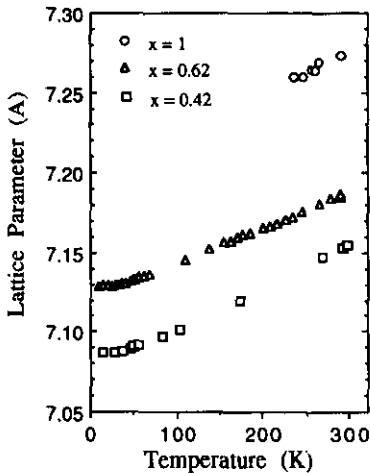


Figure 2. Temperature variation in the lattice parameter measured in the FCC phase of $K_{1-x}(ND_4)_xI$ single crystals.

This discrepancy is explained by the fact that pure ammonium halides in phase I can be easily supercooled (say about 60 K in the case of NH_4I [9]). Since the ND_4I sample is irreversibly destroyed by the phase transition, no neutron measurements have been performed in the phases of lower symmetry. The values of $a(x)$ at ambient temperature are 7.154 Å, 7.185 Å and 7.273 Å for $x = 0.42$, $x = 0.62$ and $x = 1$, respectively. As usually observed in ionic mixed crystals, Vegard's rule is satisfied for the $K_{1-x}(ND_4)_xI$ compounds. An expression of the form $a(x, T = 295 \text{ K}) = 7.07 + 0.19x$ Å reproduces the $a(x)$ -dependence well. It attests moreover to the accurate determination of lattice parameter and concentration.

3.2.2. $x = 0.42$. CINS data have already been partially reported for the $x = 0.42$ crystal [3]. We concentrate here on the main features revealed by this preliminary study and recall the specific analysis performed on the inelastic spectra. We first examine in more detail the [001] TA branch versus temperature and composition. The phonon energies are shown in figure 3 for $x = 0$ [10], for $x = 1$ and, at two temperatures ($T = 293 \text{ K}$ and $T = 103 \text{ K}$), for $x = 0.42$. For this last compound, an anomalous temperature softening is observed typically for $q^* > 0.6$, the effect being the largest at the zone-boundary X point.

Owing to the above results, the $q = 2\pi/a$ phonon was then placed under scrutiny, using a much better energy resolution than in figures 1 and 3. This was achieved by changing the incident k_i from 2.66 to 1.97 \AA^{-1} . This choice of 1.97 \AA^{-1} results from a compromise between the requirements of good resolution and reliable statistics. Moreover it allowed measurements in the frequency range from -1.5 THz to $+1 \text{ THz}$, which was necessary for an accurate determination of the different contributions (see below). Finally it prevented the ' $\lambda/2$ ' contamination arising from the $Q = (4, \bar{2}, 0)$ Bragg peak reasonably well (the transmission of the graphite filter is only 18% at $k_i = 3.94 \text{ \AA}^{-1}$). The inelastic neutron spectra of $K_{1-x}(ND_4)_xI$ as received from measurements at $Q = (2, \bar{1}, 0)$ are shown in figure 4 at different temperatures between $T = 293 \text{ K}$ and $T \simeq 15 \text{ K}$. Basically, a 'three-peak' structure is found, indicating the occurrence of a dynamical central peak besides the phonon groups. Asymmetries in the Stokes and anti-Stokes sides are due to the resolution

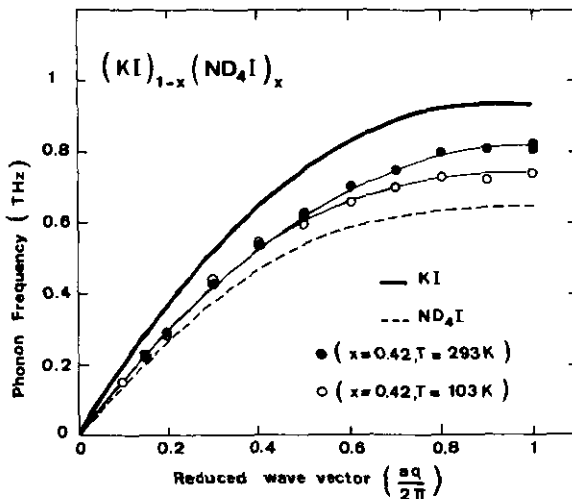


Figure 3. The TA branch of phonons propagating along the [001] direction in $K_{1-x}(ND_4)_xI$ single crystals with $x = 0$, $x = 0.42$ and $x = 1$. The experiments were performed at around $Q = (q^*, 2, 2)$ using a constant incident wavevector ($q^* = aq/2\pi$). The data for KI are from [10].

effect superimposed by the use of the constant- k_i method. In order to account for the overall neutron scattering cross section, four contributions were assumed [3].

