

A neutron powder diffraction study of $\text{Rb}_x(\text{NH}_4)_{1-x}\text{AlF}_4$ mixed compounds

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

1989 J. Phys.: Condens. Matter 1 1577

(<http://iopscience.iop.org/0953-8984/1/9/004>)

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

Download details:

IP Address: 171.66.16.90

The article was downloaded on 10/05/2010 at 17:52

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

A neutron powder diffraction study of $\text{Rb}_x(\text{NH}_4)_{1-x}\text{AlF}_4$ mixed compounds

A Jouanneaux^{†‡}, A Leble[†], J Pannetier[§] and J L Fourquet^{||}

[†] Laboratoire de Spectroscopie du Solide (Unité associée au CNRS 807), Faculté des Sciences, Université du Maine, 72017 Le Mans Cédex, France

[§] Institut Laue–Langevin, 156X, 38042 Grenoble Cédex, France

^{||} Laboratoire des Fluorures (Unité associée au CNRS 449), Faculté des Sciences, Université du Maine, 72017 Le Mans Cédex, France

Received 31 May 1988, in final form 28 September 1988

Abstract. The neutron powder profile refinement method has been used to determine the structures of mixed compounds $\text{Rb}_x(\text{NH}_4)_{1-x}\text{AlF}_4$ for $x \leq 0.10$ at 290 and 5 K. At 290 K, the average structure for $x \leq 0.10$ is refined in the space group $I4/mcm$ as is pure NH_4AlF_4 . The introduction of rubidium ions leads essentially to a variation in the cell parameters and to a slight decrease in the fluorine octahedra tilts. At 5 K for $x = 0.03$, the long-range order of the ammonium ions settles as in NH_4AlF_4 . For $x = 0.07$ and $x = 0.10$, it is shown that the low-temperature phase does not exhibit any 3D order in the ammonium network. This result precludes the hypothesis of $A3NNI$ phases and tends to suggest the existence of a structural spin-glass behaviour. Then very small rubidium concentrations are sufficient to destroy the long-range order in the ammonium sublattice.

1. Introduction

NH_4AlF_4 is known to undergo an order–disorder phase transition in the vicinity of 155 K, associated with a full ordering of the NH_4^+ ions below T_c (Leble *et al* 1982). The structure consists of (001) layers of corner-sharing $(\text{AlF}_6)^{3-}$ octahedra separated by layers of NH_4^+ ions. In both high-temperature and low-temperature (LT) phases, the fluorine octahedra exhibit tilts around the c axis with antiferro rotational order along c . At room temperature (RT), the space group is $I4/mcm$ (Fourquet *et al* 1979, Leble *et al* 1982) (figure 1) and the NH_4^+ tetrahedra randomly occupy two equivalent orientations related by a rotation of $\pi/2$ around c . These two equivalent positions can represent the eigenstates of a pseudo-Ising spin operator ($\sigma_z = \pm 1$). At LTs, the ammonium ions exhibit a parallel order in the (001) layers and an antiparallel order along the c axis (figure 2). The space group $P4_2/mbc$ was predicted by EPR (Leble *et al* 1982) and confirmed by neutron powder profile refinement (Bulou *et al* 1982).

Recently, the RT and LT phases of mixed crystals $\text{Rb}_x(\text{NH}_4)_{1-x}\text{AlF}_4$ have been studied by EPR (Jouanneaux *et al* 1987). RbAlF_4 exhibits nearly the same atomic structure as NH_4AlF_4 , except for the rotational order of the fluorine octahedra along c , which is of the ferro type (Bulou and Nouet 1982). In the mixed crystals at RT, it has been found

[‡] Present address: Laboratoire de Chimie des Solides (Unité associée au CNRS 279), Université de Nantes, 2 rue de la Houssinière, 44072 Nantes Cédex, France.

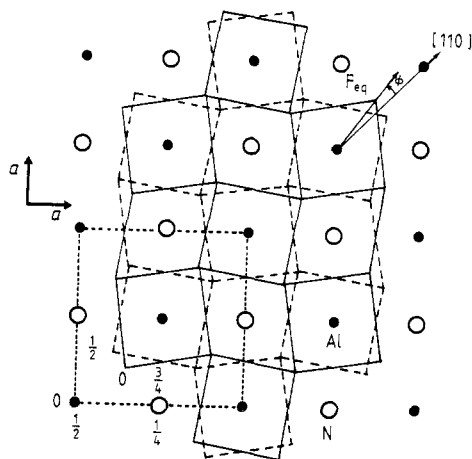


Figure 1. Projection of the RT structure of NH_4AlF_4 on the (001) layer. H and F_{ax} atoms are omitted for clarity. $|\varphi|$ corresponds to the tilting angle of the AlF_6 octahedra around the c axis.

