# Diffuse scattering in K1-x(ND4)x I mixed crystals

Jean-François Berret, S. Ravy, B. Hennion

Classification
*Physics Abstracts*
64.70P — 61.12 — 61.10

# Diffuse scattering in $K_{1-x}(ND_4)_xI$ mixed crystals

J.-F. Berret ([1]), S. Ravy ([2]) and B. Hennion ([3])

([1]) Groupe de Dynamique des Phases Condensées (*)
([2]) Laboratoire de Physique des Solides (**)
([3]) Laboratoire Léon Brillouin, F-91190 Gif-sur-Yvette, France

(*Received 10 September 1992, accepted in final form 15 December 1992*)

**Abstract.** — We have used thermal neutron scattering and x-ray diffraction to investigate the short range order correlations in the orientational glassy phase of $K_{1-x}(ND_4)_xI$. Single crystals with ammonium concentrations $x = 0.42$ and $x = 0.62$ have been studied between ambient temperature and 10 K. Both experiments exhibit diffuse scattering patterns characteristic of the low-temperature phase of $K_{1-x}(ND_4)_xI$. The diffuse signal peaks at the Brillouin zone-boundary and is strongly anisotropic. Its intensity does not diverge as $T \to 0$ *K*, indicating that only on a local state, the f.c.c. symmetry is broken through the short-range antiferroelectric correlations. As a result of the comparison between the different cross-sections obtained by x-ray and neutron scattering, it is concluded that static displacements of one or several atoms away from the lattice sites (most probably the iodide ions) are involved in the dipolar freezing. The dependences of the diffuse signal as functions of wave-vector, temperature and concentration are finally discussed.

## 1. Introduction.

In an orientational glass (OG), multipolar moments (dipoles, quadrupoles, etc.) occupy randomly some of the sites of a regular lattice. These moments interact either directly *via* electric interactions, or indirectly *via* a coupling of the reorientations with the lattice modes (these are elastic iteractions). The competition between interactions which act in favor of orientational ordering and the substitutional disorder results in a freezing of the orientational degrees of freedom. An orientational glass is a system where the molecular orientations are frozen-in and disordered in the low-temperature phase. Two conditions are generally added : The translational order is preserved at all temperatures and the transition towards the glassy state is a collective process. OG's have attracted much attention these last years because the freezing of the orientational degrees of freedom shows strong similarities with the liquid-glass and the spin glass transition (for a review, see [1]).

(*) U.A. 233, Université de Montpellier II, F-34095 Montpellier, France.
(**) Université de Paris-Sud, F-91405 Orsay, France.

Recently, it has been suggested that the mixed potassium ammonium iodide crystals, $K_{1-x}(NH_4)_xI$, exhibit a dipolar glass state for intermediate compositions ($x \sim 0.50$) and low temperatures ($T < 50$ K) [2-4]. This conclusion resulted from two main observations : First a Curie-Weiss behavior of the dielectric susceptibility followed at lower temperatures by a cusp [3] ; second, the growth of diffuse scattering patterns in the elastic neutron response in the same T-range [4]. The first feature was interpreted in terms of a freezing transition, in analogy to that encountered in other OG's or in spin glasses. The second result indicated the existence of antiferroelectric (AFE) spatial correlations at low temperatures. In the original reports on this compounds [3, 4], the orientational degrees of freedom have been identified as electric dipole moments associated with the ammonium molecules. On lowering T, these dipoles were assumed to freeze collectively toward a state devoid of long range order.

Compared to other orientational glasses with dipolar degrees of freedom [1], $K_{1-x}(NH_4)_xI$ presents many advantages. i) the crystallographic structure of the mixed compounds showing disorder remain cubic face-centered (Fm3m) at all temperatures [4] ; ii) The orientational disorder is observed on a wide composition range, typically for $x < x_c \approx 0.75$. Above $x_c$ the freezing is replaced by structural transitions analogous to those of $NH_4I$ [5].

However, concerning this system, serious questions are still not elucidated such as the origin of the electric dipole moment or the microscopic description of the frozen disordered phase. It is indeed unclear whether the dipole of 1.4 Debye determined from dielectric spectroscopy [3] results from the distortions of the H-N-H angles [2, 6] or from the off-centre position of the ammonium ions [3, 7, 8].