- (1) A damped harmonic oscillator given by the expression $S_{ph}(\omega) \propto \gamma_{ph}/[(\omega^2 - \omega_{TA}^2)^2 + \gamma_{ph}^2\omega^2]$ was used for the phonon (with frequency $\omega_{TA}/2\pi$ and FWHM γ_{ph}).
- (2) A Lorentzian was employed for the component centred at zero energy transfer and due to quasi-elastic scattering (QES): $S_{QES}(\omega) \propto \Gamma_{QES}/(\omega^2 + \Gamma_{QES}^2)$ ($1/\Gamma_{QES}$ being here the mean relaxation time of the orientational fluctuations).
- (3) A Dirac delta function was utilized for the elastic incoherent scattering.
- (4) A Debye-like phonon density of states was used for the inelastic incoherent scattering.

Both inelastic contributions (1) and (4) follow Bose statistics.

The data analysis consisted in calculating the scattered intensity by folding the (q, ω) four-dimensional resolution function of the spectrometer with the scattering cross sections described above (see, e.g., [11]). This treatment accounts for the distortions of the spectra in figure 4 which are due to the large k_i^3 -dependence of the scattered intensity (it includes variations in the analyser reflectivity). We are then left with seven adjustable parameters: the intensities of the four contributions, the widths Γ_{QES} and γ_{ph} of the QES and inelastic signals, and the angular frequency ω_{TA} of the phonon. These parameters were then adjusted through a χ^2 minimization routine. The adequacy of the resolution function was checked with the vanadium calibration and by properly fitting standard phonon lineshapes far from the zone boundary ($q^* \leq 0.5$).

It is obvious that the strongest correlations occur between the linewidths of the quasi-elastic and inelastic peaks and the intensity of the incoherent inelastic signal. Fortunately, firstly, the phonon is always underdamped and its shape remains rather

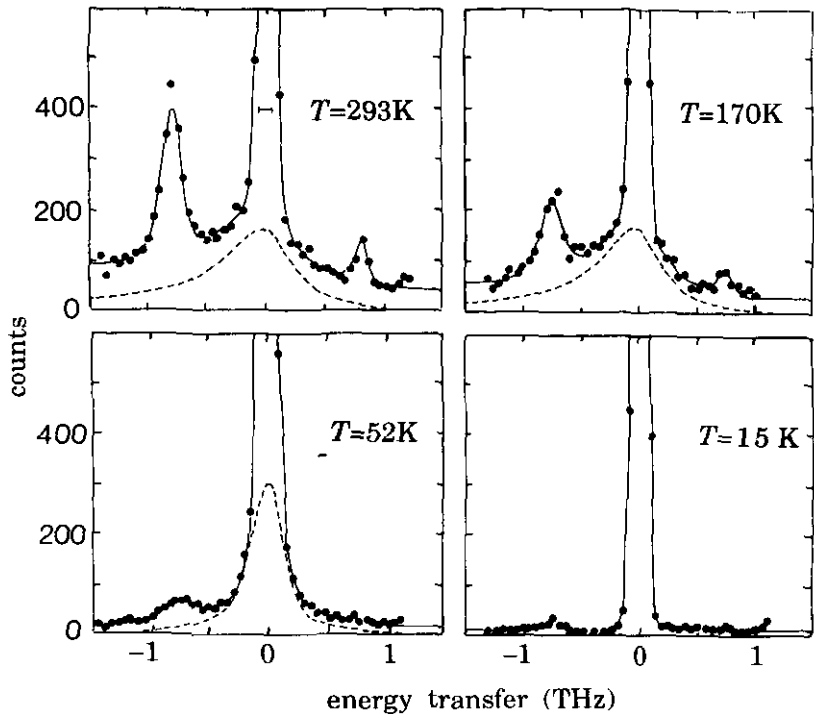


Figure 4. Coherent inelastic neutron spectra from $K_{0.42}(ND_4)_{0.58}I$ at the Brillouin zone boundary ($q^* = 1$) for [001] TA phonons. The energy resolution is 110 GHz, as shown in the first plot. The measurements were performed at different monitors, e.g. $m = 10000$ for $T = 293$ K and $m = 20000$ at $T = 52$ K; however, the intensities are shown for $m = 10000$, corresponding to a counting time of 410 s. The full curves are the results of the fitting procedure described in the text. The QES is represented by the broken curves. Note the disappearance at low temperature of both quasi-elastic and inelastic incoherent signals.

sharp at any temperature, and secondly, the incoherent signal appears to be weak and its known temperature dependence allows one to constrain its value.