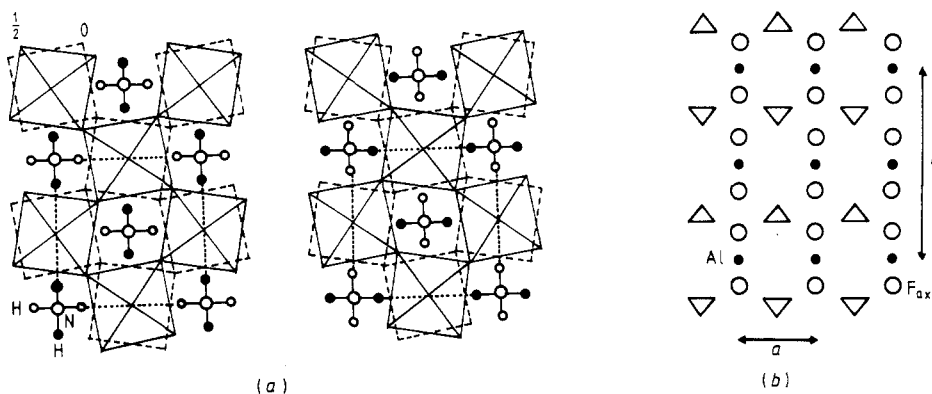


Figure 2. LT structure of NH_4AlF_4 in the space group $P4_2/mbc$. (a) Projection on the (001) layer. On the left side of the figure, N atoms are at $z = 0.25$; \bullet , H atoms below this level; \circ H atoms above this level. On the right side, N atoms are at $z = 0.75$; H atoms are represented with the same convention as above. (b) Projection on the (010) layer. Δ , ∇ , two possible orientations of the NH_4^+ ions. N and F_{eq} atoms are omitted for clarity.

that the Rb^+ ions are randomly substituted for the ammonium ions. Using the pseudo-spin representation, $\text{Rb}_x(\text{NH}_4)_{1-x}\text{AlF}_4$ may be viewed as a random Ising-like system. At LTs for $x \leq 0.028$, the EPR spectra give evidence that the long-range order settles as in NH_4AlF_4 . In the range $x = x_c$ to $x = 0.10$ ($0.028 < x_c < 0.043$), the spectra show the existence of large 2D domains with a frozen parallel order of the ammonium ions in the (001) layers below 150 K. Moreover, in this concentration range, the EPR spectra reveal a change in the ordering of adjacent ammonium layers, which are no longer fully antiparallel along c .

Since EPR local measurements cannot provide a definitive conclusion about the long-range order, two hypotheses have been proposed to interpret the EPR results in the LT phases for $x > x_c$.

(i) Structural spin-glass phases formed by large 2D parallel domains randomly stacked along c exist.

(ii) 3D ordered phases with a long wavelength along c , i.e. A3NNI phases (Selke *et al* 1985, Barreto and Yeomans 1985), occur. The main result of the 3D A3NNI model is the existence of long-period commensurate phases described by the notation $\langle lmn \dots \rangle$ corresponding to bands of l, m, n, \dots layers with the same pseudo-spin (Fisher and Selke 1980, Selke and Fisher 1981). With this notation, the LT phase of pure NH_4AlF_4 and of the mixed compounds with $x \leq 0.028$ corresponds to a phase denoted $\langle 1 \rangle$; for $x = 0.07$ and $x = 0.10$, the EPR lines are consistent with the $\langle 12 \rangle$ and $\langle 2 \rangle$ phases respectively. Finally, the EPR spectra for $x = 0.24$ show that the LT phase is not far from a $\langle \infty \rangle$ phase, corresponding to a 3D parallel order of the ammonium sublattice (Jovanneaux *et al* 1989).

Diffraction techniques are appropriate for investigating the long-range ordering. In this paper, we report a neutron powder profile refinement investigation of $Rb_x(NH_4)_{1-x}AlF_4$. Our main purpose is to determine the LT order in the ammonium sublattice and to discriminate between 3D long-range order and structural spin-glass behaviour.

2. Experimental details

The $Rb_x(NH_4)_{1-x}AlF_4$ ($x = 0.03, 0.07$ and 0.10) powdered samples were obtained from a stoichiometric mixture of the fluorides NH_4F , RbF and AlF_3 , heated at $440^\circ C$ for 48 h in gold tubes sealed under argon. The neutron diffraction patterns at 290 K for $x = 0.07$ and 0.10 and at 5 K for the three concentrations were collected on the high-resolution D1A diffractometer of the Institut Laue-Langevin at Grenoble (Hewat and Bailey 1976). The angular range of measurement was $2\theta = 6-160^\circ$ in steps of 0.05° and the incident wavelength was 1.909 \AA . The powdered sample was contained in a vanadium can ($\alpha = 10 \text{ mm}$, $h = 50 \text{ mm}$) held in a standard helium cryostat. The data collection time was about 10 h per pattern. All refinements were performed with the program of Rietveld (1969) modified for thermal anisotropy (Hewat 1973). The scattering lengths are taken from the work of Koester and Rauch (1981).

