E14-2001-171

I.Natkaniec[1], A.-J.Dianoux[2], M.L.Martinez Sarrion[3], L.Mestres[3], M.Herraiz[3], L.S.Smirnov[4], L.A.Shuvalov[5]

INFLUENCE OF CONCENTRATION AND TEMPERATURE ON TUNNELING AND ROTATIONAL DYNAMICS OF AMMONIUM IN $Rb_{1-x}(NH_4)_xI$ MIXED CRYSTALS

Submitted to «Ferroelectrics»

---

[1]On leave from H.Niewodniczanski Institute of Nuclear Physics, 31-342 Krakow, Poland
[2]Institute Laue–Langevin, 156X, 38042 Grenoble Cedex, France
[3]Inorganic Chemistry Department, University of Barcelona, Spain
[4]SSC RF Institute of Theoretical and Experimental Physics, 117259 Moscow, Russia
[5]Institute of Crystallography RAS, 117333 Moscow, Russia

1. INTRODUCTION

Ammonium-alkaline metal halides are known to have a complex x-T phase diagram [1,2]. At low temperatures the diagram has a dynamic orientational disordered α-phase in the region of small ammonium concentrations, an orientational glass state in the region of medium ammonium concentrations, and orientational ordered phases [3-8] at high ammonium concentration. With increasing ammonium concentration the NH_4^+-NH_4^+ interaction affects the barrier that controls the reorientation of ammonium ions and it also influences the dynamic properties of different phases.

The ammonium dynamics and structural phase transitions in $Rb_{1-x}(NH_4)_xI$ mixed crystals were earlier studied at 20 K in the concentration region $0.01 \le x \le 0.66$ [9] to compare them with the ammonium dynamics and structural phase transitions in $K_{1-x}(NH_4)_xI$. This revealed some difference that could be due to the inner strain in $K_{1-x}(NH_4)_xI$ as the ionic radius of ammonium is bigger than that of potassium and is approximately equal to the ionic radius of rubidium. The results presented in the papers [9] and [10] show that in general, the translational and librational ammonium dynamics in $Rb_{1-x}(NH_4)_xI$ and $K_{1-x}(NH_4)_xI$ is similar. However, the temperature of 20 K was to high for observation of the tunneling transitions and the resolution of the used spectrometer NERA-PR [11] at the IBR-2 high flux pulsed reactor (JINR, Dubna) was to low for investigations of the quasielastic incoherent neutron scattering (QINS) in more details.

In this paper we present the results of tunneling transitions and the QINS investigations of $Rb_{1-x}(NH_4)_xI$ performed on the IN6 spectrometer at the HFR ILL at Grenoble in the temperature range of 5 - 150 K.

2. EXPERIMENT AND RESULTS

Samples of $Rb_{1-x}(NH_4)_xI$ mixed crystals with the concentration x=0.01, 0.02, 0.06, 0.16, 0.40, 0.50, and 0.66 are prepared by evaporation of corresponding stoichiometric aqueous solutions. The inelastic incoherent neutron scattering (IINS) spectra are measured on the NERA-PR time-of-flight inverted-geometry neutron spectrometer in FLNP, JINR, Dubna, Russia [11] and the IN6 time-of-flight neutron spectrometer in ILL, Grenoble, France [12]. In NERA-PR the scattered neutron energy is determined with a pyrolitic graphite crystal-analyzer with λ_o=4.15 Å and the elastic peak resolution $\delta E \approx 0.66$ meV. In IN6 measurements the incident neutron wavelength λ_o=5.12 Å, the resolution $\delta E \approx 0.10$ meV, and the detectors cover the scattering angle from 13.2° to 104.77°. The detectors are divided into eight groups, which makes it possible to obtain the S(Q,E)–scattering law for the scattering vectors Q=0.282, 0.489, 0.736, 0.951, 1.164, 1.469, 1.730, and 1.943 $Å^{-1}$.