When plotted against temperature, the frequency ω_{TA} of the TA zone-boundary phonon exhibits a shallow minimum down to $T \simeq 100$ K and recovers below. This *anomalous softening* is accompanied by a maximum in γ_{ph} (i.e. acoustic damping) at a slightly lower temperature. These features, which are characteristic of the relaxation process, are illustrated in figure 5. The maximum in acoustic damping in the lower part of figure 5 corresponds to the relaxation regime $\omega_{TA}\tau_r \simeq 1$.

The temperature variation in the QES has already been described in detail in [3]. The related peak was found to grow in intensity as $1/T$ and to narrow in linewidth Γ_{QES} (see the broken curves in figure 4). We focus here on a surprising feature of the ammonium compounds, namely the q -dependence of this dynamical central peak. In figure 6 are shown the CINS spectra at the reduced q^* -values of 0.1, 0.2 and 0.5 along the [001] direction for $T = 101$ K. The energy resolution was chosen at 60 GHz ($k_i = 1.64 \text{ \AA}^{-1}$) for the first two plots, and at 110 GHz for the $q^* = 0.5$ spectrum

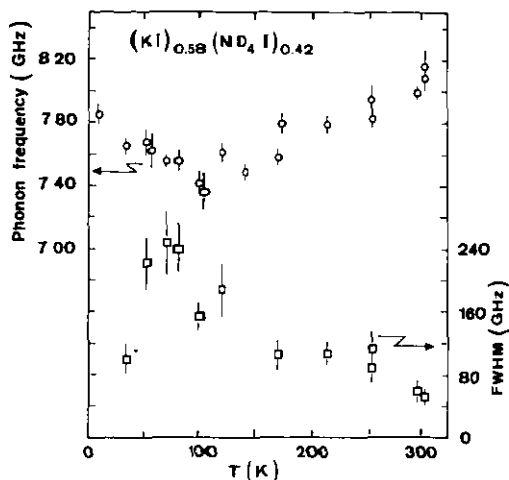


Figure 5. Temperature dependence of the [001] TA phonon frequency $\omega_{TA}/2\pi$ and linewidth γ_{ph} corresponding to the spectra in figure 4. The maximum in acoustic damping corresponds to the relaxation regime $\omega_{TA}\tau_r \approx 1$.

($k_i = 1.97 \text{ \AA}^{-1}$). Below the strong incoherent contribution, a central component clearly shows up with increasing wavevector. It is absent for the $q^* = 0.1$ spectrum but becomes resolved at $q^* = 0.5$ and culminates at the zone-boundary X point. The full curves in the lowest plot in figure 6 result from the same fitting procedure as in figure 4.

3.2.3. $x = 0.62$. The $x = 0.62$ crystal has been studied with respect to its lattice dynamics properties only. As illustrated in figure 7, the TA phonon group at the zone boundary could be resolved down to 20 K. The measurements were performed at constant $k_i = 2.66 \text{ \AA}^{-1}$ at wavevectors $Q = (4, 1, 0)$ and $(1, 2, 0)$. The incomplete softening revealed at lower x is still present, but its magnitude does not depend on the ND_4^+ content. The difficulty in clearly measuring the phonon groups at low temperatures is probably due to their relaxational coupling with the ND_4^+ reorientations.

3.2.4. $x = 1$. As already mentioned, no anomaly has been observed at the phase transition on the acoustic branches, nor at the centre or the edge of the Brillouin zone. The former result corroborates recent Brillouin scattering data on protonated ammonium iodide, which for example exhibits a constant $c_{44}(T)$ on approaching T_c [12].