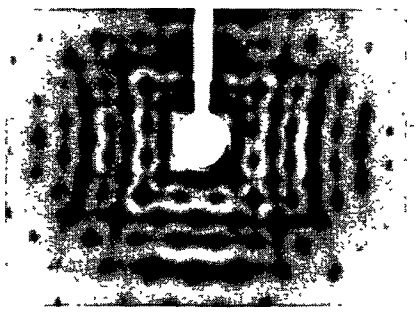
In the present paper, we report x-ray diffraction and coherent neutron scattering measurements on deuterated homologs, $K_{1-x}(ND_4)_xI$ with concentration $x = 0.42$ and $x = 0.62$. Both systems fall in the x-range where the transition between the plastic and frozen phase is a collective process. We give here a comprehensive account of the coherent neutron studies undertaken on $K_{1-x}(ND_4)_xI$, and partially published elsewhere [4]. In addition, the neutron data are compared to new x-ray diffraction patterns obtained on the same crystals. Qualitative comparisons between the diffuse intensities received from the two experiments enable us to establish that the glassy phase of $K_{1-x}(ND_4)_xI$ does not correspond to the naïve picture of frozen $ND_4^+$ tetrahedra slightly distorted and randomly distributed on a f.c.c. sub-lattice. The short range order which establishes on lowering temperature also reflects correlations in atomic displacements.

## 2. Experimental details and results.

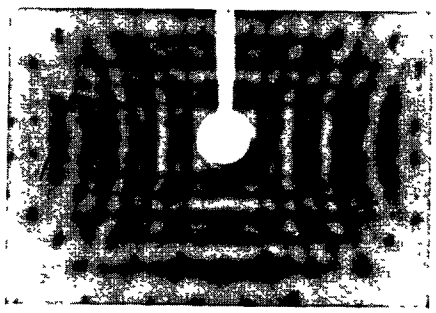
Deuterated single crystals are required for coherent neutron scattering experiments. Two samples ($\sim 0.5$ cm$^3$) have been investigated at $x = 0.42$ and $x = 0.62$. They were grown from aqueous solutions by Haussühl at the Universität zu Köln with nominal concentrations $x = 0.5$ and 0.75. The true ammonium contents were determined afterwards by estimating the mass fraction of nitrogen atoms from small pieces (see Ref. [9]).

X-RAY DIFFRACTION. — X-ray investigations were performed with the Mo $K_\alpha$ ($\lambda = 0.711$ Å) radiation after a (002) reflection on a simply bend graphite monochromator. Two crystals of size ($3.2 \times 1.3 \times 0.7$ mm$^3$) and ($2 \times 2 \times 0.3$ mm$^3$) were studied, the latter being thinned by ethanol. The crystals were attached on the cold tail of a displex cryocooler and were cooled down to about 20 K. Figure 1 displays the x-ray patterns taken at 300 K, 70 K and 20 K from the second sample with the normal to the platelet ([001] direction) parallel to the x-ray beam.

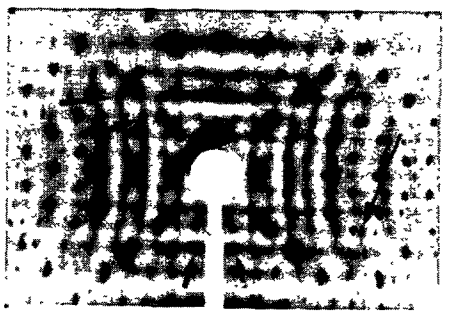
As shown in figure 1c, strong diffuse scatterings at the f.c.c. forbidden ($h$, $k$, $\ell$) positions (X-point of the zone boundary) are clearly visible at low temperatures. More precisely, three types of scattering are present at positions $\mathbf{Q}_B + \mathbf{q}_{ZB}$, where $\mathbf{q}_{ZB}$ is $2\pi/a(1, 0, 0)$,



a)



b)



c)

Fig. 1. — X-ray patterns taken at 300 K (a), 70 K (b) and 20 K (c). The $c$ axis is along the x-ray beam, and the $b$ axis is vertical. On the low-temperature photographs the thin arrows point toward the $(\bar{7}, 3, 4) = (\bar{7}, 3, 3) + (0, 0, 1)$ scatterings, medium arrows toward the $(4, \bar{3}, 1) = (3, \bar{3}, 1) + (1, 0, 0)$ and the $(5, \bar{4}, 2) = (4, \bar{4}, 2) + (1, 0, 0)$ ones, and the small arrows toward the $(1, \bar{4}, 1) = (1, \bar{3}, 1) + (0, 1, 0)$ scatterings.

$2\pi/a(0, 1, 0)$ or $2\pi/a(0, 0, 1)$, $\mathbf{Q}_B$ the position of the Bragg spot and $a$ the lattice parameter ($a \approx 7.1$ Å). In figure 1 the arrows point toward diffuse peaks of each type. The diffuse scattering decreases rapidly below 50 K, but it is still observable at higher temperatures, down to 100 K (although superimposed to the diffuse thermal scattering). As shown in figure 1, the diffuse patterns are thinner in one direction, but the confirmation of strong anisotropy observed by neutrons (see below) would demand a more thorough x-ray study.