3. Room-temperature structures

Figure 3 shows a part of the RT neutron diffraction pattern for $x = 0.10$. Owing to the large incoherent diffuse scattering from hydrogen atoms, the background of the patterns is rather high, which limits the accuracy of the structure determination. For $x \leq 0.10$, the diffraction patterns are similar to that observed for NH_4AlF_4 (same reflections and almost identical intensities). Therefore all refinements have been performed in the space group $I4/mcm$ (table 1). The rubidium ions are considered to be statistically distributed, on the positions of the N atoms (4b position). The calculated patterns at 290 K for $x = 0.10$ and for pure NH_4AlF_4 (given for comparison) are shown in figures 3(a) and 3(b), respectively. The results of the refinements for $x = 0.07$ and $x = 0.10$ are listed in table 2, and the distances and angles between atoms are given in table 3.

One can see that the lattice parameter a increases with x while c decreases. The decrease in the c/a ratio (figure 4) is consistent with the fact that c/a is larger in pure NH_4AlF_4 ($c/a = 2.503$) than in pure $RbAlF_4$ ($2c/a = 2.452$). Moreover, the linear

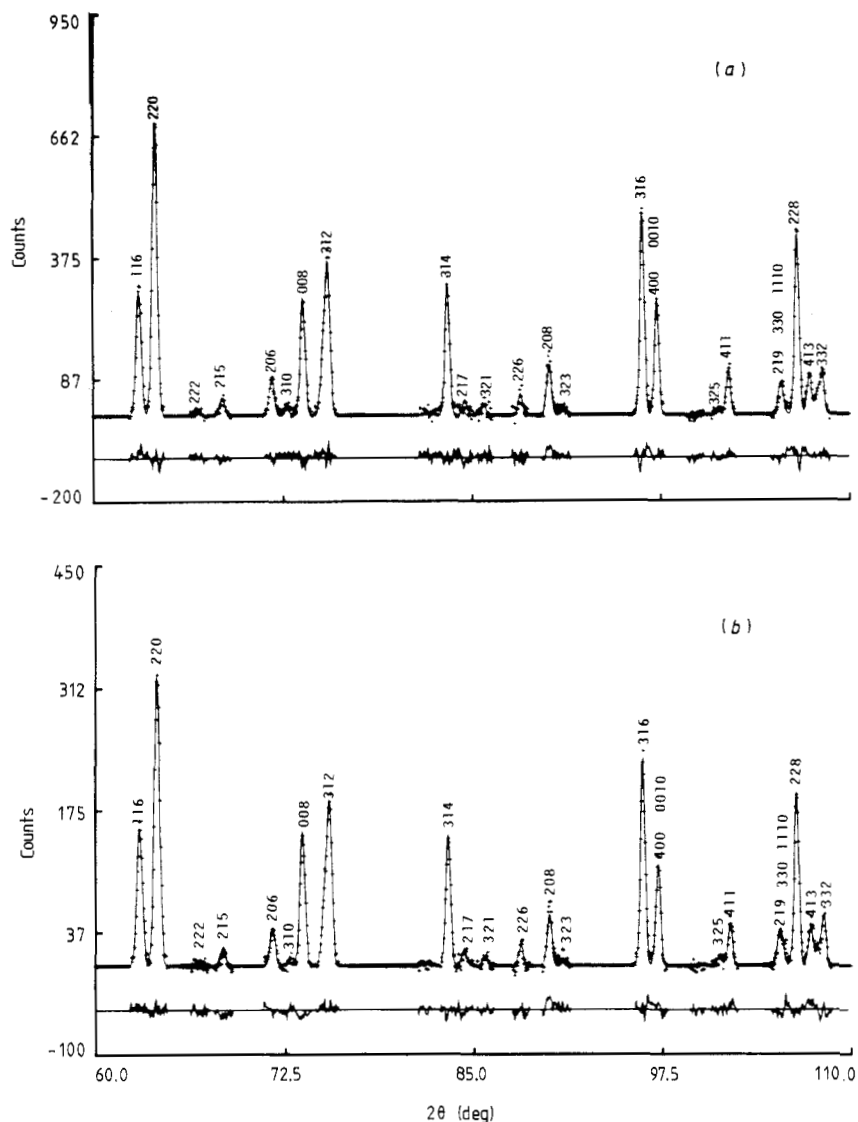


Figure 3. Parts of experimental (+) and calculated (—) (space group $I4/mcm$) neutron powder diffraction patterns at 290 K: (a) for $x = 0.10$; (b) in pure NH_4AlF_4 (Bulou *et al* 1982).

