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# The high-resolution crystal structure of potassium ammonium dihydrogen phosphate mixed crystals: $K_{0.11}(NH_4)_{0.89}H_2PO_4$ at 154 K, 164 K, 192 K and 295 K

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**Abstract.** The x-ray crystal structure of a mixed crystal of potassium dihydrogen phosphate (KDP) and ammonium dihydrogen phosphate (ADP),  $K_{1-X}(NH_4)_X H_2PO_4$  ( $KADP_X$ ) with  $X = 0.89$ , has been refined in the paraelectric phase at 154, 164, 192 and 295 K, against high-resolution data ( $((\sin \theta)/\lambda)_{\max} \approx 1.2 \text{ \AA}^{-1}$ ) with multipolar pseudoatom form factors. The phase transition temperature is observed to lie at  $T_c = 132 \pm 1 \text{ K}$ ; a linear temperature dependence of the atomic vibration amplitudes of P and O is observed; extrapolation of  $U^{33}$  curves to  $T = 0 \text{ K}$  suggests a distribution of P between two sites separated by 0.2 Å. The structure of  $KADP_{0.89}$  is compared with ADP and KDP structural data.

## 1. Introduction

It is well known that potassium dihydrogen phosphate  $KH_2PO_4$  (KDP) undergoes a paraferroelectric (PE–FE) phase transition at 123 K [1–3] whereas the ammonium dihydrogen phosphate (ADP) shows a paraelectric–antiferroelectric (PE–AFE) phase transition at 148 K [4–6]; both compounds crystallize in the same space group,  $I42d$ , in their paraelectric phase; in the ferroelectric phase KDP is orthorhombic, space group  $Fdd2$ , and ADP in its antiferroelectric phase crystallizes in the  $P2_12_12_1$  space group. Mixed ferroelectric and antiferroelectric crystals may show a glassy behaviour analogous to a spin–glass system at intermediate  $X$  compositions.  $Rb_{1-X}(NH_4)_X H_2PO_4$  ( $RADP_X$ ) constitutes the best and most intensively investigated system [7].  $K_{1-X}(NH_4)_X H_2PO_4$  ( $KADP_X$ ) has been established to be analogous to  $RADP_X$  but has been investigated less well.  $KADP_X$  is ferroelectric for  $X < 0.23$  below transition temperatures lower than that of KDP, whereas for  $X > 0.85$ , it exhibits an antiferroelectric transition below a critical temperature which is lower than that of ADP. However, contrary to  $RADP_X$ , the phase diagram remains unsymmetric and is not actually known accurately [8, 9]. The disappearance of the FE or AFE phase transition has been observed in the composition range  $0.20 < X < 0.85$  [6], and dielectric measurements on  $KADP_{0.23}$  have shown the glassy low-frequency dispersion of the dielectric constant [10]. Furthermore, structural studies have established that these latter mixed crystals maintain their paraelectric tetragonal  $I42d$  structure down to 20 K [11, 12] in agreement with infrared

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reflectivity studies [13]. However no x-ray nor neutron structure analysis in the range  $0.23 < X < 1$  has ever been carried out at any temperature.

The purpose of this present paper is to describe the x-ray structure of  $\text{KADP}_{0.89}$  and to determine the variation of the thermal parameters, with respect to those of KDP [14–16] and ADP [17].

## 2. Experimental details

### 2.1. Data collection

Single crystals of  $\text{KADP}_X$ ,  $X = 0.89$  were grown from an aqueous solution of ADP and KDP at a fixed temperature (294 K) by slow evaporation; the mass percentages ( $m_{\text{ADP}} = 103.74$  g,  $m_{\text{KDP}} = 13.35$  g) were deduced from Ono *et al* [8]. The single crystal used for the x-ray experiment was selected at the very beginning of the crystallization process, in order to avoid any change in the starting stoichiometry. The habit of the crystal was determined by optical goniometry and later checked on the CAD4F Enraf Nonius diffractometer (programs Micros, Micror [18]) that was used for the data collection. The crystal geometry given in table 1 presents a symmetry very close to that of the tetragonal holohedral  $4/mmm$  point group, despite its  $42m$  point group.

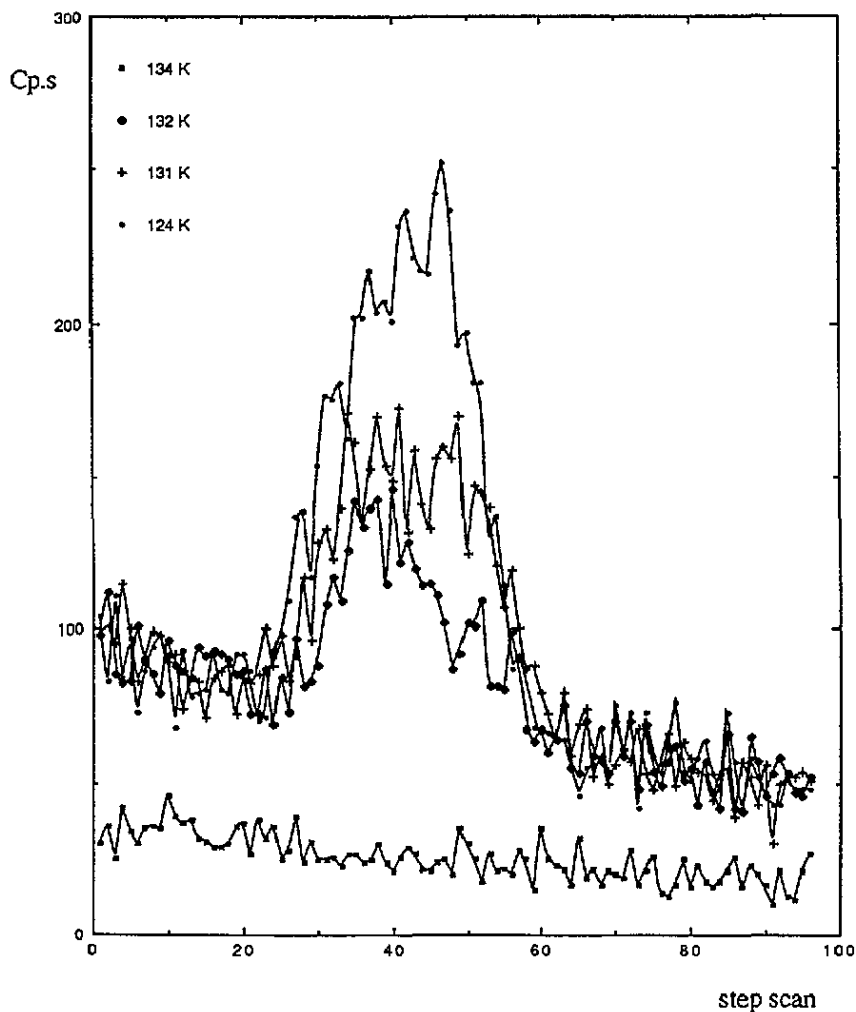
Table 1. Crystal geometry and distances (mm) from the centre of mass of the crystal.