COHERENT ELASTIC NEUTRON SCATTERING. — The measurements were performed at the Laboratoire Léon Brillouin on a triple axis spectrometer installed on the thermal source of the Orphée reactor. The (graphite-filtered) wave-vector of 2.66 $Å^{-1}$ was selected for the incident neutrons. In its standard configuration, the neutron spectrometer is mounted with a double (PG002) monochromator, a PG002 analyser and with horizontal collimations fixed at -/-/-/60/60, equivalent to a simple monochromator with -/23/60/60. In order to observe diffuse scattering, the spectrometer was utilized at zero energy transfer with an energy resolution $\Delta E = 280\ GHz$. This last quantity is important since collective excitations characterized by correlation times longer than $h/\pi\ \Delta E \sim 1$ ps will appear as frozen. The measured elastic scattering intensity $I(\mathbf{Q}, \omega = 0)$ is then the folding of the dynamical structure factor $S(\mathbf{Q}, \omega = 0)$ integrated over the energy $\Delta E$ with the resolution function.

In the chronology of this work, neutron scattering were carried out prior x-ray diffraction. This is the converse to what is usually done in the search for spatial correlations. This can be explained easily : At the origin of this work, the idea was to search for anomalies in the dispersion curves of $K_{1-x}(ND_4)_xI$ mixed crystals, and actually anomalies in the dynamics were evidenced. The transverse acoustic phonon exhibits a relaxation behavior due to its coupling with the rotational modes of the ammonium ions. However scanning in energy at the Brillouin zone-boundary also revealed a quasi-elastic central peak strongly temperature dependent. It was hence logicial to check that this dynamical central peak condenses at low temperatures, resulting in diffuse scattering. A complete discussion of the dynamical aspect of the reorientations in $K_{1-x}(ND_4)_xI$ has been given recently [10].

*Wave-vector dependence.* — Elastic scattering measurements in the reciprocal $(h, k, 0)$-plane have evidenced diffuse patterns in the neighborhood of antiferroelectric points with $h + k$ odd [4]. They correspond to the X-boundary points, that is for reduced wave-vector $q^* = aq_{ZB}/2\ \pi = 1$. The location and contour of the diffuse peaks which have been indeed measured by neutron are schematically drawn in figure 2. These peaks were obtained at different $q_{ZB}$-values of the $(h, k, 0)$-plane for $T \sim 10$ K and $x = 0.42$. Their elongated shapes are discussed below.

Figures 3 and 4 show the diffuse peaks more in detail around $\mathbf{Q} = (2, \bar{1}, 0)$ for $x = 0.42$ and $x = 0.62$, respectively. The «$\lambda/2$»-contamination arising from the $Q = (4, \bar{2}, 0)$-Bragg peak has been carefully checked and avoided using graphite filters on incident and scattered beams. Both figures are constructed in a similar way : in the upper part maps of $I(Q)$ are plotted in the $\ell = 0$-plane whereas in the lower part, the contours of equi-intensity are drawn in the vicinity of the AFE wave-vector. In order to distinguish clearly the coherent diffuse signal in the $x = 0.42$-sample, room-temperature $I(\mathbf{Q})$ has been subtracted. Such a calculation was not necessary for $x = 0.62$, the diffuse signal being enhanced of more than one decade (indeed, due to experimental reasons, an absolute comparison between peaks of Figs. 3 and 4 cannot be achieved precisely).

For both compositions however, the diffuse intensity looks similar : it is characterized by a cigar-shaped pattern elongated in the h-direction. In the perpendicular direction, no broadening could be detected compared to the wave-vector resolution ($\Delta q_{res} = 0.035\ Å^{-1}$, FWHM).

*Temperature evolution.* — In figure 5 for $K_{0.38}(ND_4)_{0.62}I$ are displayed the elastic spectra performed in the $k$-direction around $\mathbf{Q} = (1, 2, 0)$ at several temperatures between 9 K and 68 K. Subtraction of the room-temperature incoherent scattering explains the Q-independent background of each spectrum. As illustrated in figure 5, the diffuse contribution merges typically below ~ 60 K.