Table 1. Positions and atomic coordinates for NH_4AlF_4 at 290 K in the space group $I4/mcm$.

Atom	Position	x	y	z
N(Rb)	4b	0	$\frac{1}{2}$	$\frac{1}{4}$
Al	4c	0	0	0
F _{ax}	8f	0	0	z
F _{eq}	8h	x	$x + \frac{1}{2}$	0
H	32m	x	y	z

Table 2. Atomic coordinates for $Rb_{0.07}(NH_4)_{0.93}AlF_4$ and $Rb_{0.10}(NH_4)_{0.90}AlF_4$ at 290 K in the space group $I4/mcm$. $B = 8\pi(u^2)$ is the Debye–Waller factor, where $\langle u^2 \rangle$ is the mean-square atomic displacement in square ångströms Å^2 . To take into account the effect of absorption (Hewat 1979), the Debye–Waller factors given in tables 2, 4 and 6 have been corrected by a factor $\Delta B = 0.32(5) \text{ Å}^2$. The R -factors are defined by $R_{\text{mc}} = 100 \sum |I(\text{obs.}) - S I(\text{calc.})| / \sum I(\text{obs.})$ and $R_{\text{prof}} = 100 \sum |Y(\text{obs.}) - SY(\text{calc.})| / \sum Y(\text{obs.})$ and $I(\text{calc.})$ are the integrated intensities of reflection, $Y(\text{obs.})$ and $Y(\text{calc.})$ are the intensity data points and S is the scale factor. R_{exp} is the profile R -factor expected from statistics. The standard deviations are given in parentheses.

x	a (Å)	c (Å)	R_{mc} (%)	R_{prof} (%)	R_{exp} (%)
0.07	5.0881(2)	12.7245(4)	7.03	16.25	13.22
0.10	5.0893(1)	12.7177(3)	6.28	14.08	7.39

x	$z(F_{\text{an}})$	$x(F_{\text{eq}})$	$x(H)$	$y(H)$	$z(H)$	$B(N, Rb)$	$B(Al)$	$B(F_{\text{an}})$	$B(F_{\text{eq}})$	$B(H)$
0.07	0.1386(2)	0.2108(6)	-0.0004(17)	0.3353(13)	0.2049(6)	1.11(10)	0.49(13)	1.75(9)	1.21(9)	4.08(17)
0.10	0.1386(2)	0.2113(4)	-0.0015(14)	0.3360(5)	0.2057(5)	0.80(8)	0.61(14)	1.42(8)	0.90(8)	3.87(18)

Table 3. Selected distances and angles in pure NH_4AlF_4 (Bulou 1982) for $x = 0.07$ and $x = 0.10$ at 290 K. Values marked with an asterisk correspond to nearest neighbours. $|\varphi|$ denotes the tilting of the AlF_6 octahedra around the c axis (see figure 1). $V = a^2c$ is the volume of the unit cell.

	$x = 0$	$x = 0.07$	$x = 0.10$
Al-F_{ax} (Å)	1.765(3)	1.764(4)	1.763(3)
Al-F_{eq} (Å)	1.821(2)	1.821(2)	1.821(2)
N-F_{ax}^* (Å)	2.912(1)	2.912(1)	2.912(1)
N-F_{eq}^* (Å)	3.523(1)	3.524(1)	3.524(1)
H-F_{ax}^* (Å)	1.900(4)	1.903(5)	1.911(4)
H-F_{eq}^* (Å)	2.820(5)	2.828(8)	2.836(5)
H-N (Å)	1.019(4)	1.016(6)	1.007(4)
H-N-H (deg)	111.0(4)	111.2(6)	111.9(4)
	108.7(4)	108.6(6)	108.2(4)
$\text{F}_{\text{ax}}\text{-H-N}^*$ (deg)	171.7(5)	171.7(7)	172.3(5)
$ \varphi $ (deg)	9.11(8)	8.91(10)	8.80(8)
V (Å ³)	329.47(2)	329.42(2)	329.40(2)

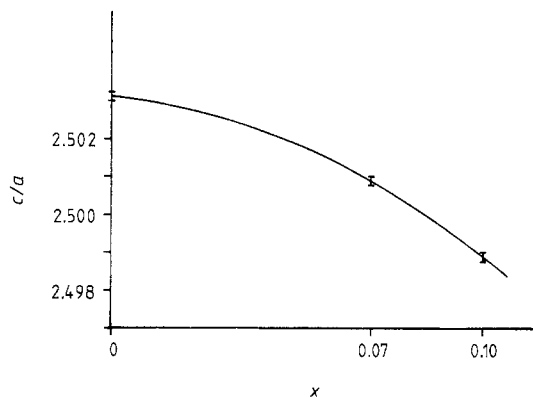


Figure 4. Evolution of the c/a ratio at 290 K with increase in concentration x .

decrease in the volume $V = a^2c$ with concentration indicates a progressive contraction of the unit cell (see table 3).