| <i>hkl</i>   | 100   | $\bar{1}00$ | 010   | $0\bar{1}0$ | 101   | $\bar{1}0\bar{1}$ | $10\bar{1}$ | $\bar{1}01$ | 011   | $0\bar{1}\bar{1}$ | $0\bar{1}1$ | $0\bar{1}\bar{1}$ |
|--------------|-------|-------------|-------|-------------|-------|-------------------|-------------|-------------|-------|-------------------|-------------|-------------------|
| Dist. from 0 | 0.070 | 0.070       | 0.113 | 0.113       | 0.154 | 0.154             | 0.124       | 0.124       | 0.154 | 0.154             | 0.154       | 0.154             |

Four data collections using graphite monochomatized Mo  $K\alpha$  radiation were carried out above the paraelectric–antiferroelectric transition temperature at 295, 192, 164 and 154 K, with the same crystal on the CAD4F diffractometer equipped with a liquid nitrogen vapour stream apparatus and installed in a dry box to prevent ice formation on the crystal. The gas stream temperature was maintained constant with 1 K as monitored by a copper–constantan thermocouple positioned  $\sim 5$  mm upstream from the crystal. The temperature was scaled using the phase transition temperatures of KDP (123 K) and ADP (148 K): for KDP, a reversible splitting of the (200), (400) and (040) peaks is easily observed at the transition, whereas the (012), (311) tetragonal forbidden reflections due to the I Bravais lattice begin to grow at 148 K for ADP. Lattice parameters obtained by least-squares fit to the optimized setting angles of the  $K\alpha_1$  peaks on 22 reflections with  $20^\circ < 2\theta < 40^\circ$  are given in table 2. Data were recorded in one octant of the Ewald sphere ( $0 \leq h \leq 19$ ;  $0 \leq k \leq 19$ ;  $0 \leq l \leq 19$ ) as  $\omega$ - $2\theta$  profiles to a resolution of  $(\sin \theta)/\lambda = 1.29, 1.22, 1.22$  and  $1.15 \text{ \AA}^{-1}$  for the 295, 192, 164 and 154 K experiments, respectively. During the data collections, four standard reflections: ( $5\bar{1}6$ ), (460), (040) and (400) were measured at two-hour intervals. No decline was observed. The total  $\Delta\omega$  (deg) for each measurement was  $(3/2)(1 + 0.35 \tan \theta)$  with a constant detector aperture of  $6 \times 3 \text{ mm}^2$ . A prescan speed ( $d\omega/dt$ ) of  $2.75^\circ \text{ min}^{-1}$  and a final scan speed depending on the signal-to-noise ratio ( $1.1 < v < 2.75^\circ \text{ min}^{-1}$ ) were used. The total exposure time was 57, 49, 48 and 42 hours, respectively, for the four data collections. No temperature nor diffractometer problem occurred. After these data collections, the transition temperature was determined at the temperature where the forbidden tetragonal reflections (012), (311) and (111) appear with crystal cooling. As shown in figure 1, the (012) reflection begins to grow at 132 K, which is taken as the transition temperature; the crystal did not crack during cooling below  $T_c$ .

**Table 2.** Lattice parameters ( $\text{\AA}$ ) and standard deviations at  $T = 295, 192, 164$  and  $154$  K.

| $T$ (K) | 295        | 192        | 164        | 154        |
|---------|------------|------------|------------|------------|
| $a = b$ | 7.4971(12) | 7.4731(16) | 7.4707(12) | 7.4694(14) |
| $c$     | 7.471(3)   | 7.462(3)   | 7.456(3)   | 7.456(3)   |

**Figure 1.** Profiles of the (012) reflection of  $KADP_{0.89}$  versus temperature (K). For clarity, the (012) reflection 134 K has been shifted to  $-70$  cps.

## 2.2. Data processing

Data reduction and error analysis were done using the program DREAR of Blessing [19]. Reflection integration limits were from a Lorentzian model for the peak width variation. The instrumental instability coefficients  $p$  (for the calculation of  $\sigma^2(|F|^2) = \sigma_c^2(|F|^2) + (p|F|^2)^2$ ) are  $0.0, 2.9 \times 10^{-4}, 0.0$  and  $3.3 \times 10^{-3}$  for the 295, 192, 164 and 154 K experiments, respectively;  $\sigma_c^2$  is calculated from the propagation of error calculations in which counting

statistics and scan angle uncertainties ( $\sigma(\omega) = 0.01^\circ$ ) made the most important contributions. Absorption corrections were done using the ABSORB program [20]: with a single crystal of  $8.8 \times 10^{-3} \text{ mm}^3$  volume and of  $0.64 \text{ mm}^{-1}$  absorption coefficient, the minimal and the maximal transmission factors are 0.847 and 0.901, respectively. The optical path varies from 0.14 to 0.31 mm; hence, the absorption corrections improve dramatically the internal agreements between symmetry-equivalent structure factors, as shown in table 3.

**Table 3.** Internal agreement factors with and without absorption corrections.  $R_1 = \Sigma(|Y - \bar{Y}|)/\Sigma|Y|$ ,  $R_2 = [\Sigma(Y - \bar{Y})^2/\Sigma Y^2]^{1/2}$ ,  $R_w = [\Sigma_w(Y - \bar{Y})^2/\Sigma_w Y^2]^{1/2}$ .

| T (K) | Without absorption corrections |           |           | With absorption corrections |           |           | Total reflect. | Unique reflections $I > 3\sigma$ | $(\sin \theta/\lambda)_{\max} (\text{\AA}^{-1})$ |
|-------|--------------------------------|-----------|-----------|-----------------------------|-----------|-----------|----------------|----------------------------------|--|
|       | $R_1$ (%)                      | $R_2$ (%) | $R_w$ (%) | $R_1$ (%)                   | $R_2$ (%) | $R_w$ (%) |                |                                  |  |
| 295   | 2.37                           | 2.37      | 2.79      | 1.33                        | 0.89      | 2.22      | 2290           | 506                              | 1.29   |
| 192   | 2.00                           | 2.23      | 2.82      | 1.36                        | 1.00      | 2.47      | 1875           | 605                              | 1.22   |
| 164   | 1.67                           | 1.81      | 3.09      | 1.32                        | 1.20      | 2.71      | 1828           | 650                              | 1.22   |
| 154   | 1.66                           | 1.84      | 3.09      | 1.25                        | 1.20      | 2.70      | 1552           | 594                              | 1.15   |