An other way to show the strong increase of the diffuse scattering with lowering T consists in measuring the neutron counts at a given AFE point and to scan the temperature. The results are

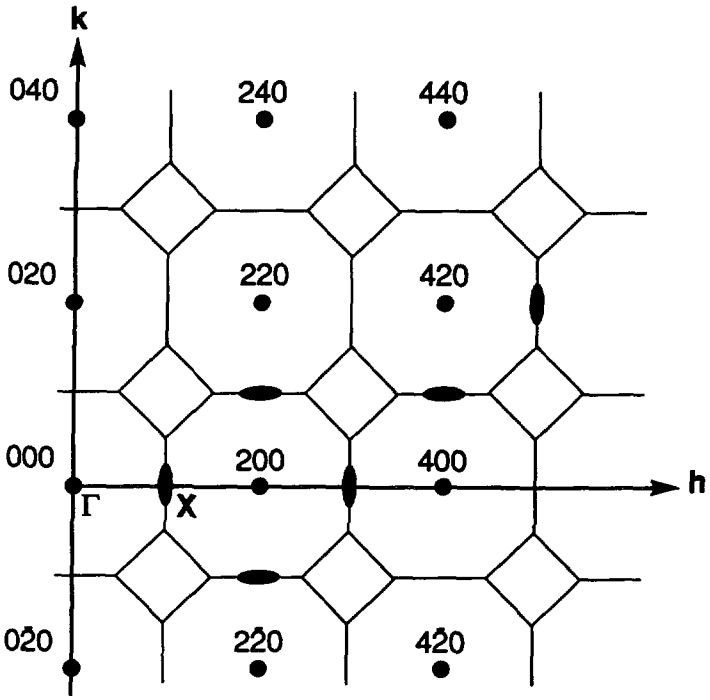


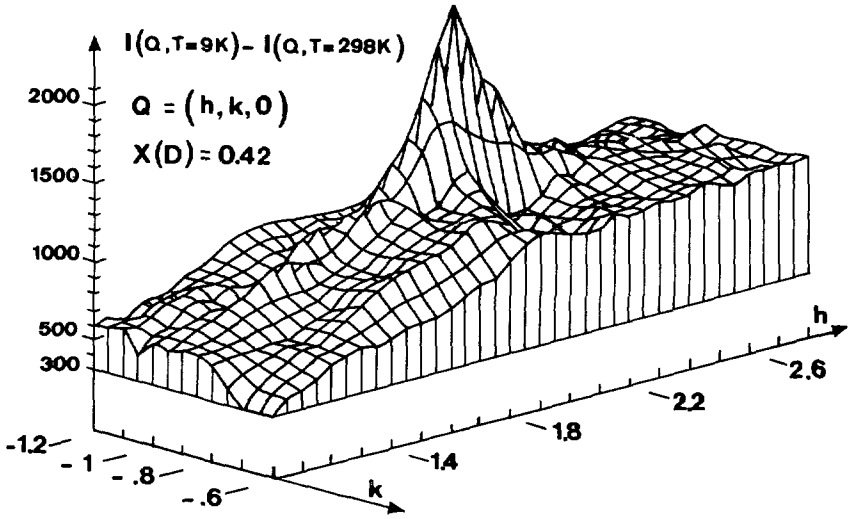

Fig. 2. — Location of the diffuse peaks (shaded ellipses) in the ($h$, $k$, 0) reciprocal plane obtained by coherent elastic neutron scattering on a $K_{0.58}(ND_4)_{0.42}I$ single crystal ($T \sim 10$ K).

shown in figure 6 at wave-vectors $\mathbf{Q} = (4, 1, 0)$ and $\mathbf{Q} = (2, 1, 0)$ for $x = 0.42$ and $x = 0.62$, respectively. Defining the freezing temperature as the temperature at which the spatial correlations develop, one gets $T_F = 34 \pm 2$ K and $T_F = 58 \pm 2$ K. Note that the absolute intensity is strongly Q-dependent, however the relative temperature evolution has been checked to be the same for different $\mathbf{Q}_B + \mathbf{q}_{ZB}$. An other important result of figure 5 is that the increase of the diffuse scattering occurs continuously and without hysteresis effect (as usually revealed for the structural changes above $x_c$ [5]). Within the accuracy of the neutron detection, no discontinuity could be observed at $T_F$.

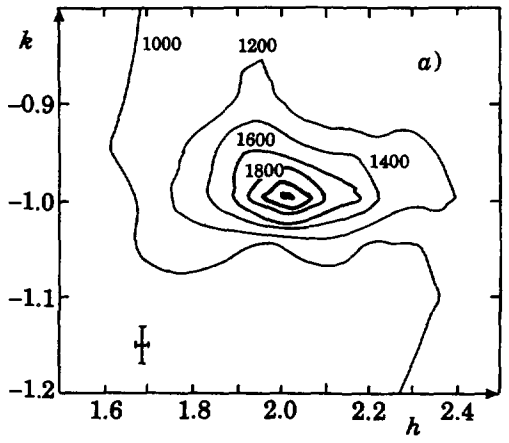
### 3. Analysis and discussion.