In figure 8 are displayed three examples of CINS spectra collected between ambient temperature and approximately T_c . The experimental conditions are identical with those in figures 1 and 3. As for the $x = 0.42$ sample, a 'three-peak' structure developed, indicating again a QES contribution. The full curves in figure 8 are best fits to the data using the analysis described for $x = 0.42$ (the elastic component has been subtracted here). It reveals the growth and the narrowing of the QES peak on approaching the transition (as shown in figure 8), but no critical behaviour. From the linewidth Γ_{QES} in ND_4I , one estimates a dipolar correlation time which increases from 0.37 to 0.52 ps between 300 and 242 K.

4. Discussion

Coherent QES is a common feature of molecular crystals in their disordered phases

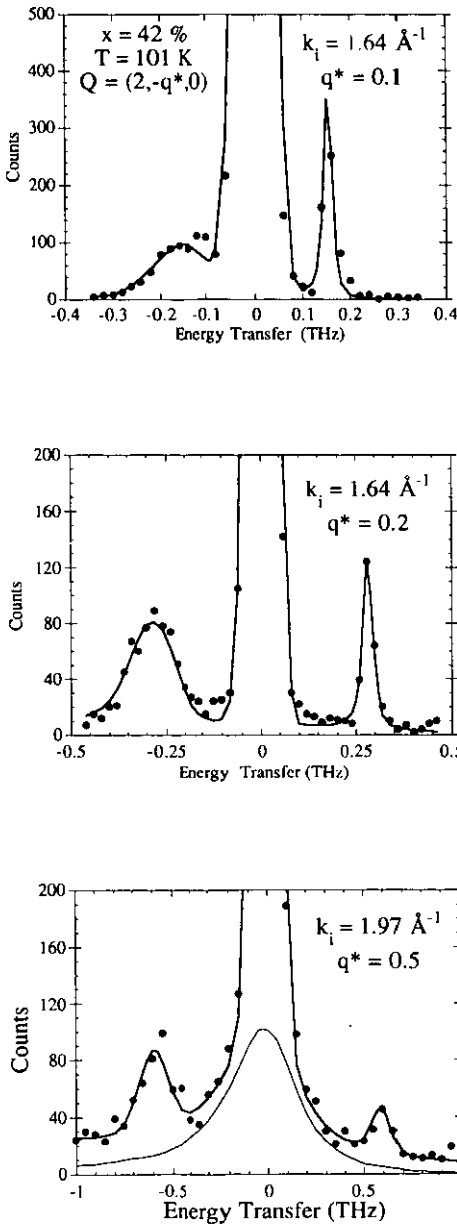


Figure 6. Neutron spectra for $K_{0.42}(ND_4)_{0.58}I$ as a function of the wavevector q^* . The temperature was set at 101 K. The spectra were taken with different incident k_i , 1.64 \AA^{-1} for the first two plots (using $m = 1000$ and 2000 , respectively) and 1.97 \AA^{-1} for the lower graph ($m = 4000$). The full curves are the fits according to the analysis explained in the text. For $q^* = 0.1$ and 0.2 , no central peak has been assumed.

[13]. It indicates the existence of orientational correlations between different molecules and reflects their collective behaviours. These phenomena have been extensively studied at the order-disorder phase transition (as in CD_4 [14] and ND_4Br [15]), or more recently in orientational glasses at the freezing transition (e.g. in the

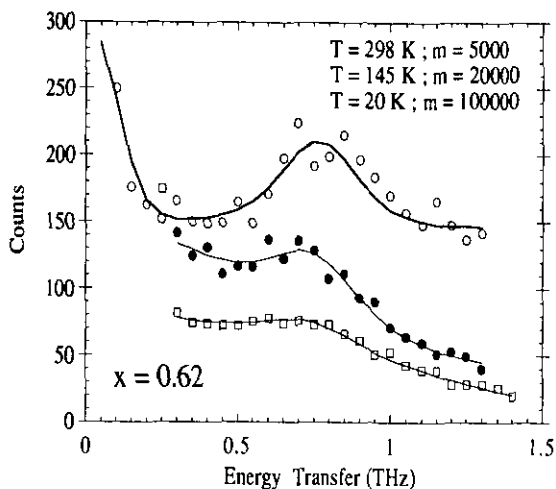


Figure 7. The TA phonons in $K_{0.62}(ND_4)_{0.38}I$ observed at the zone boundary ($Q = (4, 1, 0)$ for the upper curve and $Q = (1, 2, 0)$ for the other two curves) as a function of temperature. The measurements were performed at constant $k_f = 2.66 \text{ \AA}^{-1}$. For clarity, the data points (given for $m \approx 100000$) have been shifted with respect to each other and the upper (lower) intensity has been divided (multiplied) by a factor of 2.