### 2.3. Crystal structure refinements

First a conventional spherical atom refinement was performed on the 192 K data ( $0 < (\sin \theta)/\lambda < 1.22 \text{ \AA}^{-1}$ ) with the following starting parameters: P (0, 0, 0); K (or N) (0, 0,  $\frac{1}{2}$ ;  $X = 0.9$ ). Fourier difference maps gave the approximate positions for the oxygen and hydrogen atoms. The hydrogen H(O) linked to the oxygen atom (figure 2) was split as found on Fourier maps and therefore was not constrained to stay on the two-fold axis ( $x, \frac{1}{4}, \frac{1}{8}$ ); after several cycles of refinement of the  $xyz$  and  $U$  parameters the partial occupancy  $X$  was allowed to be refined together with the other parameters; the final value for  $x$  is 0.887(6) compared with the starting value of 0.9 ( $R(F) = 2.74\%$ ,  $R_w(F) = 3.43\%$ ,  $\text{GOF} = 3.24$ ). The occupancy  $X$  was held constant during all further refinements. In order to obtain the best set of unbiased thermal parameters, high-order (HO) refinements ( $(\sin \theta)/\lambda > 0.8 \text{ \AA}^{-1}$ ) were performed against the four data sets; the HO refinement uses data above a value for  $(\sin \theta)/\lambda$  at which the contribution of valence electron scattering is estimated to be negligible compared with the core contribution; the refinement is then expected to obtain thermal parameters for non-hydrogen atoms that are unbiased by the non-spherical valence electron density. As shown in table 4, these refinements converge very well with a goodness of fit very close to the expected value (1.0), contrary to the GOF obtained for the full data refinement (3.24). This latter high value for the GOF shows that an improvement of the refinement can be performed by using aspherical form factors; hence, non-sphericity of the atoms may be taken into account by performing a multipole refinement (program Molly [21]). In this model, the atomic density is calculated as a sum of pseudoatomic multipolar densities:

$$\rho(r) = \rho_c(r) + P_v \kappa^3 \rho_v(\kappa r) + \kappa^3 \sum_{l=0}^4 R_{nl}(\kappa' r) \sum_{m=-l}^{+l} P_l^m y_l^m(\theta, \varphi)$$

where  $\rho_c$  and  $\rho_v$  are spherically averaged Hartree-Fock core and valence densities,  $y_l^m$  are the multipolar spherical harmonic angular functions in real form and  $R_{nl} = N_l r^{n_l} \exp(-\kappa' \xi r)$  are Slater-type radial functions, in which  $N_l$  is a normalization factor; the  $n_l$  and  $\xi$  values

for the atoms are given in table 5. The refinement variables are  $P_v$ ,  $P_l^m$  and Kappas ( $\kappa$ ,  $\kappa'$ ) parameters;  $\kappa$  and  $\kappa'$  are related to the extension contraction of the atomic electron density. The net atomic charge is obtained by  $N - P_v$  where  $N$  is the number of electrons of the free atom. The asphericity is described by the  $P_l^m$  population parameters which are constrained by the site symmetry of the atom [22]. Furthermore, the  $P_v$  parameters are constrained in order to have a neutral unit cell. The starting positional and thermal parameters were those obtained from HO refinement for the heavy atoms and those calculated from a conventional refinement for the H atoms. The multipolar expansion was truncated at  $l = 4$  for the phosphorus atom, at  $l = 3$  for the oxygen and nitrogen atoms and  $l = 1$  for the hydrogen atoms. The  $P_v$  and  $P_l^m$  parameters for the potassium atom were not refined. The strategy for the refinement was as follows: at the first stage of the multipolar refinement ( $P_v$ ,  $\kappa$  refinement), the HO scale factor was fixed. Then all the electron density parameters were refined together with the scale factor. This process was recycled until convergence. Then, the  $xyz$  and the anisotropic thermal parameters for the non-H atoms as well as the positional and isotropic thermal motion parameters for the H atoms were refined together with the density parameters. The statistics of fit are given in table 4. The goodness of fit decreases from a value close to 3.0 to an average value of 1.36, when the aspherical model of the electron density is used.

**Table 4.** Statistical agreements of the refinements.  $S = (\sin\theta)\lambda$ ;  $R(F) = \Sigma\|F_0| - K|F_c|\|/\Sigma|F_0|$ ;  $R_w(F) = [\Sigma_w(|F_0| - K|F_c|)^2/\Sigma_w|F_0|^2]^{1/2}$ ;  $GOF = [\Sigma_w(|F_0| - K|F_c|)^2/N_{obs} - N_v]^{1/2}$ ;  $N_{obs}$  data and  $N_v$  parameters;  $N_v(HO) = 19$ ;  $N_v(\text{multipolar refinement}) = 74$ .

| $T$ (K) | Type of refinement | $S$               | $N_{obs}$<br>$I > 3\sigma(I)$ | $R(F)$ (%) | $R_w(F)$ (%) | GOF  | Scale factor |
|---------|--------------------|-------------------|-------------------------------|------------|--------------|------|--------------|
| 295     | HO                 | $0.8 < S < 1.29$  | 259                           | 5.00       | 3.77         | 1.15 | 1.251(3)     |
|         | Multipolar         | $0.09 < S < 1.29$ | 506                           | 2.02       | 1.36         | 1.36 | 1.2526(8)    |
| 192     | HO                 | $0.8 < S < 1.22$  | 355                           | 3.37       | 2.55         | 1.22 | 1.275(2)     |
|         | Multipolar         | $0.09 < S < 1.22$ | 605                           | 1.92       | 1.41         | 1.47 | 1.2754(9)    |
| 164     | HO                 | $0.8 < S < 1.22$  | 401                           | 3.30       | 2.46         | 1.05 | 1.271(2)     |
|         | Multipolar         | $0.09 < S < 1.22$ | 650                           | 1.92       | 1.67         | 1.33 | 1.2734(8)    |
| 154     | HO                 | $0.8 < S < 1.15$  | 345                           | 2.75       | 2.35         | 1.06 | 1.268(2)     |
|         | Multipolar         | $0.09 < S < 1.15$ | 594                           | 1.68       | 1.59         | 1.40 | 1.2695(8)    |