In the present discussion, we first provide a detailed analysis of the neutron data collected on the $K_{0.38}(ND_4)_{0.62}I$ crystal and then compare the results with the x-ray patterns of figure 1 as well as with earlier reports. For instance, $K_{1-x}(ND_4)_xI$ systems exhibit strong similarities with the $Rb_{1-x}(NH_4)_xH_2PO_4$ proton glass [11]. Extensively studied during the last decade, this mixed compound is considered as a model for competing interactions yielding a degenerated groundstate (and related to site disorder within the hydrogen bound network). Diffuse peaks are also present, but they appear at wave-vector $q^* \sim 1/3$ from the zone center [12].

*Analysis of the neutron spectra.* — In order to shed some light on the dipolar freezing process, both temperature and wave-vector variations of the short range correlations have been examined. In a first approximation, an Ornstein-Zernicke (OZ) profile has been utilized. An




a)




b)

Fig. 3. — a) Map of the elastically scattered neutron intensity around $\mathbf{Q} = (2, \bar{1}, 0)$ in $K_{0.58}(ND_4)_{0.42}I$ taken at 10 K. b) Equi-intensity contour related to the diffuse peak shown in a). The wave-vector resolution is given by the cross. Both figures exhibit the strong anisotropy in the direction perpendicular to the AFE wave-vector $\mathbf{q}_{ZB}$.

expression of the form [13] :

$$S(q) = \frac{I_{ZB}/\xi^2}{(q - q_{ZB})^2 + 1/\xi^2} \tag{1}$$

was considered, where $(q - q_{ZB})$ denotes the distance from the next $X$ points in the direction of anisotropy and $\xi$ the correlation length. According to the OZ assumption, the maximum intensity $I_{ZB}$ in equation (1) is expected to vary quadratically with $\xi$. The data analysis consisted in calculating the scattered intensity by folding the four-dimensional resolution

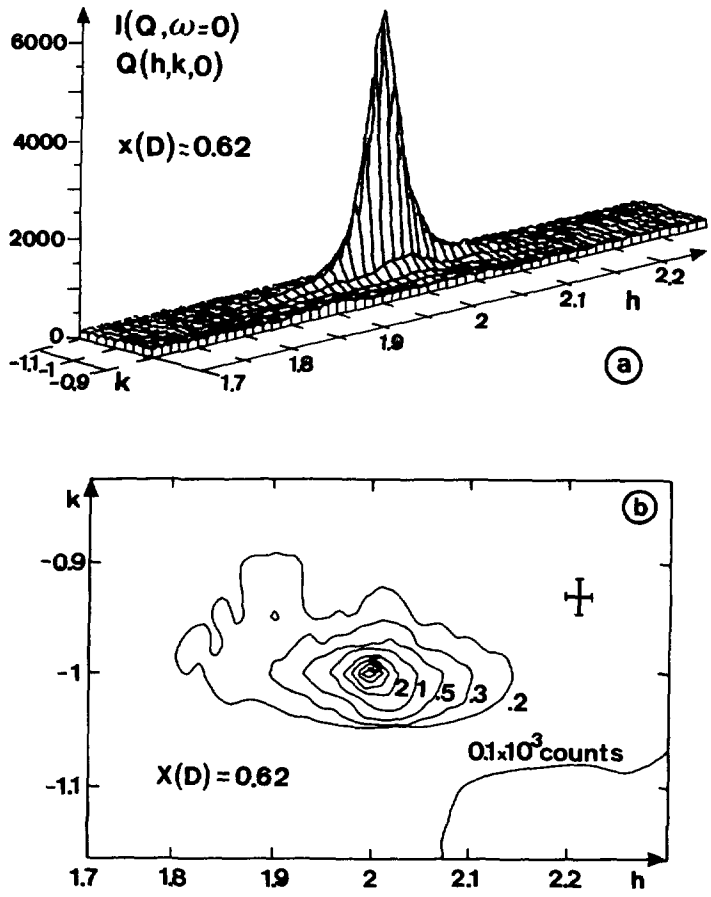



Fig. 4. — As in figure 3, but for the $K_{0.38}(ND_4)_{0.62}I$ single crystal.

function of the spectrometer with $S(q)$ in equation (1). Treating $I_{ZB}$ and $\xi$ as fitting parameters, the results of the convolution accounts well for the AFE diffuse peaks, as those displayed in figure 5 for Q = (1, 2, 0). The inverse width received from best fit calculations is shown as function of temperature in figure 7. $\xi$ increases on cooling but saturates at a value of about 10 lattices parameters – $\xi(T = 10\ K) = 62$ Å. This value is much larger that the correlation length found in the $x = 0.42$ crystal [4], which does not exceed 2 lattice cells at comparable temperatures. It should be emphasized that in the perpendicular direction, the AFE correlations are at much longer range (say, more than ~ 200 Å) but cannot be resolved within the present experiments.