For illustration, the QINS spectra of $Rb_{1-x}(NH_4)_xI$ measured with NERA-PR for the ammonium concentration x=0.06, 0.16, 0.40, and 0.66 at 20 K in the energy transfer region $-3 \le x \le 3$ meV are shown in Fig. 1a and corresponding IN6 spectra measured in the region $-2 \le x \le 3$ meV are in Fig. 1b. The intensities of the spectra (at ΔE=0) are normalized to 1 to enable a comparison of QINS spectra measured with different spectrometers.

The QINS spectra of $Rb_{1-x}(NH_4)_xI$ as a function of concentration, $0.06 \le x \le 0.66$, at 20 K in the energy transfer region $-3 < x < 3$ meV show that the quasielastic contribution increases with increasing ammonium concentration from x=0.06(o) to x=0.16(◊) and then it decreases at x=0.40(Δ) and x=0.66(-●-). This behaviour is explained by the fact that on the x–T phase diagram at 20 K, samples with x=0.06 and 0.16 are in the region of the dynamic disordered α-phase, sample with x=0.40 is in the orientational glass state, and with x=0.66 is in the ordered phase. The QINS spectra for x=0.66 measured with two spectrometers can be correspond through their resolution functions. The satellite maximums at $\Delta E \approx \pm 0.6$ meV in the QINS spectrum of IN6 for x=0.06 (Fig. 1b) correspond to rotational tunneling transitions not observed in the QINS spectrum measured with NERA-PR because the IN6 energy resolution is higher.

QINS spectra from IN6 are exemplified for two ammonium concentrations, x=0.16 (Fig. 2a) and x=0.40 (Fig. 2b), as the temperature changes from 5 to 150 K. A series of maximums is seen in the QINS spectra of the sample with x=0.16 at 5 K corresponding to inelastic neutron scattering on the rotational tunneling levels of ammonium ions. As the temperature increases tunneling transitions disappear in QINS spectra at 20 K, which corresponds to a transition of neutron scattering from quantum motion of ammonium ions to their classical motion described by jump reorientation [13].

Studies of the influence of ammonium concentrations, $0.01 \leq x \leq 0.66$, on the rotational tunneling levels of NH_4^+ in the energy transfer region $-2<x<0$ meV at 5 K are illustrated in Fig. 3. An increase of the ammonium concentration is accompanied with a modification of the tunneling levels pattern and disappearance of the tunneling levels contribution to QINS spectra. This disappearance of tunneling transitions in the QINS spectra at 5 K for x=0.40 corresponds to a transition to the concentration region of the orientational glass state on the x-T phase diagram of $Rb_{1-x}(NH_4)_xI$ mixed crystals.

The positions of the tunneling levels as a function of ammonium concentration at 5 K are determined and summarized in Table 1. If the situations of the tunneling levels for the ammonium concentration x=0.01, 0.02, or 0.06 are similar and are observed at ΔE=0.56, 0.67, 1.19, 1.38, and 1.74 meV, the new additional tunneling levels appear for the concentration x=0.16 at ΔE=0.42 and 0.93 meV. Absence of contribution from tunneling levels in the QINS spectra for the concentration x=0.40, 0.50 or 0.66 is the result of the influence of the NH_4-NH_4 collective interaction on the growth of the potential barrier to reorientations, which leads to “freezing” of orientational degrees of freedom. The areas under the maximums of the tunneling levels are determined and their ratios to the maximum area of the tunneling level with the energy E=0.56 meV are given in Table 2. The tunneling levels with the energies E=0.56, 0.67 and 1.19 are similar to the earlier observed levels for $Rb_{97.1}(NH_4)_{0.029}I$ [14].

The QINS spectra are treated on the basis of scattering law with two components: the elastic, Ie(Q)G(E), and quasielastic, Iqe(Q)L(E), where G(E) and L(E) are Gaussian and Lorenzian functions, respectively [15], Q is scattering vector and E is energy transfer. Then QINS spectra are fitted by a non-linear least-square procedure, program “Fullprof”, with the help of parameters, describing positions G(E) and L(E), intensities Ie and Iqe, and full width at half of maximum (FWHM) of L(E). An analysis of FWHM calculated for QINS spectra at each concentration and all scattering vectors as a function of temperature shows that FWHM does not depend on the scattering vector. This confirms the correctness of the decomposition of the observed QINS spectra into a G(E) function and a single Lorenzian function.