**Table 5.**  $n_1$  and  $\zeta$  (Bohr $^{-1}$ ) values for the Slater-type valence electron density radial functions.

|   | $\zeta$ | $n_0$ | $n_1$ | $n_2$ | $n_3$ | $n_4$ |
|---|---------|-------|-------|-------|-------|-------|
| P | 3.6     | 4     | 6     | 6     | 6     | 6     |
| O | 4.5     | 2     | 2     | 2     | 3     |       |
| N | 3.8     | 2     | 2     | 2     | 3     |       |
| H | 2.26    | 0     | 1     |       |       |       |

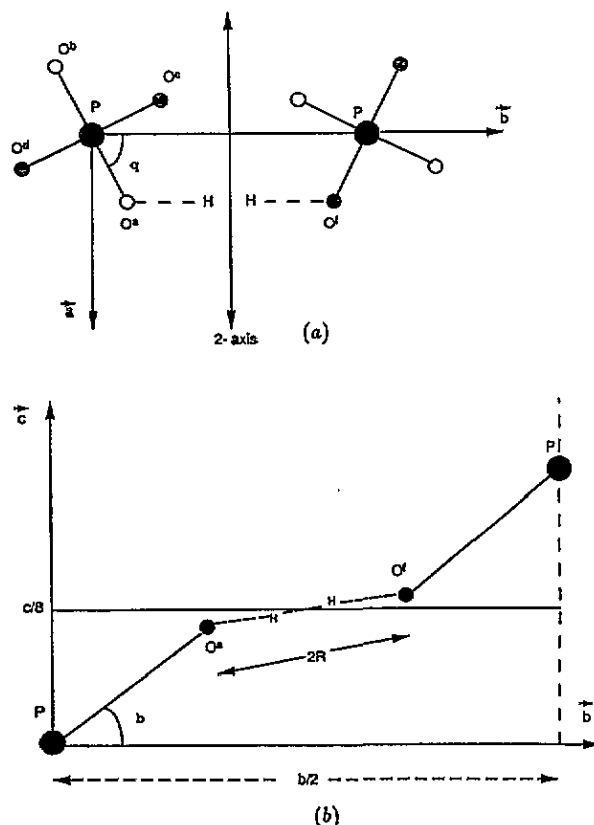


Figure 2. The projection of the phosphate group in  $\text{KADP}_{0.89}$  (a) along the  $c$  axis, and (b) along the  $a$  axis: a,  $x, y, z$ ; b,  $\bar{x}, \bar{y}, z$ ; c,  $\bar{y}, x, \bar{z}$ ; d,  $y, \bar{x}, \bar{z}$ ; e,  $y, \frac{1}{2} + x, \frac{1}{4} + z$ ; f,  $x, \frac{1}{2} - y, \frac{1}{4} - z$ .

### 3. Results and discussion

Atomic coordinates and thermal parameters at the four temperatures are given in table 6; bond distances and angles are shown in table 7 together with the corresponding distances and angles in KDP [15–16] and ADP [17]. The multipole parameters are given in tables 8 and 9. This paper will discuss the position and thermal parameters; the electron density, dipole moment, and electrostatic potential will be discussed in another paper for several  $X$ -values.

Figure 2 gives the projections of the  $\text{H}_2\text{PO}_4$  group along the  $a$  and  $c$  axes which are to be compared with that given by Nelmes and co-workers [14, 15]. In our mixed crystal, owing to the 0.89  $X$ -value, the crystal structure is closer to that of ADP than to that of KDP. The  $z$ -coordinate of the oxygen atom is 0.116 97(8) versus 0.148 39(3) in KDP due to the elongation of the  $c$ -parameter.

In  $\text{KADP}_{0.89}$ , no significant shift of the average of the heavy-atom positions as a function of temperature is observed. The P–O distance does not depend on the temperature. The same observation was made by Nelmes and co-workers in KDP [14]. The O—O<sup>f</sup> distance ( $2R$  on figure 2) decreases by 0.01 Å (14 ESD) when the temperature decreases from room temperature to 154 K. This observation is related to the contraction of the  $a(b)$  cell parameter (0.023 Å) and to the slight increase of the  $\theta$  angle (0.18 (1)°). This latter value is close to that observed in ADP (0.25 (3)°) and larger than that observed in KDP (table 7).

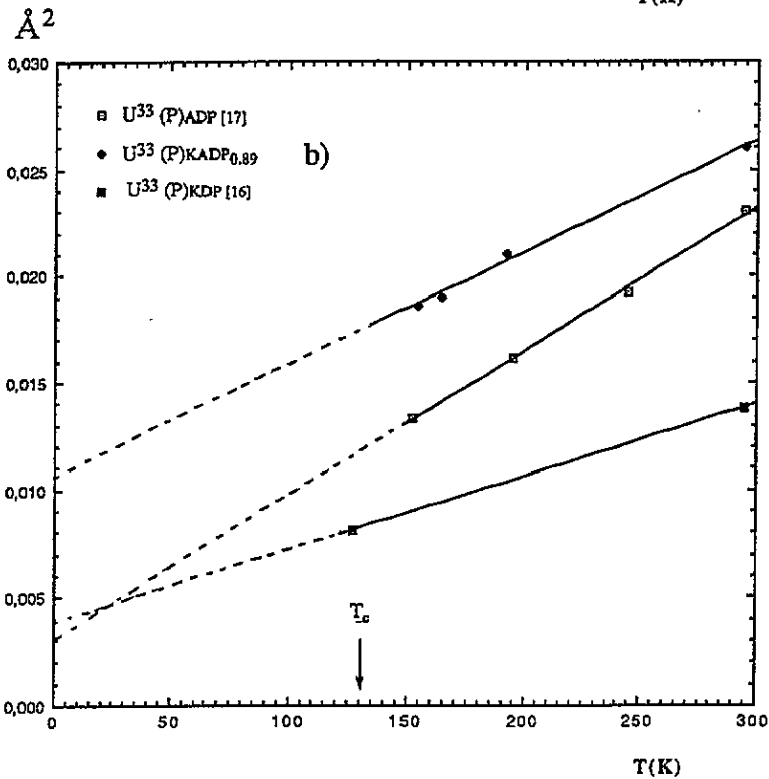
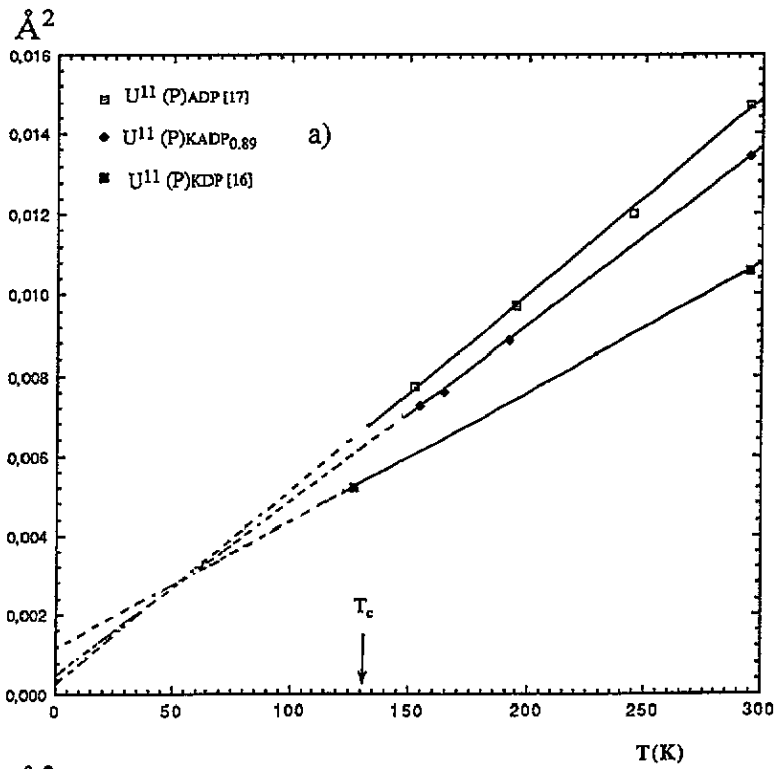