As mentioned above, a $I_{ZB} \propto \xi^2$-variation is expected from the OZ approximation. This behavior has been tested by eliminating the temperature from the $I_{ZB}(T)$ and $\xi(T)$ dependences (Figs. 6 and 7). The result shown in figure 8 indicates well an increase of $I_{ZB}$ with increasing $\xi$. However, a closer inspection reveals two different regimes : below $\xi \leqslant 30$ Å, this increase is nearly linear, and above it goes typically as $\xi^3$ (shown by solid line). The observation of power laws in the $I_{ZB}(\xi)$ variation can be interpreted in terms of nucleation process characterized by $\xi(T)$ as unique scaling length. The cubic dependence observed for $\xi \geqslant 30$ Å in figure 8 is typical for coalescence phenomena [14]. Although these results are qualitative, they could indicate different physical processes in the growth of correlations, one

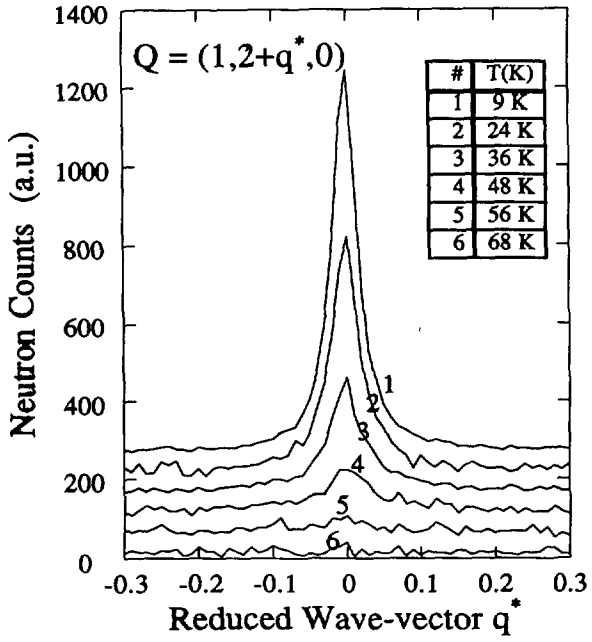



Fig. 5. — Elastic neutron spectra at $x = 0.62$ and performed in the k-direction around $\mathbf{Q} = (1, 2, 0)$ at several temperatures between 9 K and 68 K. The room-temperature incoherent scattering has been subtracted in order to get a $\mathbf{q}^*$-independent background. The diffuse contribution merges below $T_F = 58$ K.

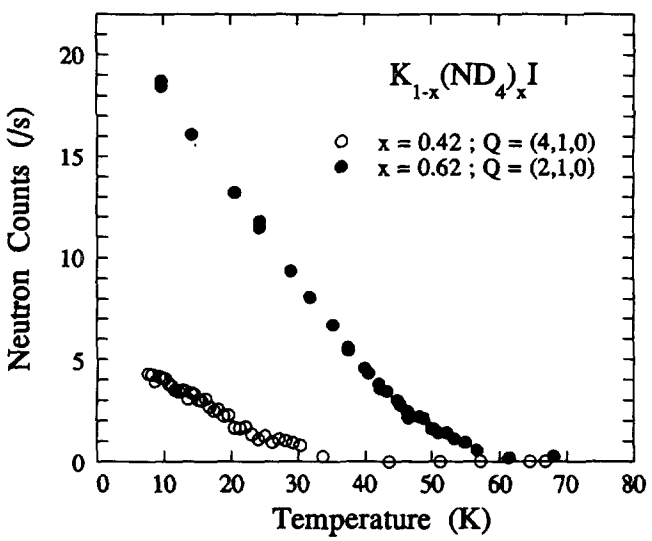



Fig. 6. — Temperature dependences of the diffuse intensities $I_{ZB}$ at wave-vector $\mathbf{Q} = (4, 1, 0)$ and $\mathbf{Q} = (2, 1, 0)$ for $x = 0.42$ and $x = 0.62$, respectively. Note that the increase of the diffuse scattering occurs continuously and without hysteresis effect.