A small decrease in the tilting angle φ of the AlF_6 octahedra around c is observed (see table 3). This decrease is concomitant with the increase in the lattice parameter a . It must also be pointed out that, in spite of the modification of the lattice parameters, the N-F_{ax}^* distance (the asterisk indicates that the distance corresponds to the nearest-neighbour distance) and the $\text{F}_{\text{ax}}\text{-H-N}$ angle remain almost unchanged. Therefore the contraction of the unit cell leads to a decrease in the H-N bond length, and a correlated increase in the H-F_{ax}^* distance. This suggests that the hydrogen bonding becomes weaker, which could induce a 'relaxation' of the fluorine octahedra tilts and thereby an increase in the lattice parameter a .

4. Low-temperature phases ($T = 5$ K)

4.1. Structure refinement for $x = 0.03$

The diffraction pattern for $x = 0.03$ is analogous to that obtained for NH_4AlF_4 at the

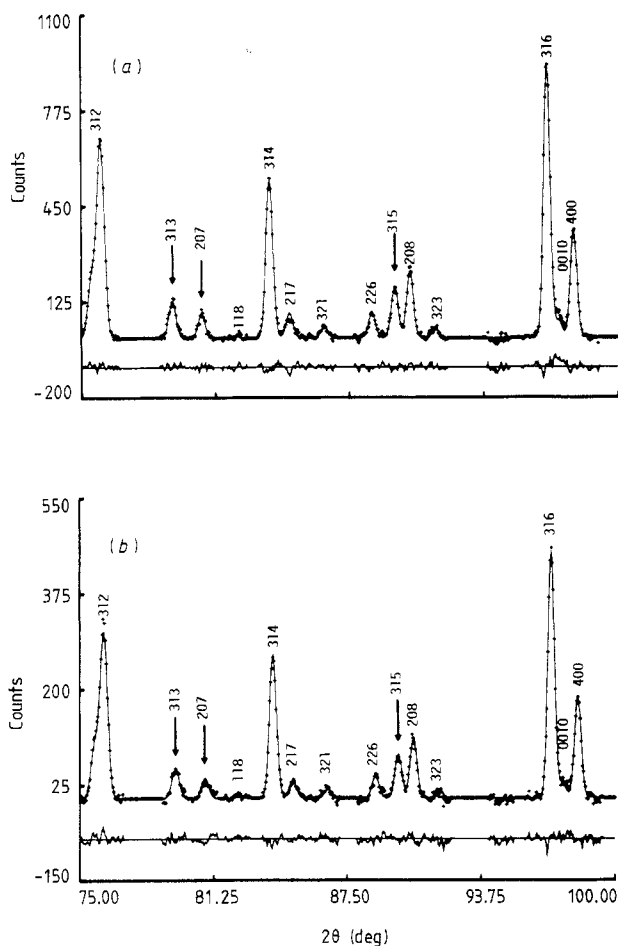


Figure 5. Parts of experimental (+) and calculated (—) (space group $P4_2/mbc$) neutron powder diffraction patterns at 5 K: (a) in pure NH_4AlF_4 (Bulou *et al* 1982); (b) for $x = 0.03$.

same temperature (Bulou *et al* 1982). In particular, one also observes the same set of diffraction lines characterised by the condition $h + k + l \neq 2n$, which indicates that the I translation is lost (figure 5). The intensity of this set of reflections arises essentially from H atoms and is characteristic

- (i) of the parallel ordering of the ammonium tetrahedra in the (001) layers and
- (ii) of the antiparallel order along the c axis (see figure 2).

Then, the LT structure of $Rb_{0.03}(NH_4)_{0.97}AlF_4$ has been refined in the centrosymmetric space group $P4_2/mbc$ (figure 5(b)) already used to refine the structure of pure NH_4AlF_4 .

The results of the refinement, given in table 4, are very close to those obtained in pure NH_4AlF_4 ; the distances and angles between atoms are not significantly modified (table 5). This means that the random substitution of the rubidium ions for $x \leq 0.03$ does not disturb the long-range order in the ammonium sublattice, i.e. the (1) phase. This result is in good agreement with previous EPR measurements for $x \leq 0.028$.