Figure 3. Anisotropic displacement parameters ( $\text{\AA}^2$ ):  $U^{11}$  (a),  $U^{33}$  (b) for the phosphorus atom as a function of temperature (K).



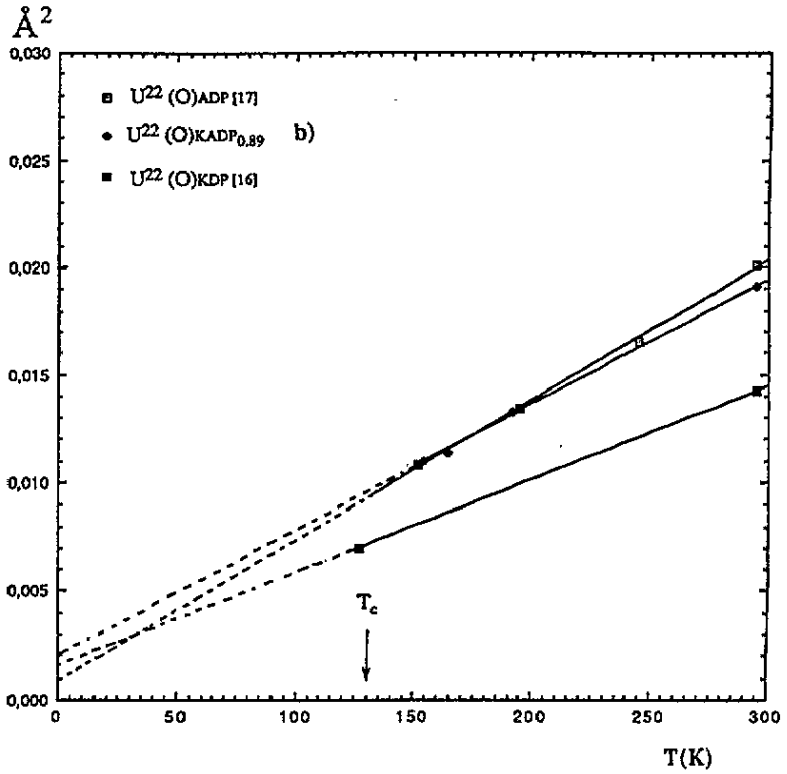
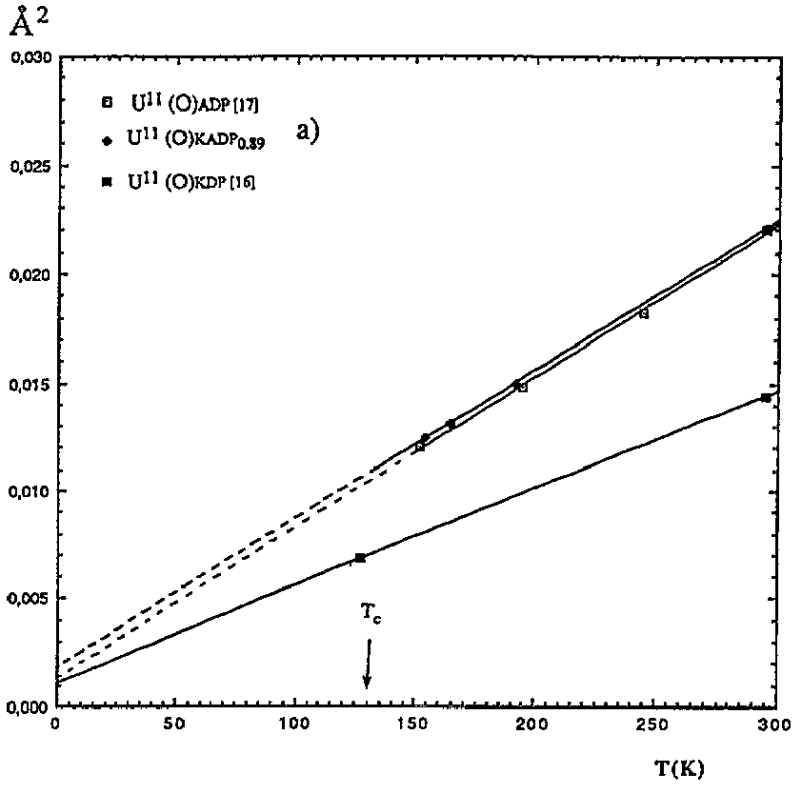
Table 6. Fractional coordinates and thermal parameters at 154, 164, 192 and 295 K for KADP<sub>89</sub>.