A comparison of the obtained FWHM shows that their temperature behaviour is determined by the ammonium concentration. So the FWHM(T) curves as a function of the ammonium concentration are divided into three groups: a group of FWHM(T) curves for the concentration x=0.01, 0.02, 0.06 whose slopes are close and are approximately equal to 0.0018 meV/K, a group for the concentration x=0.40, 0.50 and 0.66 with slopes close to

Table. 1. Comparison of tunneling transition energies of $Rb_{1-x}(NH_4)_xI$ mixed crystals, obtained at 5 K in present study, with the results for $Rb_{1-x}(NH_4)_xI$ [14] and $K_{1-x}(NH_4)_xBr$ [15].

Specimen	$Rb_{1-x}(NH_4)_xI$			$Rb_{1-x}(NH_4)_xI$ [14]	$K_{1-x}(NH_4)_xBr$ [15]	
x	0.01	0.02	0.16	0.029	0.005	Transition
E, meV			0.42			
	0.56	0.56	0.55	0.56	0.53	$\bar{A}_1A_1 \rightarrow \bar{T}_1T_1$
	0.67	0.68		(0.66)	0.67	$\bar{T}_1T_1 \rightarrow \bar{T}_2E,\ \bar{E}T_2$
			0.93			
	1.19	1.19	1.20	1.21	1.20	$\bar{A}_1A_1 \rightarrow \bar{T}_2E$
	1.38	1.4	1.37			
	1.74	1.74	1.72		1.70	$\bar{A}_1A_1 \rightarrow \bar{T}_2T_2$

Table 2. Relative intensities of different tunneling transitions related to the 0.56 meV tunneling transition in $Rb_{1-x}(NH_4)_xI$ mixed crystals.

		x=0.01	x=0.02	x=0.06	x=0.16
N	E, meV observed	S_i/S_2	S_i/S_2	S_i/S_2	S_i/S_2
1	0.42				0.15
2	0.56	1	1	1	1
3	0.67	0.24	0.25	0.22	
4	0.93				0.08
5	1.19	0.19	0.20	0.17	0.15
6	1.39	0.007	0.006	0.007	0.03
7	1.74	0.018	0.019	0.022	0.023

0.007 meV/K, and a FWHM(T) for x=0.16 found between two above groups of curves with an approximate slope of 0.0047 meV/K if one uses the linear approximation of experimental points. These curves are shown in Fig. 4.

The group with x=0.01, 0.02 and 0.06 is characterized by similar tunneling levels at low temperatures and lies in the region of the dynamic disordered α-phase on the x–T phase diagram. The group with x=0.16 is characterized by a modified tunneling levels pattern in comparison with that of the group with a smaller ammonium concentration. The group with x=0.40, 0.55, and 0.66 corresponds to the orientational state (x=0.40) and the region with an ordered crystalline structure (x=0.50 and 0.66). This shows that obviously, there is an intermediate concentration region (x=0.16) between the dynamic orientational disordered α-phase (x=0.01-0.06) and the region of the orientational glass state (x=0.40). The temperature curves of FWHM for different concentrations are found to be in correspondence with the concentration curves of the tunneling levels. Namely, the behaviour of the tunneling levels and the temperature dependence of FWHM for $0.01 \leq x \leq 0.06$ are similar and do not depend on the ammonium concentration. This means that IINS spectra for $0.40 \leq x \leq 0.66$ do not have contributions from the tunneling transitions and their temperature dependence slopes are similar. However, for x=0.16 an intermediate situation is observed when the described properties vary between the properties characteristic for these limited concentration regions.