$Rb_{1-x}(NH_4)_xH_2PO_4$ proton glass [16] and in Ar-N₂ mixtures [17]). In the second class of systems, the QES peak shows no critical behaviour but rather a saturation effect below freezing.

The present results supply additional information on the lattice and rotational dynamics of $K_{1-x}(ND_4)_xI$. For the three compounds investigated, the CINS data can be interpreted in terms of coupling between the dipolar orientational fluctuations and TA phonons propagating along the fourfold axis. This interpretation has already been provided in [3] where only the $x = 0.42$ sample was studied in detail. This so-called rotation-translation (R-T) coupling is manifested experimentally by

(i) a relaxational behaviour of the phonon energy and acoustic damping for the two crystals which undergo no structural changes, namely $x = 0.42$ and $x = 0.62$, and

(ii) the presence already at ambient temperature of a quasi-elastic central peak in the mixed and pure systems (the overall behaviour of the central and side components also suggest a collective slowing down of the ND_4^+ dynamics on decreasing the temperature).

This interpretation is based on a microscopic theory due to Michel and Rowe [18] who studied the coupling between rotational and translational degrees of freedom in orientationally disordered crystals. These authors were able to predict that a coupling of the dipolar orientational and translational modes would be the strongest at the Brillouin zone boundary. In $K_{1-x}(ND_4)_xI$ indeed, as emphasized by recent Brillouin scattering [12] and ultrasonic [19] measurements, the R-T coupling is weak at the zone centre. The present neutron results demonstrate that this coupling is efficient for wavevectors $q^* \geq 0.5$, but its strength is the largest at the X point (see figures 4 and 6).

According to the above arguments, one is led to the first conclusion: the QES in $K_{1-x}(ND_4)_xI$ is not connected to the driving mechanism yielding the NaCl-to-

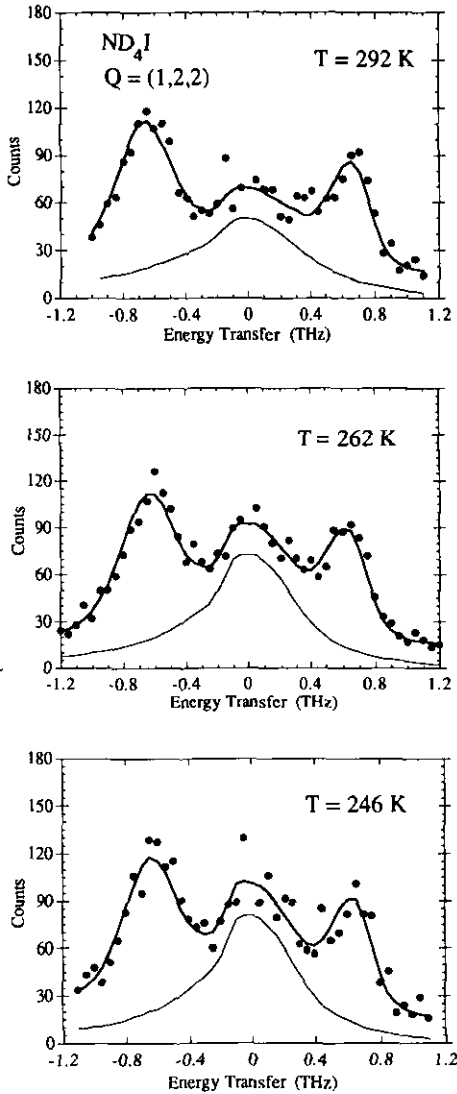


Figure 8. Neutron spectra for ND_4I at wavevector $\mathbf{Q} = (1, 2, 2)$ as a function of temperature ($k_i = 2.66 \text{ \AA}^{-1}$; energy resolution, 280 GHz). The measurements have been performed with comparable monitors and are shown for $m = 3000$ (counting time, about 150 s). The same fitting procedure was employed as given in the text (the elastic contribution has been subtracted). The HWHM of the QES decreases from 440 GHz at room temperature to 300 GHz near $T_c = 235 \text{ K}$.