| Atom  | x          | y          | z          | U <sup>11</sup> | U <sup>22</sup> | U <sup>33</sup> | U <sup>12</sup> | U <sup>13</sup> | U <sup>23</sup> |
|-------|------------|------------|------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 154 K |            |            |            |                 |                 |                 |                 |                 |                 |
| N     | 0.0000     | 0.0000     | 0.5000     | 0.0169(2)       | 0.0169(2)       | 0.0135(4)       | 0.0000          | 0.0000          | 0.0000          |
| K     | 0.0000     | 0.0000     | 0.5000     | 0.0185(4)       | 0.0185(4)       | 0.0125(6)       | 0.0000          | 0.0000          | 0.0000          |
| P     | 0.0000     | 0.0000     | 0.0000     | 0.00725(5)      | 0.00725(5)      | 0.0186(1)       | 0.0000          | 0.0000          | 0.0000          |
| O     | 0.14767(5) | 0.08446(5) | 0.11662(7) | 0.0124(1)       | 0.0110(1)       | 0.0204(1)       | 0.0018(1)       | -0.0056(1)      | -0.0034(1)      |
| H(O)  | 0.151(4)   | 0.238(1)   | 0.120(1)   | 0.046(9)        |                 |                 |                 |                 |                 |
| H(N)  | 0.089(2)   | 0.012(2)   | 0.565(1)   | 0.019(2)        |                 |                 |                 |                 |                 |
| 164 K |            |            |            |                 |                 |                 |                 |                 |                 |
| N     | 0.0000     | 0.0000     | 0.5000     | 0.0183(2)       | 0.0183(2)       | 0.0134(4)       | 0.0000          | 0.0000          | 0.0000          |
| K     | 0.0000     | 0.0000     | 0.5000     | 0.0187(4)       | 0.0187(4)       | 0.0134(6)       | 0.0000          | 0.0000          | 0.0000          |
| P     | 0.0000     | 0.0000     | 0.0000     | 0.00763(5)      | 0.00763(5)      | 0.0190(1)       | 0.0000          | 0.0000          | 0.0000          |
| O     | 0.14759(5) | 0.08437(5) | 0.11663(7) | 0.0131(1)       | 0.0114(1)       | 0.0213(2)       | 0.0021(1)       | -0.0060(1)      | -0.0037(1)      |
| H(O)  | 0.154(4)   | 0.243(1)   | 0.121(1)   | 0.056(1)        |                 |                 |                 |                 |                 |
| H(N)  | 0.097(2)   | 0.014(2)   | 0.568(1)   | 0.017(2)        |                 |                 |                 |                 |                 |
| 192 K |            |            |            |                 |                 |                 |                 |                 |                 |
| N     | 0.0000     | 0.0000     | 0.5000     | 0.0198(2)       | 0.0198(2)       | 0.0155(4)       | 0.0000          | 0.0000          | 0.0000          |
| K     | 0.0000     | 0.0000     | 0.5000     | 0.0228(4)       | 0.0228(4)       | 0.0160(7)       | 0.0000          | 0.0000          | 0.0000          |
| P     | 0.0000     | 0.0000     | 0.0000     | 0.00887(5)      | 0.00887(5)      | 0.0210(1)       | 0.0000          | 0.0000          | 0.0000          |
| O     | 0.14738(5) | 0.08445(5) | 0.11663(6) | 0.0150(1)       | 0.0132(1)       | 0.0233(1)       | 0.0022(1)       | -0.0068(1)      | -0.0041(1)      |
| H(O)  | 0.147(3)   | 0.238(1)   | 0.119(1)   | 0.047(7)        |                 |                 |                 |                 |                 |
| H(N)  | 0.091(1)   | 0.010(2)   | 0.567(1)   | 0.019(2)        |                 |                 |                 |                 |                 |
| 295 K |            |            |            |                 |                 |                 |                 |                 |                 |
| N     | 0.0000     | 0.0000     | 0.5000     | 0.0285(2)       | 0.0285(2)       | 0.0231(5)       | 0.0000          | 0.0000          | 0.0000          |
| K     | 0.0000     | 0.0000     | 0.5000     | 0.0342(7)       | 0.0342(7)       | 0.0222(9)       | 0.0000          | 0.0000          | 0.0000          |
| P     | 0.0000     | 0.0000     | 0.0000     | 0.01341(6)      | 0.01341(6)      | 0.0260(1)       | 0.0000          | 0.0000          | 0.0000          |
| O     | 0.14649(6) | 0.08441(6) | 0.11697(8) | 0.0221(1)       | 0.0191(1)       | 0.0333(2)       | 0.0037(1)       | -0.0106(2)      | -0.0065(1)      |
| H(O)  | 0.161(2)   | 0.234(3)   | 0.118(1)   | 0.071(9)        |                 |                 |                 |                 |                 |
| H(N)  | 0.105(2)   | 0.006(2)   | 0.568(1)   | 0.019(3)        |                 |                 |                 |                 |                 |

Table 7. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) in  $KADP_{89}$  ( $T = 154, 164, 192, 295$  and  $295$  K) compared with those of KDP and ADP.