Reorientations of ammonium ions is described through the elastic incoherent structure factor EISF(Q) determined as a ratio of elastic scattering Ie(Q) to elastic scattering Ie(Q) plus quasielastic scattering Iqe(Q) [16], i.e.,

$$EISF(Q) = Ie(Q)/(Ie(Q) + Iqe(Q)),$$

The EISF(Q) temperature curves are calculated for all ammonium concentrations and an analysis of the curves makes it possible to identify their three general types. The first type of the observed EISF(Q) is presented in Fig. 5a and characterizes the $Rb_{1-x}(NH_4)_xI$ mixed crystals with x in the region from 0.01 to 0.16, the second type is illustrated in Fig. 5b for x=0.40, and the third one is in Fig. 5c being similar for x=0.50 and 0.66. It is worth noting that the scattering vector region where EISF(Q) are obtained is not sufficient for the determination of an axis around which ammonium ions reorient contributing to quasielastic scattering. The temperature curves for the observed three types of EISF(Q) are, however, different and image the properties of different concentration regions on the x–T phase diagram of $Rb_{1-x}(NH_4)_xI$ mixed crystals. Thus, they can be used for the identification of concentration regions on the x–T phase diagram of $Rb_{1-x}(NH_4)_xI$ mixed crystals.

3. DISCUSSION AND CONCLUSIONS

The results of a recent study of the ammonium ion dynamics in the $Rb_{1-x}(NH_4)_xI$ mixed crystals in the concentration region $0.01 \leq x \leq 0.66$ at the temperature region from 5 to 150 K obtained by quasielastic incoherent neutron scattering (QINS) on the IN6 neutron spectrometers are presented. Interesting concentration dependence curves of the tunneling levels in mixed crystals at 5 K are obtained. The tunneling levels for the ammonium

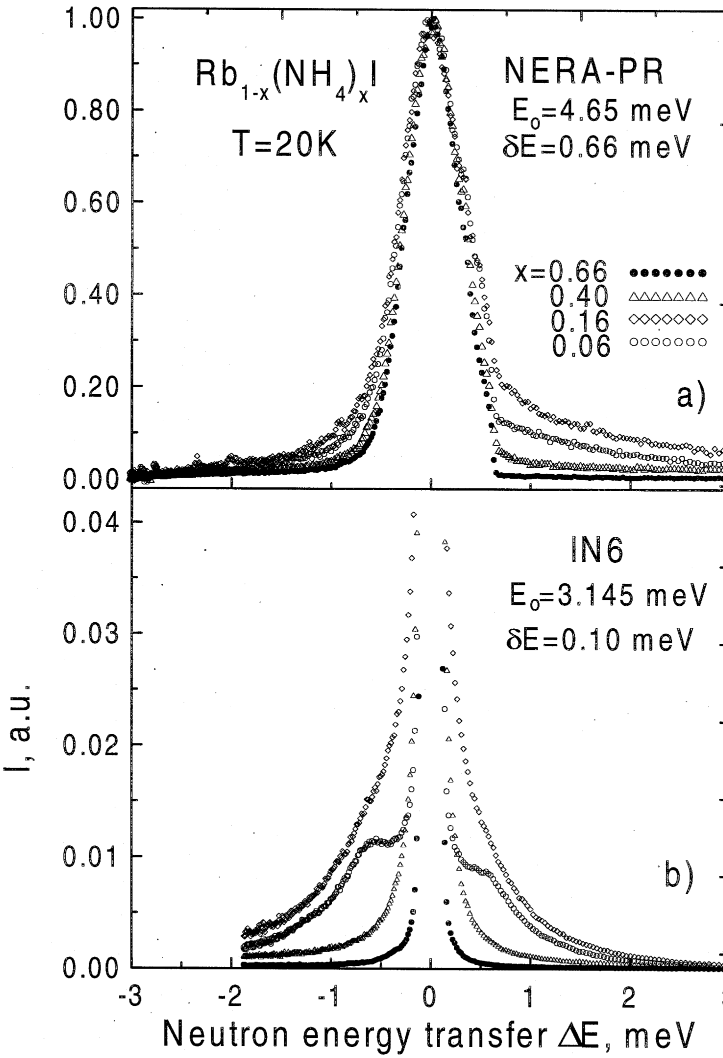

Fig. 1. Quasielastic incoherent neutron scattering (QINS) spectra of $Rb_{1-x}(NH_4)_xI$ mixed crystals measured with neutron spectrometers at 20 K: (a) - NERA-PR and (b) - IN6.