CsCl structural transformation of ND_4I . On the contrary, the R-T coupling and the orientational correlations are essential mechanisms for the freezing transition in these mixed compounds. This has been clearly shown by elastic neutron scattering [3, 5]. At low temperatures, the dynamical central peak condenses at the zone boundary, resulting in spatial correlations of an antiferroelectric local order [5].

One has thus for $\text{K}_{1-x}(\text{ND}_4)_x\text{I}$ a situation which is the converse to that encountered in mixed alkali cyanides. In KCN, the linear coupling between the shear elastic constant and the quadrupolar T_{2g} susceptibility is the driving mechanism of the first-order transition at 168 K [20]. The role of substitution (CN^- by Br^-) is to diminish this coupling and hence to dilute the elastic quadrupolar interactions. In $(\text{KBr})_{1-x}(\text{KCN})_x$, below x_c , orientational long-range order ceases to occur. In the potassium ammonium iodide systems, structural transitions in the pure system and the freezing process in the mixtures have two separate physical origins.

ND_4Br in the CsCl structure is another model system for which an R-T coupling drives the transition to an orientationally ordered phase ($T_c = 215$ K). As investigated by Yamada *et al* [15], the dynamical critical behaviour of ND_4Br above T_c was ascribed to coupled relaxation motions of Br^- displacements and the flipping of the ND_4^+ ions. As in $K_{1-x}(ND_4)_xI$ systems, this coupling was found to occur at the zone boundary.

The present CINS spectra (in the plastic phase, see figures 4 and 6-8) show some qualitative similarities with those observed in ND_4Br on approaching T_c . For example the scattering cross section exhibits a 'triple-peak' structure, and the phonon mode is noticeably broadened by the coupling. However, the pseudo-spin-phonon-coupled approach of [15] should not be directly applicable to $K_{1-x}(ND_4)_xI$, for at least two major reasons. First, the model of Yamada *et al* does not take into account the dipolar nature of the interacting moments. Second, in contrast to ammonium bromide where the molecules have a finite number of well defined orientations (two in its CsCl phase), the orientations in $K_{1-x}(ND_4)_xI$ are best described in terms of probability functions [21].

The preceding sections have stressed the importance of the coupling between the [001] TA phonon and the ND_4^+ dipolar reorientations in $K_{1-x}(ND_4)_xI$. In order to visualize the different motions involved by this coupling, the atomic displacements related to this zone-boundary [001] TA wave have been represented schematically by arrows in figure 9 for a ND_4I lattice cell. For clarity, only one ND_4^+ ion placed in the octahedral symmetry is shown. Its orientation has been taken in agreement with the 'triple-approach' model [22]. Within this picture, one N-D bond points along the cube diagonals whereas the remaining bonds are along the fourfold axis. In such an environment, the dipolar moment results from the distortions of the tetrahedra. The thermally activated jumps of the ammonium molecule resulting in a 180° flip of the dipole could possibly couple to the atomic motions indicated by arrows.

All these assumptions need evidently to be supported by quantitative calculations.

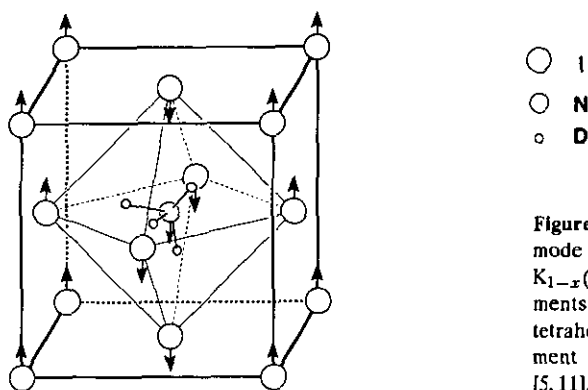


Figure 9. Schematic representation of the TA mode which couples to the ND_4^+ reorientations in $K_{1-x}(ND_4)_xI$. The arrows indicate the displacements of the iodide ions. For clarity, only one tetrahedron is shown. Its orientation is in agreement with the so-called 'triple-approach' model [5, 11].

5. Concluding remarks

We have made a study of the molecular and lattice dynamics of the $K_{1-x}(ND_4)_xI$ mixed crystals at three concentrations ($x = 0.42$, $x = 0.62$ and $x = 1$) by means

of CINS. As the temperature decreases, anomalies in the behaviour of TA phonons propagating along the fourfold axis have been found. These are as follows.