| Dist. angle                         | $KADP_{89}$ |           |           |           |           | ADP [17]  |            |            | KDP [16]   |            |
|-------------------------------------|-------------|-----------|-----------|-----------|-----------|-----------|------------|------------|------------|------------|
|                                     | T (K)       | 154       | 164       | 192       | 295       | 152       | 195        | 296        | 127        | 293(1)     |
| P-O                                 |             | 1.5397(4) | 1.5391(4) | 1.5390(4) | 1.5395(5) | 1.5416(7) | 1.5419(15) | 1.5403(8)  | 1.5429(3)  | 1.5403(4)  |
| O-O <sup>b</sup>                    |             | 2.5410(7) | 2.5396(7) | 2.5388(7) | 2.5350(9) | 2.544(2)  | 2.545(3)   | 2.5391(15) | 2.5363(3)  | 2.5315(3)  |
| O-O <sup>f</sup>                    |             | 2.4761(7) | 2.4780(7) | 2.4775(8) | 2.4858(9) | 2.481(2)  | 2.483(3)   | 2.4899(15) | 2.4829(4)  | 2.4946(6)  |
| O-H(O)                              |             | 1.13(1)   | 1.15(1)   | 1.15(1)   | 1.13(2)   | 1.249(7)  | 1.245(6)   | 1.249(5)   | 1.0712(7)  | 1.0677(16) |
| H(O)-O <sup>f</sup>                 |             | 1.35(1)   | 1.32(1)   | 1.33(1)   | 1.36(2)   | 1.249(7)  | 1.245(6)   | 1.249(5)   | 1.4120(6)  | 1.4276(15) |
| H(O)H(O) <sup>f</sup>               |             | 0.24(3)   | 0.18(2)   | 0.20(2)   | 0.26(4)   |           |            |            | 0.3428(12) | 0.3647(28) |
| N-H(N)                              |             | 0.83(1)   | 0.88(1)   | 0.85(1)   | 0.94(1)   | 0.88(3)   | 0.87(3)    | 0.85(4)    |            |            |
| N-O <sup>a</sup>                    |             | 3.1279(5) | 3.1279(4) | 3.1297(4) | 2.1298(6) | 3.1712(8) | 3.173(15)  | 3.1719(8)  |            |            |
| N-O <sup>h</sup>                    |             | 2.8833(4) | 2.8842(4) | 2.8867(4) | 2.9004(4) | 2.8905(7) | 2.896(2)   | 2.9104(8)  |            |            |
| H(N) <sup>c</sup> -O <sup>h</sup>   |             | 2.10(1)   | 2.04(2)   | 2.09(1)   | 2.01(2)   | 2.08(3)   | 2.09(4)    | 2.11(4)    |            |            |
| H(N)-O <sup>f</sup>                 |             | 2.65(1)   | 2.64(1)   | 2.64(1)   | 2.62(1)   | 2.64(3)   | 2.69(5)    | 2.69(4)    |            |            |
| O-P-O <sup>b</sup>                  |             | 111.21(3) | 111.18(3) | 111.13(3) | 110.83(4) | 111.22(6) | 111.2(1)   | 111.02(6)  | 110.58(3)  | 110.52(3)  |
| O-P-O <sup>c</sup>                  |             | 108.61(2) | 108.62(2) | 108.64(2) | 108.80(2) | 108.60(3) | 108.61(5)  | 108.70(3)  | 108.92(1)  | 108.95(1)  |
| P-O-H(O)                            |             | 117(1)    | 119(1)    | 117(1)    | 121(1)    | 122(2)    | 120(3)     | 120(2)     | 112.34(6)  | 112(1)     |
| P-O-N                               |             | 100.43(2) | 100.46(2) | 100.51(2) | 100.69(2) | 100.73(3) | 100.75(6)  | 100.89(3)  |            |            |
| O-H(O)-O <sup>f</sup>               |             | 173(2)    | 173(2)    | 176(2)    | 169(2)    | 166(5)    | 171(6)     | 171(5)     | 178.22(16) | 177.23(40) |
| H(N)-N-H(N) <sup>b</sup>            |             | 108(1)    | 110(2)    | 108(1)    | 115(1)    | 108(3)    | 109(3)     | 107(4)     |            |            |
| H(N)-N-H(N) <sup>e</sup>            |             | 110(1)    | 109(1)    | 110(1)    | 107(1)    | 110(2)    | 110(2)     | 111(2)     |            |            |
| N-H(N) <sup>c</sup> -O <sup>h</sup> |             | 157(1)    | 157(1)    | 156(1)    | 157(1)    | 153(3)    | 154(4)     | 157(3)     |            |            |
| $\theta$                            |             | 60.22(1)  | 60.24(1)  | 60.18(1)  | 60.04(1)  | 60.32(3)  | 60.24(7)   | 60.07(3)   | 60.98(1)   | 60.89(1)   |
| $\beta$                             |             | 34.39(2)  | 34.41(2)  | 34.43(2)  | 34.58(2)  | 34.38(3)  | 34.39(6)   | 34.49(4)   | 34.71(1)   | 34.74(1)   |

<sup>a</sup>  $x, y, z$ .<sup>b</sup>  $\bar{x}, \bar{y}, z$ .<sup>c</sup>  $\bar{y}, x, \bar{z}$ .<sup>d</sup>  $y, \bar{x}, \bar{z}$ .<sup>e</sup>  $y, \frac{1}{2} + x, \frac{1}{4} - z$ .<sup>f</sup>  $x, \frac{1}{2} - y, \frac{1}{4} - z$ .<sup>g</sup>  $y, \frac{1}{2} + x, \frac{1}{4} + z$ .<sup>h</sup>  $\bar{y}, \frac{1}{2} - x, \frac{1}{4} + z$ .



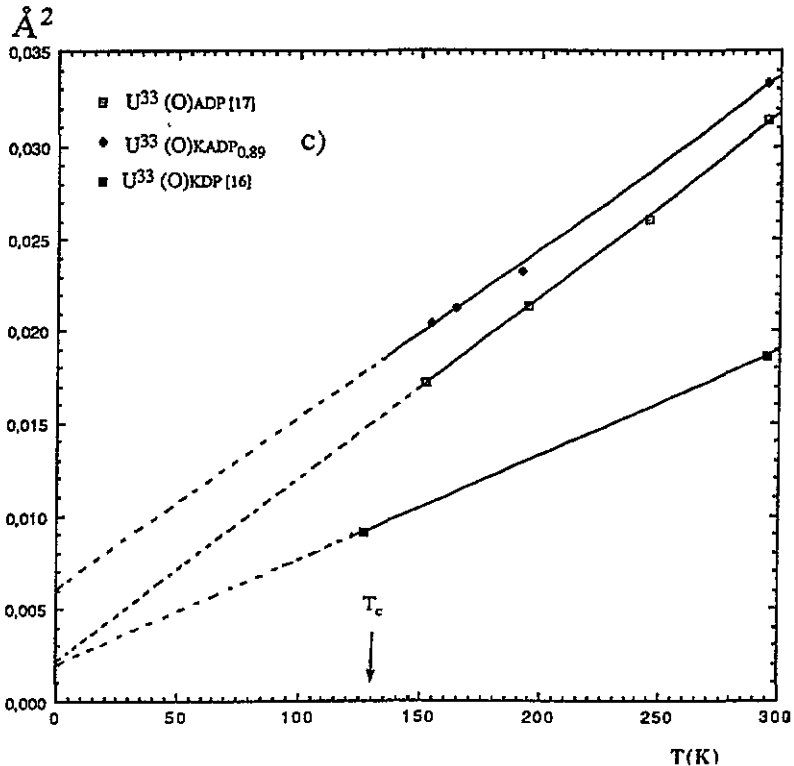


Figure 4. Anisotropic displacement parameters ( $\text{\AA}^2$ ):  $U^{11}$  (a),  $U^{22}$  (b),  $U^{33}$  (c) for the oxygen atom versus temperature (K)