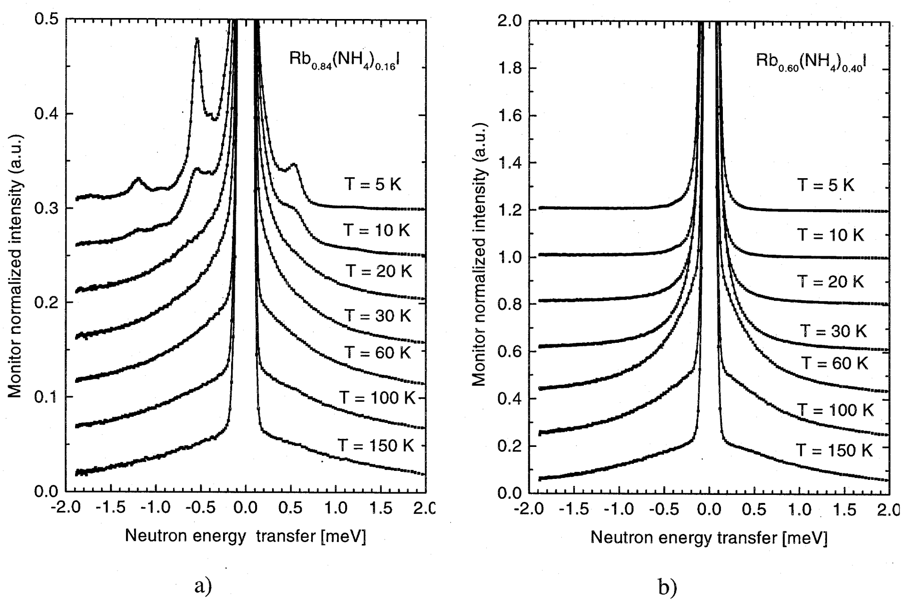

Fig. 2. Quasielastic incoherent neutron scattering spectra of $Rb_{1-x}(NH_4)_xI$ as a function of temperature: (a)-x=0.16, (b)-x=0.40 (measured on IN6 spectrometer).