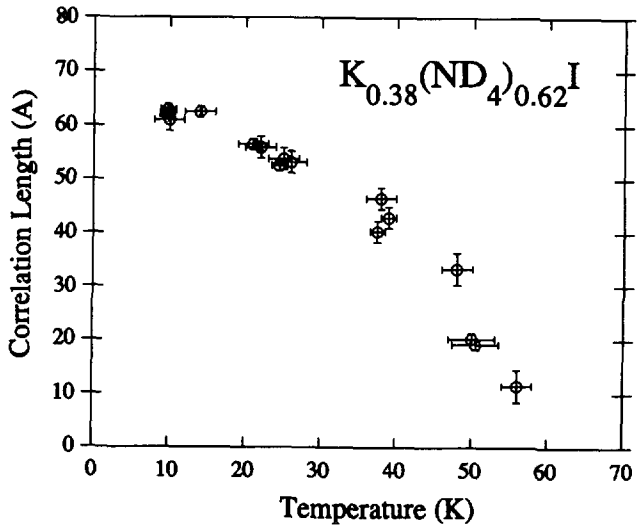



Fig. 7. — Correlation lengths as a function of temperature in $K_{0.38}(ND_4)_{0.62}I$. The $\xi$-values are results of best fit calculations using an Ornstein-Zernicke assumption (Eq. (1)) which accounts well for the diffuse profiles. $\xi$ saturates as $T \to 0$ K at a value of about 10 lattice parameters, $\xi \sim 62$ Å.

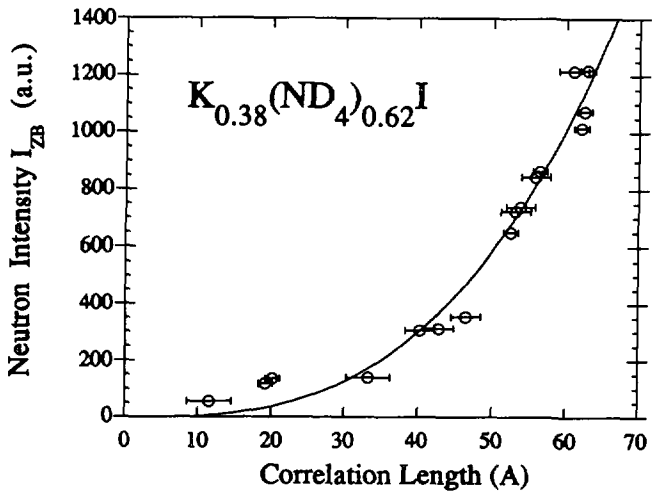



Fig. 8. — Variation of the zone-boundary diffuse intensity $I_{ZB}$ (see Eq. (1)) for $x = 0.62$ as a function of the correlation length $\xi$. The observation of a power laws $I_{ZB} \propto \xi^3$ above 30 Å could indicate a coalescence phenomenon in the correlation growth processes [14].

occuring near the freezing, the second at much lower $T$. More experimental informations are obviously needed to verify this assumption.

*Comparison between x-ray and neutron scattering.* — The x-ray and neutron data on the $K_{0.38}(ND_4)_{0.62}I$ crystal are consistent with each other. Both experiments establish the occurence at low temperatures of strong diffuse scattering at the X-point of the Brillouin zone. Nevertheless, as the x-ray scattering is roughly proportional to the square of the atomic number of the constituents, the contribution of the light elements such as deuterium or nitrogen and

thus that of the $ND_4^+$ dipoles, is almost negligible. This remark rules out the possibility of a pure ordering of the $ND_4^+$ species without displacements of one (or several) atom(s) away from its face-centered position. Such a conclusion could not be derived from the neutron results only, the coherent scattering length of the four elements involved being comparable (from 0.37 for $K^+$ to 0.94 for $D^+$). Moreover, since the iodide ions are the strongest x-ray scatterers, we suggest that displacement modes of the $I^-$ species are most likely involved in the freezing. The possibility of off-center displacements in the plastic phase of $NH_4I$ was already speculated by Seymour and Pryor [7].

Finally, it cannot be decided from the x-ray measurements whether the modulated patterns are static or dynamic. This is because all the dynamical modes with wave-vector $\mathbf{q}_{ZB}$ contributes to the cross-section. This could explain the persistence of the diffuse signal above $T_F$, as revealed on the x-ray photograph at 70 K (Fig. 1b). It corroborates indirectly the dynamical nature of the freezing in $K_{0.38}(ND_4)_{0.62}I$.

*Comparison with dielectric data.* — It is also of importance to test that the onset of short-range ordering coincides with the dipolar freezing probed by dielectric spectroscopy [3]. From dielectric loss measurements on $K_{0.57}(NH_4)_{0.43}I$, it was concluded that the temperatures of maximal absorption relate to the frequency of measurements through the usual Arrhenius law, $\nu = \nu_0 \exp(E_a/k_B T)$, with an attempt frequency $\nu_0 = 10^{26}$ Hz and an activation energy $E_a = 460$ K. An extrapolation of the above expression at $\nu = 280$ GHz yields $T_F \sim 14$ K, in clear contradiction with the results of figure 6. For the deuterated crystal at comparable $x$, the onset of freezing is estimated at $T_F = 34$ K and the same $T_F$-value was derived for an $x = 0.43$ protonated sample studied by Raman scattering [9]. This discrepancy could have two explanations : first, in reference [3], the Arrhenius law is determined on a temperature range which does not exceed 1 K ! Second, and this is surely more fundamental, the dielectric experiment measures a macroscopic susceptibility averaged on the whole crystal, that is at wave-vector $q \ll 2\pi/a$. Contrary to that, the anomaly revealed in the $K_{1-x}(ND_4)_xI$ system is a local ordering process at the Brillouin zone boundary, at $q = 2\pi/a$.