Table 4. Atomic coordinates for $\text{Rb}_{0.03}(\text{NH}_4)_{0.97}\text{AlF}_4$ at 5 K in the space group $\text{P4}_2/\text{mbc}$.

	a (Å)	c (Å)	R_{nuc} (%)	R_{prof} (%)	R_{exp} (%)
	5.0569(1)	12.7091(3)	5.95	15.28	10.13

Atom	Position	Symmetry	x	y	z	B (Å ²)
N, Rb	4b	$\bar{4}$	0	0	$\frac{1}{4}$	0.31(7)
Al	4c	2/m	0	$\frac{1}{2}$	0	0.02(10)
F _{ax}	8f	2	0	$\frac{1}{2}$	0.1389(1)	0.35(6)
F _{eq}	8h	m	0.2937(13)	0.2966(14)	0	0.76(6)
H	16i	1	-0.0004(10)	0.8295(8)	0.2036(3)	1.94(7)

Table 5. Selected distances and angles in pure NH_4AlF_4 (Bulou *et al* 1982) for $x = 0.03$ at 5 K. $|\varphi|$ is defined in table 3.

	$x = 0$	$x = 0.03$
Al-F _{ax} (Å)	1.772(1)	1.765(1)
Al-F _{eq} (Å) (1)	1.811(3)	1.807(5)
(2)	1.827(3)	1.827(5)
N-F _{ax} * (Å)	2.893(1)	2.896(1)
N-F _{eq} * (Å)	3.494(1)	3.499(2)
H-F _{ax} * (Å)	1.852(2)	1.858(3)
H-F _{eq} * (Å)	2.781(3)	2.791(4)
H-N (Å)	1.043(2)	1.045(3)
F _{eq} -Al-F _{eq} (deg)	90.1(1)	90.1(1)
	89.9(1)	89.9(1)
H-N-H (deg)	110.1(2)	111.3(2)
	109.2(2)	108.6(2)
F _{ax} -H-N* (deg)	171.4(2)	171.7(2)
$ \varphi $ (deg)	10.66(10)	10.30(20)

4.2. Structure refinements for $x = 0.07$ and $x = 0.10$

The experimental diffraction patterns of the mixed compounds with $x = 0.07$ and $x = 0.10$ are almost identical at $T = 5$ K but are different from that observed for $x \leq 0.03$ at the same temperature. In particular, the hkl reflections with $h + k + l \neq 2n$, which are characteristic of the LT order for $x \leq 0.03$ (see figure 5), have now completely disappeared. Finally, the LT diffraction patterns for these two concentrations look identical with those obtained for the same compounds at RT (see figure 3), and all the reflections can be indexed in the space group $\text{I4}/\text{mcm}$ (figure 6(a)). The RT and LT patterns differ only by small variations in the lattice parameters between 290 and 5 K, which shift the position of the reflections.

In the hypothesis of A3NNI phases, new lines ought to appear in the LT experimental diagrams. For example, the space group Pbam , a subgroup of $\text{P4}_2/\text{mbc}$, would be expected for the $\langle 2 \rangle$ phase, with the cell dimensions $(a, a, 2c)$. The expected pattern has