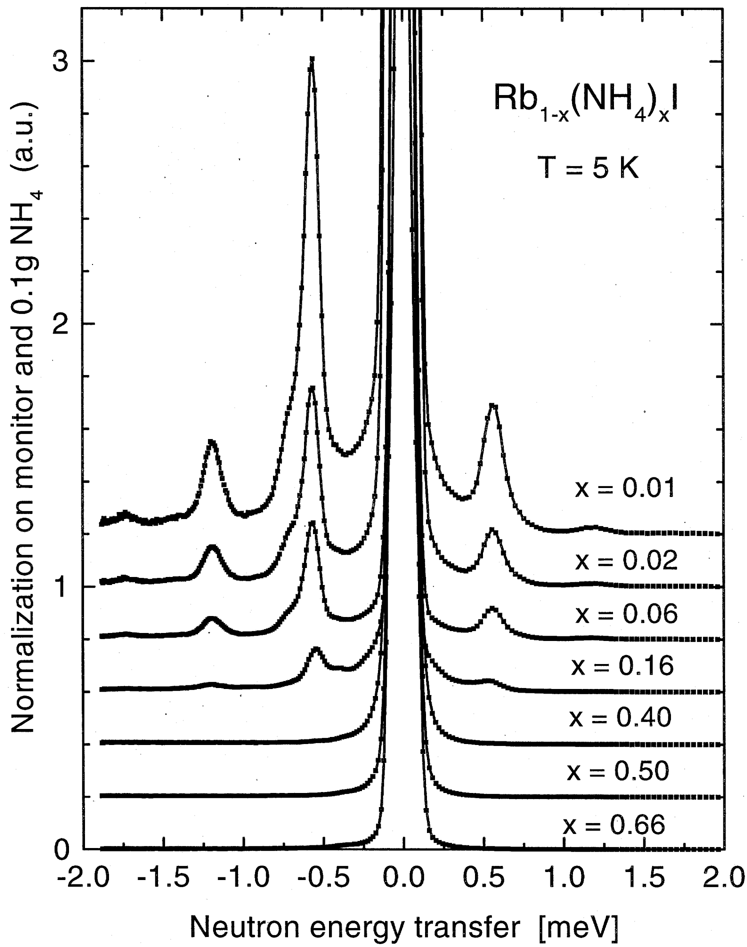

Fig. 3. Tunneling spectra of $Rb_{1-x}(NH_4)_xI$ as a function of ammonium concentration at 5 K (measured on IN6 spectrometer).

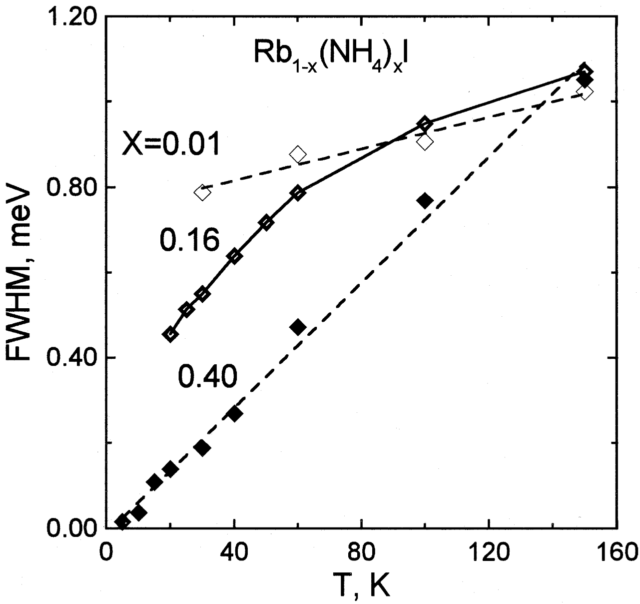

Fig. 4. FWHM temperature dependence of quasielastic reflections for $Rb_{1-x}(NH_4)_xI$ (x=0.01, 0.16 and 0.40).

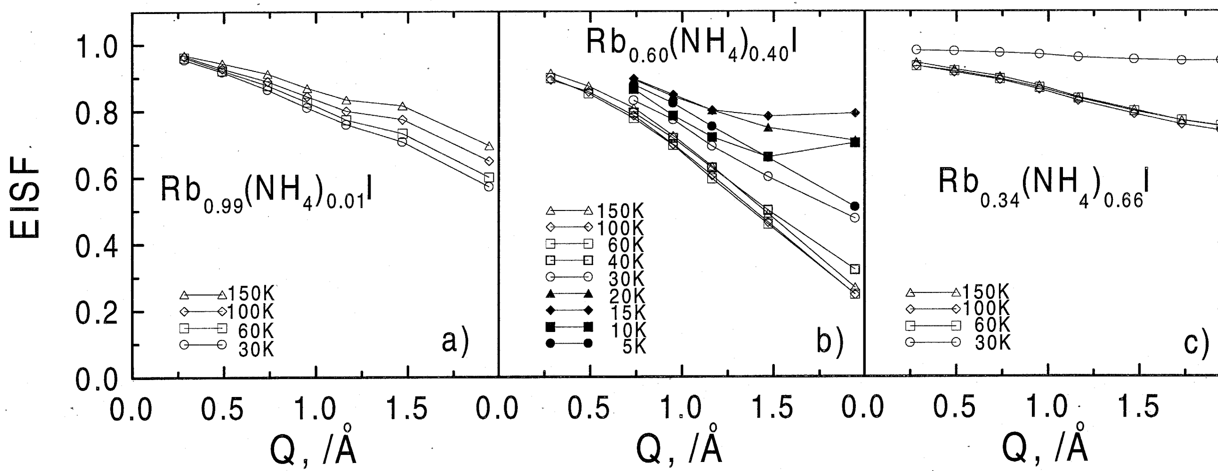

Fig. 5. EISF(Q) temperature curves of $Rb_{1-x}(NH_4)_xI$ (a-x=0.01, b-x=0.40, c-x=0.66).

concentration x=0.01, 0.02, and 0.06 are similar and almost all tunneling levels can be described by the levels observed in $K_{1-x}(NH_4)_xBr$ with x=0.005 and described in [17]. The comparison is illustrated in Table 1. The first three levels observed in this study were earlier observed in $Rb_{1-x}(NH_4)_xI$ with x=0.0029 [14].