## 4. Concluding remarks.

Diffuse scattering patterns obtained using x-ray and neutron measurements have been shown to characterize the low-temperature phase of $K_{1-x}(ND_4)_xI$ with $x < x_c$. The essential features of the diffuse signal are the followings :

i) It peaks below $T_F$ at the zone-boundary X-point (i.e. at $\mathbf{Q}_B + \mathbf{q}_{ZB}$) and forms cigar-shaped contours elongated in the direction orthogonal to $\mathbf{q}_{ZB}$.

ii) The diffuse intensity does not diverge as $T \to 0$ K. This means that no macroscopic change in the crystal symmetry occurs down to the lowest $T$ investigated. However, on a local scale, the fcc symmetry is broken through the short-range correlations. Note that the absence of saturation in the diffuse scattering suggests that at such low temperature as ~ 10 K the $ND_4^+$ dynamics is not completly frozen in.

iii) It is plausible that static displacements of one or several atoms away from the lattice sites (most probably the iodide ions) are involved in the freezing. This is a crucial result for the KI : $ND_4I$ dipolar glass. It appears as a direct consequence of the different x-ray and neutron scattering cross-sections. These findings rule out the assumption of an electric dipole moment in $K_{1-x}(ND_4)_xI$ solely due to the distortions of the H-N-H angles, as originally believed [2]. Accordingly, static disorder might also increase the value of the bare dipole of the $ND_4^+$ groups.

iv) The freezing of the dipolar degrees of freedom is a dynamical process.

Measurements of the diffuse structure factor as function of Q in the whole reciprocal space

are underway in order to fully characterize the structural aspects of the freezing and of the dipolar glass state.

**Acknowledgments.**

It is a pleasure to acknowledge K. H. Michel, C. Bostoen and M. Descamps for fruitful discussions. We also wish to thank Jean-Pierre Fluxench for the drawings.

## References

[1] HÖCHLI U., LOIDL A. and KNORR K., *Adv. Phys.* **39** (1990) 405.
[2] BOSTOEN C., CODDENS G. and WEGENER W., *J. Chem. Phys.* **91** (1989) 6337.
C. Bostoen, Ph. D. Thesis, Univerity of Antwerpen (1991), unpublished.
[3] FEHST I., BÖHMER R., OTT W., LOIDL A., HAUSSÜHL S. and BOSTOEN C., *Phys. Rev. Lett.* **64** (1990) 3139.
[4] BERRET J.-F., BOSTOEN C., SAUVAJOL J.-L., HENNION B. and HAUSSÜHL S., *Europhys. Lett.* **16** (1991) 91.
[5] PARSONAGE N. G. and STAVELEY L. A. K., Disorder in Crystals (Oxford, Oxford University Press, 1978).
[6] BERRET J.-F., BRUCHHÄUSER F., FEILE R., BOSTOEN C. and HAUSSÜHL S., *Solid State Commun.* **74** (1990) 1041.
[7] SEYMOUR R. S. and PRYOR A. W., *Acta Cryst.* **B 26** (1970) 1487.
[8] TOMKINSON J., DASANNACHARYA B. A., GOYAL P. S. and CHAKRAVARTHY R., *J. Chem. Soc. Faraday Trans.* **87** (1991) xxx.
[9] BERRET J.-F., SAUVAJOL J. L. and HAUSSÜHL S., *J. Chem. Phys.* **92** (1992) 4896.
[10] BERRET J.-F., SAUVAJOL J.-L. and HENNION B., *J. Phys. . Cond. matter* **4** (1992) 9235.
[11] For a review, see : GRIMM H., ILL-Workshop on Dynamics of disorderd Materials (Springer-Verlag, 1988) p. 274.
[12] COWLEY R. A., RYAN T. and COURTENS E., *J. Phys. C* **18** (1985) 2793.
GRIMM H. and MARTINEZ J., *Z. Phys. B* **13** (1986) 64.
[13] STANLEY H. E., Introduction to Phase Transitions and Critical phenomena (Oxford University Press, 1971).
[14] DESCAMPS M. and CAUCHETEUX C., *J. Phys. C* **20** (1985) 5073.