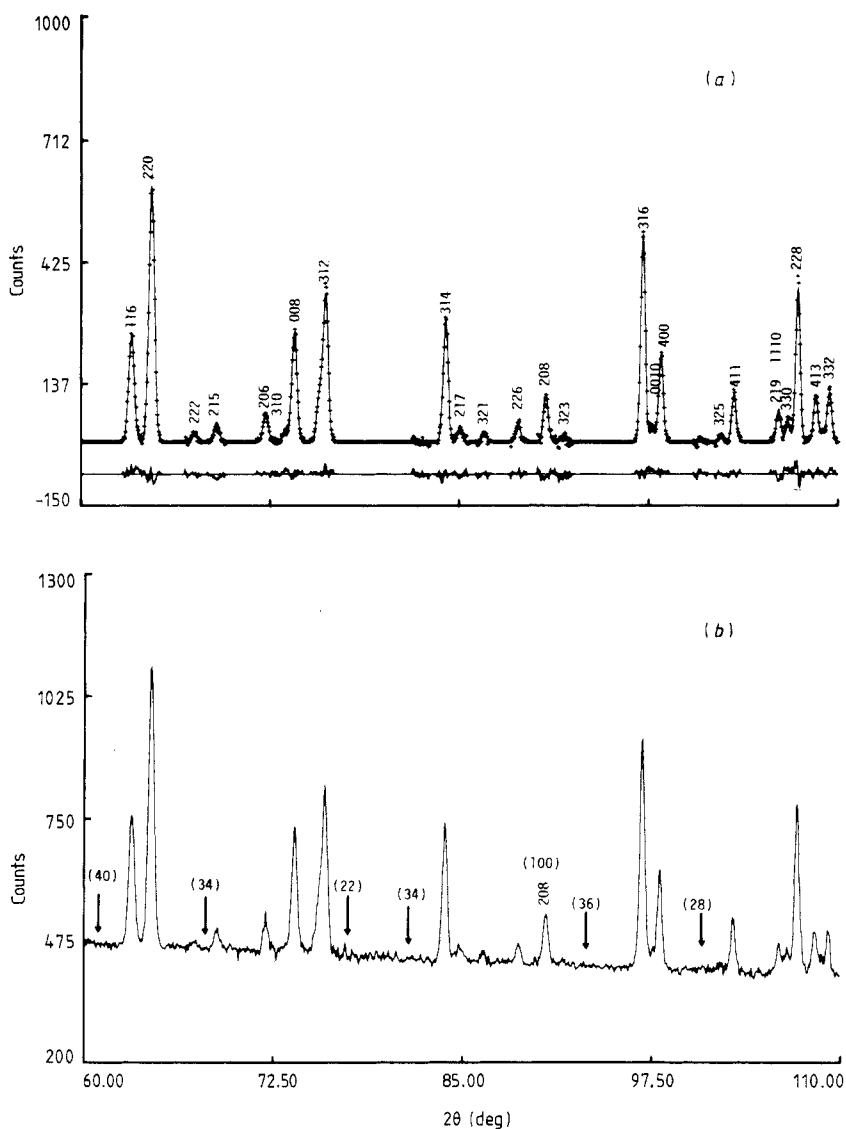


Figure 6. Parts of the neutron powder diffraction patterns at 5 K. (a) Experimental (+) and calculated (—) data (space group $I4/mcm$) for $x = 0.07$. (b) Part of the experimental pattern for $x = 0.10$. The arrows indicate the most intense reflections expected for a $\langle 2 \rangle$ phase. Their calculated intensities, given in parentheses, are normalised to that of the observed reflection $I(208) = 100$.

been calculated with *LAZY PULVERIX* (Yvon *et al* 1977). Owing to the doubling of the unit cell along c , new hkl reflections appear in the $\langle 2 \rangle$ phase. The most intense reflections, indicated by arrows in figure 6(b), are not observed experimentally, which seems to preclude the occurrence of a phase of type $\langle 2 \rangle$.

Finally, the LT average structures for $x = 0.07$ and $x = 0.10$ have been refined in the space group $I4/mcm$ (figure 6(a)). The results of the refinements and the distances between atoms are given in tables 6 and 7, respectively. The refinement in the space

Table 6. Atomic coordinates for $x = 0.07$ and $x = 0.10$ at 5 K in the space group I4/mcm (see table 1).

x	a (Å)	c (Å)	R_{mic} (%)	R_{prof} (%)	R_{exp} (%)	$B(\text{N, Rb})$	$B(\text{Al})$	$B(\text{F}_{\text{ax}})$	$B(\text{F}_{\text{eq}})$	$B(\text{H})$
0.07	5.0579(1)	12.7003(2)	4.70	11.00	7.43					
0.10	5.0601(1)	12.6977(3)	4.57	11.96	8.15					
x	$z(\text{F}_{\text{ax}})$	$x(\text{F}_{\text{eq}})$	$x(\text{H})$	$y(\text{H})$	$z(\text{H})$	$B(\text{N, Rb})$	$B(\text{Al})$	$B(\text{F}_{\text{ax}})$	$B(\text{F}_{\text{eq}})$	$B(\text{H})$
0.07	0.1389(1)	0.2041(3)	0.0002(9)	0.3319(9)	0.2043(4)	0.36(7)	0.22(9)	0.59(6)	0.70(6)	1.82(8)
0.10	0.1395(2)	0.2042(3)	0.0005(9)	0.3326(9)	0.2046(4)	0.31(8)	0.21(11)	0.49(7)	0.68(7)	2.08(12)

Table 7. Selected distances and angles for $x = 0.07$ and $x = 0.10$ at 5 K. $|\varphi|$ is defined in table 3.

	$x = 0.07$	$x = 0.10$
Al–F _{ax} (Å)	1.764(1)	1.772(1)
Al–F _{eq} (Å)	1.818(1)	1.819(1)
N–F _{ax} [*] (Å)	2.896(1)	2.893(1)
N–F _{eq} [*] (Å)	3.495(1)	3.495(1)
H–F _{ax} [*] (Å)	1.873(3)	1.875(3)
H–F _{eq} [*] (Å)	2.799(3)	2.803(3)
H–N (Å)	1.030(2)	1.025(2)
H–N–H (deg)	111.4(2)	111.5(2)
F _{ax} –H–N [*] (deg)	108.5(2)	108.5(2)
F _{ax} –H–N [*] (deg)	171.7(2)	171.7(2)
$ \varphi $ (deg)	10.40(10)	10.39(10)

group I4/mcm indicates that the NH_4^+ tetrahedra are statistically distributed over half of the 32m positions, thus presenting the two possible orientations in a disordered manner. This further confirms that the LT phases of $\text{Rb}_x(\text{NH}_4)_{1-x}\text{AlF}_4$ with $x = 0.07$ and $x = 0.10$ do not exhibit any 3D ordering of the ammonium network as expected in the A3NNI model. It must be pointed out that the orientational disorder of the NH_4^+ ions is static at 5 K whereas it is purely dynamic at RT.