An increase of the ammonium concentration is accompanied with a change of the tunneling level pattern. For example, for x=0.16 two additional levels appear at ΔE=0.42 and 0.93 meV. The change of the tunneling level patterns may result from formation of clusters with two adjacent ammonium ions in mixed crystal. This leads to the new specific splitting of T-states [18]. Then, clusters with three adjacent ammonium ions, whose interaction changes the tunneling level pattern, form in mixed crystals [19]. Finally, at some ammonium concentrations tunneling transitions cannot arise because an increase in the ammonium concentration is accompanied with the growth of the barrier to reorientation and the orientational degrees of freedom of ammonium ions "freeze" forming the orientational glass state.

The observed dependence of the tunneling levels in $Rb_{1-x}(NH_4)_xI$ mixed crystals on the ammonium concentration shows that a transition from dynamic orientational disordered to orientational glass state region takes place in the medium concentration region which is characterized by clusters with different tunneling levels and will be investigated in detail in near future.

Quasielastic incoherent neutron scattering results obtained for $Rb_{1-x}(NH_4)_xI$ mixed crystals in the concentration region $0.01 \leq x \leq 0.66$ at 5 to 150 K show that such characteristics of QINS as FWHM and EISF(Q) are specific for different concentration regions which are the dynamic orientational disorder region, static orientational disorder (orientational glass state) region, and the orientational order region.

Acknowledgments

The authors thank Mr. S.Jenkins for technical assistance and Dr.G.Cicognani for useful discussions.

References:

1. R.J.Havighurst, E.Mack Jr. and F.C.Blake, J.Am.Chem.Soc., **47**, 29 (1925).
2. P.Brauer and I.R.Jahn, Z.Naturforsch., **33**a, 1093 (1978).
3. I.Fehst, R.Bohmer, W.Ott, A.Loidl, S.Haussuhl and C.Bostoen, Phys.Rev.Lett., **64**, 3139 (1990).
4. J.F.Berret, C.Bostoen and B.Hennion, Phys.Rev., B **46**, 13747 (1992).
5. M.Winterlich, R.Bohmer and A.Loidl, Phys.Rev.Lett., **75**, 1783 (1995).
6. M.Paasch, G.J.McIntyre, M.Reehuis, R.Sonntag and A.Loidl, Z.Phys., B **99**, 339 (1996)
7. M.Ohl, M.Reehuis and A.Krimmel, BENSC Experimental reports 1998, p. 150.
8. F.Guthoff, M.Ohl, M.Reehuis and A.Loidl, Physica B **266**, 310 (1999).
9. I.Natkaniec, M.L.Martinez Sarrion, L.Mestres and L.S.Smirnov, Physica B **276-278**, 294 (2000).
10. I.Natkaniec and L.S.Smirnov, Physica B **234-236**, 409 (1997).
11. I.Natkaniec, S.I.Bragin, J.Brankowski and J.Mayer, ICANS-XII, Abingdon, 1993, RAL Report 94-025, v.I, p. 89.
12. R.Scherm, C.Carlile, A.J.Dianoux, J.Suck and J.White, ILL Report 76S23S, 1976.