(i) There is a relaxational behaviour of the phonon energy and acoustic damping for $x = 0.42$ and $x = 0.62$. This indicates that coupling occurs between dipolar orientational and translational degrees of freedom at the antiferroelectric wavevector $q^* = 1$.

(ii) A dynamical central peak occurs for the mixed and pure systems. This QES indicates the existence of orientational correlations between molecules and reflects their collective behaviours. At $x = 0.42$, its temperature dependence reveals a slowing down of the ND_4^+ dynamics. At $x = 1$, no critical behaviour is obtained near the NaCl-to-CsCl phase transition ($T_c = 235$ K). High-resolution neutron scattering measurements on larger samples are planned in order to characterize this quasi-elastic component fully.

The temperature and composition dependences of the CINS response have also provided some insight into this system. The structural transition occurring in ND_4I and the freezing process in the mixtures (at $x = 0.42$ and $x = 0.62$) have two separate physical origins. This is not usual for orientational glasses obtained by substitutional disordering as in $(\text{KBr})_{1-x}(\text{KCN})_x$ or $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$. Finally, any theoretical model of $\text{K}_{1-x}(\text{ND}_4)_x\text{I}$ mixed crystals will have to account for dynamical correlations and local ordering at the Brillouin zone boundary. This is a crucial feature of the $\text{K}_{1-x}(\text{ND}_4)_x\text{I}$ orientational glasses.

References

- [1] Bostoen C, Coddens G and Wegener W 1984 *J. Chem. Phys.* **91** 6337
Bostoen C 1991 *PhD Thesis* University of Antwerp
- [2] Fehst I, Böhmer R, Ott W, Loidl A, Haussühl S and Bostoen C 1990 *Phys. Rev. Lett.* **64** 3139
- [3] Berret J-F, Bostoen C, Sauvajol J-L, Hennion B and Haussühl S 1991 *Europhys. Lett.* **16** 91
- [4] Goyal P S and Dasannacharya B A 1979 *J. Phys. C: Solid State Phys.* **12** 209, 218
- [5] Berret J-F, Bostoen C and Hennion B 1992 *Phys. Rev. B* **46** at press
- [6] Parsonage N G and Staveley L A K 1978 *Disorder in Crystals* (Oxford: Oxford University Press)
- [7] Vagelatos N, Rowe J M and Rush J J 1975 *Phys. Rev. B* **12** 4522
- [8] Blaschko O, de Podesta M and Pintschovius L 1988 *Phys. Rev. B* **37** 4258
- [9] Dultz W and Ihlefeld H 1973 *J. Chem. Phys.* **58** 3365
- [10] Dolling G, Cowley R A, Schittenhelm C and Thorson I M 1966 *Phys. Rev.* **147** 577
- [11] Hennion B, Hennion M, Hippert S and Murani A P 1984 *J. Phys. F: Met. Phys.* **14** 489
- [12] Berret J-F, Bruchhäuser F, Feile R, Bostoen C and Haussühl S 1990 *Solid State Commun.* **74** 1041
- [13] Dörner B 1981 *Structural Phase Transitions* ed K A Müller and H Thomas (Berlin: Springer) p 93
- [14] Press W, Hüller A, Stiller H, Stirling W and Currat R 1974 *Phys. Rev. Lett.* **32** 1354
- [15] Yamada Y, Takatera H and Huber D L 1973 *J. Phys. Soc. Japan* **36** 641
Yamada Y, Noda Y, Axe J D and Shirane G 1974 *Phys. Rev. B* **9** 4429
- [16] Grimm H and Martinez J 1986 *Z. Phys. B* **64** 13
- [17] Press W, Janik B and Grimm H 1982 *Z. Phys. B* **49** 9
- [18] Michel K H and Rowe J M 1985 *Phys. Rev. B* **32** 5818
- [19] Berret J-F, Bostoen C, Doussineau P, Frénois C, Haussühl S and Levelut A 1992 *Ferroelectrics* **127** 275 (*Proc. 7th Eur. Meet. on Ferroelectricity (Dijon, 1991)*)
- [20] Michel K H and Naudts J 1977 *Phys. Rev. Lett.* **39** 212
- [21] Rush J J and Rowe J M 1986 *Physica B* **137** 169
- [22] Ozaki Y, Maki K, Okada K and Morrison J A 1985 *J. Phys. Soc. Japan* **54** 2595
Ozaki Y 1987 *J. Phys. Soc. Japan* **56** 1017