4.3. Discussion

The LT neutron powder diffraction results tend to suggest a structural spin-glass behaviour in $\text{Rb}_x(\text{NH}_4)_{1-x}\text{AlF}_4$. Our results are similar to those observed, for example, in magnetic alloys with ferromagnetic–antiferromagnetic competing interactions (Aharony 1978) or in the dipolar glass $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ (Courtens 1982, Cowley *et al* 1985). In these mixed crystals at LTS, the frustration of the dipoles, in the spin-glass phase, is due to randomly distributed ferroelectric–antiferroelectric competing interactions and the crystals remain the para-electric structure, as at RT.

In $\text{Rb}_x(\text{NH}_4)_{1-x}\text{AlF}_4$, the static disorder of the NH_4^+ ions observed for $x = 0.07$ and $x = 0.10$ probably does not result from direct competing interactions between the pseudo-spins. Indeed, the short-range octupole–octupole interaction between the NH_4^+ tetrahedra is not strong enough to explain the LT phase in pure NH_4AlF_4 . The ordering of the ammonium sublattice is necessarily coupled to the rotation of the AlF_6 octahedra (Bulou *et al* 1982). In pure NH_4AlF_4 , this rotation is alternated along the *c* axis (antiferro type) whereas it is of ferro type in RbAlF_4 . Therefore the mixed compounds will probably have to accommodate random competing interactions inducing either a ferro or an antiferro rotational ordering of the fluorine octahedra. These competing interactions would modify the average coupling between the NH_4^+ ions and lead to frozen random orientations of the pseudo-spins for $x > x_c$. It is worth mentioning that very small amounts of rubidium are sufficient to destroy the long-range ordering of the ammonium network. The spin-glass phases would then be formed by large 2D parallel domains, according to EPR results, exhibiting static disorder along the *c* axis. However, in the absence of 3D ordering of the NH_4^+ sublattice for $x > x_c$, such parallel domains cannot be evidenced by neutron powder diffraction. In order to determine the range of

the 2D order in the spin-glass phases, neutron diffraction experiments will have to be performed on single crystals.

5. Conclusion

We have reported a neutron powder diffraction investigation on $\text{Rb}_x(\text{NH}_4)_{1-x}\text{AlF}_4$ for $x \leq 0.10$, which tends to suggest a structural spin-glass behaviour in these mixed compounds. Further neutron diffraction measurements will lead to a more detailed description of the phase diagram (x, T), particularly for $x = 0.24$, where the EPR spectra show that the ammonium sublattice exhibits essentially a 3D parallel order.

Acknowledgments

We are specially indebted to Dr A Bulou and Dr A Gibaud for helpful discussions. Thanks are due to A M Mercier for the preparation of the powder samples.

References

- Aharony A 1978 *J. Magn. Magn. Mater.* **7** 198
Barreto M and Yeomans J 1985 *Physica A* **134** 84
Bulou A 1982 private communication
Bulou A, Leble A, Hewat A W and Fourquet J L 1982 *Mater. Res. Bull.* **17** 391
Bulou A and Nouet J 1982 *J. Phys. C: Solid State Phys.* **15** 183
Courtens E 1982 *J. Physique Lett.* **43** L199
Cowley R A, Ryan T and Courtens E 1985 *J. Phys. C: Solid State Phys.* **18** 2793
Fisher M E and Selke W 1980 *Phys. Rev. Lett.* **44** 1502
Fourquet J L, Plet F, Courbion G, Bulou A and De Pape R 1979 *Rev. Chim. Mineral.* **16** 490
Hewat A W 1973 *Harwell Report AERE-R 7350*
——— *Acta Crystallogr. A* **35** 248
Hewat A W and Bailey I 1976 *Nucl. Instrum. Methods* **137** 463
Jouanneaux A, Leble A, Fayet J C and Fourquet J L 1987 *Europhys. Lett.* **3** 61
——— 1989 *J. Phys.: Condens. Matter* at press
Koester L and Rauch H 1981 *Summary of Neutron Scattering Lengths* IAEA Contract 2517/RB
Leble A, Rousseau J J, Fayet J C, Pannetier J, Fourquet J L and De Pape R 1982 *Phys. Status Solidi a* **69** 249
Rietveld H M 1969 *J. Appl. Crystallogr.* **2** 65
Selke W, Barreto M and Yeomans J 1985 *J. Phys. C: Solid State Phys.* **18** L393
Selke W and Fisher M E 1981 *Phil. Trans. R. Soc.* **302** 1
Yvon K, Jeitschko W and Parthe E 1977 *J. Appl. Crystallogr.* **10** 73