A.J.Dianoux, R.E.Ghosh, H.Hervet and R.E.Lechner, IN5 Program Package, Institute Laue Langevin report, 1975.
13. A.Huller and L.Baetz, In: Quantum aspects of molecular motions in solids. Ed. by H.Heidemann, A.Magerl, M.Prager, D.Richter and T.Springer, N.Y., 1987, p.2.
14. A.Heidemann, J.Howard, K.J.Lushington, J.A.Morrison, W.Press and J.Tomkinson, J.Phys.Soc.Japan, **52**, 2401 (1983).
15. F.Volino, A.J.Dianoux and H.Hervet, J.Physique, Colloq. **37**, C3-55 (1976).
16. H.Hervet, A.J.Dianoux, R.E.Lechner and F.Volino, J.Physique, **37**, 587 (1976).
17. A.Inaba, H.Chihara, J.A.Morrison, H.Blank, A.Heidemann and J.Tomkinson, J.Phys.Soc.Japan, **59**, 522 (1990).
18. M.Prager, W.Press and K.Roessler, J.Mol.Struc., **60**, 173 (1980).
19. A.Heidemann, In: Quantum aspects of molecular motions in solids. Ed. by H.Heidemann, A.Magerl, M.Prager, D.Richter and T.Springer, N.Y., 1987, p.44.

Received by Publishing Department
on August 13, 2001.

Натканец И. и др. E14-2001-171

Влияние концентрации и температуры на туннельные переходы и вращательную динамику аммония в смешанных кристаллах $Rb_{1-x}(NH_4)_xI$

Смешанные кристаллы $Rb_{1-x}(NH_4)_xI$ изучались с помощью неупругого некогерентного рассеяния нейтронов с использованием спектрометров времени пролета в концентрационной области $x-T$ фазовой диаграммы $0{,}01 \leq x \leq 0{,}66$ в температурном интервале $5 \leq T \leq 150$ K, где находятся динамически и статически ориентационно разупорядоченные фазы. Показано, что при 5 K вращательные туннельные уровни для концентраций аммония $x=0{,}01$, 0,02 и 0,06 аналогичны. Для $x=0{,}16$ наблюдались дополнительные туннельные уровни, которые могут быть объяснены как результат расщепления T-состояний за счет NH_4-NH_4-взаимодействия. Для $x=0{,}40$ туннельные уровни не наблюдались в результате образования состояния ориентационного стекла. Упругие некогерентные структурные факторы для концентраций $0{,}01 \leq x \leq 0{,}16$ (динамически ориентационно разупорядоченная α-фаза), $x=0{,}40$ (состояние ориентационного стекла) и $0{,}50 \leq x \leq 0{,}66$ (ориентационно упорядоченное состояние) имеют разные температурные зависимости.

Работа выполнена в Лаборатории нейтронной физики им. И.М.Франка ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна, 2001

Natkaniec I. et al. E14-2001-171

Influence of Concentration and Temperature on Tunneling and Rotational Dynamics of Ammonium in $Rb_{1-x}(NH_4)_xI$ Mixed Crystals

The $Rb_{1-x}(NH_4)_xI$ mixed crystals are studied by inelastic incoherent neutron scattering using time-of-flight spectrometers in the concentration region of the $x-T$ phase diagram $0.01 \leq x \leq 0.66$ at $5 \leq T \leq 150$ K, where dynamic and static orientational disorder phases are generally found. It is shown that at 5 K rotational tunneling levels for ammonium concentrations $x=0.01$, 0.02 and 0.06 are similar. Additional tunneling levels are observed for $x=0.16$ which can be explained as the result of T-states splitting for account of NH_4-NH_4 interaction. Tunneling levels are not observed for $x=0.40$ as the result of forming orientational glass state. The elastic incoherent structure factors for concentrations $0.01 \leq x \leq 0.16$ (dynamic orientational disordered α-phase), $x=0.40$ (orientational glass state) and $0.50 \leq x \leq 0.66$ (orientational ordered state) have different temperature dependences.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

Preprint of the Joint Institute for Nuclear Research. Dubna, 2001

Макет Т.Е.Попеко

Подписано в печать 29.08.2001
Формат 60 × 90/16. Офсетная печать. Уч.-изд. л. 1,72
Тираж 300. Заказ 52838. Цена 2 р.

Издательский отдел Объединенного института ядерных исследований
Дубна Московской области