### 3.1. Hydrogen bonds

The average P–O–H(O) angle is equal to  $119^\circ$  (1) in  $KADP_{0.89}$  compared with a mean value of  $112^\circ$  (1) in the paraelectric phase of KDP [16] and  $116^\circ$  calculated from the ADP room-temperature neutron data [5]. The positioning of hydrogen atoms from x-ray data may be questionable but these x-ray diffraction structure factors are very accurate; they allow the positioning of the centre of the hydrogen electron distribution, which gives the direction of the O–H(O) bond; furthermore, the non-dispersion of the P–O–H(O) angles (table 7) confirms also this last statement. On the other hand, in an x-ray experiment, the O–H(O) bond distance is generally underestimated by  $\approx 0.1 \text{ \AA}$ . In this solid solution, whatever the temperature, the average O–H distance ( $1.14(1) \text{ \AA}$ ) is always larger than that observed by neutrons in ADP [5] and KDP [16] ( $1.07 \text{ \AA}$ ). This result is surprising because one would expect the x-ray distance to be smaller than that given by neutrons in KDP or ADP if the behaviour of the H atom is the same in the pure compounds and in the mixed crystals. A definitive answer will be given by a planned neutron experiment. However, it is clear that this latter hydrogen atom occupies two different sites with equal probabilities, which can be interpreted in KDP [14, 16] as asymmetric configurations of the hydrogen bonds O–H(O)–O and O–H(O)–O related by the two-fold axis (figure 2(a)). This H(O) H(O) x-ray distance (table 7) implies a very short distance between the two possible hydrogen crystallographic sites which would make the displacement of the H atoms easier, explaining the lower value for  $T_c$  compared with ADP (132 K versus 148 K). This behaviour, which has to be confirmed

by other x-ray or neutron studies for several  $X$ -values from 0.1 and 0.9 could explain the vitreous phase of the solid solution ( $0.24 < X < 0.85$  [3, 18]), the hydrogen sites getting closer and closer.

The ammonium group is linked to four of the eight neighbouring  $\text{PO}_4$  tetrahedra by hydrogen bonds ( $\langle \text{N}-\text{O}^{\text{h}} \rangle 2.8887(5) \text{ \AA}$  compared with  $2.929(1) \text{ \AA}$  in ADP). This latter N–O bond does not change with temperature. The other N–O distances ( $3.1288(5) \text{ \AA}$ ) are also  $0.05 \text{ \AA}$  smaller than in ADP (table 7), due to the  $c$  parameter. They also do not change with temperature. On the other hand in both ADP and  $\text{KADP}_{0.89}$ , the  $\text{P}-\text{O}-\text{N}^{\text{b}}$  angles decrease by  $\simeq 0.2^\circ$  from room temperature to  $\simeq 150 \text{ K}$ , the  $\text{O}-\text{P}-\text{O}^{\text{b}}$  angles decrease, respectively, by  $0.2$  and  $0.4^\circ$  while the  $\text{O}-\text{P}-\text{O}^{\text{c}}$  angles increase by  $0.1^\circ$  and  $0.2^\circ$ , respectively. Such a variation does not exist in KDP. Then the deformation of the  $\text{PO}_4$  tetrahedron, which keeps the N–O distances constant with temperature, explains by itself the shortening of the  $c$ -cell parameter.

### 3.2. Thermal parameters

Residual Fourier maps calculated from multipole refinement

$$\delta\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{H}} (|F_0(\mathbf{H})| - |F_m(\mathbf{H})|) e^{i\phi_m} e^{-2\pi i \mathbf{H} \cdot \mathbf{r}}$$

(where  $m$  designates the multipolar or the HO model) never show any effect of anharmonicity. The rigid bond test [23] on the P–O bond for  $\text{KADP}_{0.89}$  indicates that thermal motion is very well deconvoluted from the asphericity of the electron density, the difference between mean square displacements along the interatomic P–O direction has a magnitude smaller than  $5.5 \times 10^{-4} \text{ \AA}^2$  ( $4.43 \times 10^{-4}$ ,  $4.31 \times 10^{-4}$ ,  $5.44 \times 10^{-4}$  and  $4.08 \times 10^{-4} \text{ \AA}^2$ , respectively, at 154, 164, 192 and 295 K).

Figure 3 and 4 compare the temperature dependence of the P and O thermal parameters  $U^{ii}$  to those of KDP [14, 24] and ADP [10]; each of the  $U^{ii}$  parameters is linearly dependent on the temperature in the paraelectric phase. As observed in KDP and ADP, the dominant vibration of the P atom is along the  $c$  axis ( $U^{33}(\text{P}) > U^{11}(\text{P})$ ). The vibration of P along the  $a(b)$  axis  $U^{11}$  ( $U^{22}$ ) is very close to that observed in the ADP predominant phase. On the other hand, the  $U^{33}$  thermal displacement of the phosphorus atom along  $c$  is much higher in  $\text{KADP}_{0.89}$  than for the two pure compounds, most certainly due to relaxation of the  $\text{H}_2\text{PO}_4$  anion in the solid solution. The same trends exist for the oxygen atom (figure 4). P and O atoms are disordered along two sites: the linear dependence of the  $U$ s in the paraelectric phase may be written, according to Nelmes [24], as  $U = U_i + (\Delta/2)^2$ , where  $\Delta$  is the distance between two positions of the atom and  $U_i$  is the intrinsic thermal atomic motion. Applied to  $\text{KADP}_x$ , the extrapolation of the  $U^{33}$  curves of P and O atoms leads to non-zero values, respectively, of  $0.20$  and  $0.11 \text{ \AA}$ , which are about three times larger than in the pure compounds. The similar behaviour of the P and O atoms implies that the main displacement of the  $\text{PO}_4$  group is along the  $c$  axis; however the O atom displacement is smaller, due to the  $\text{O}-\text{H}(\text{O})-\text{O}$  and  $\text{N}-\text{H}(\text{N})^{\text{c}}-\text{O}^{\text{b}}$  hydrogen bond network. Finally, extrapolations of the  $U^{11}$  and  $U^{22}$  curves of P and O atoms lead to a small value for  $\Delta$ .

Figures 5 and 6 give the temperature dependence of the N(K) atoms of  $\text{KADP}_{0.89}$  compared respectively with ADP and KDP. As K and N atoms lie at the same crystallographic site, there is a strong correlation between their thermal parameters and conclusions cannot be drawn with certainty; however we observed a linearity of the  $U^{ii}$ . The  $\text{NH}_4$  group has a behaviour close to that observed in ADP. Thermal motion of the potassium atom resembles also that of KDP but is not consistent with that given for the  $X = 0.23$  solid solution [12]. However, in the two mixed crystals, the  $U^{33}$  vibration is higher than in KDP, as expected.

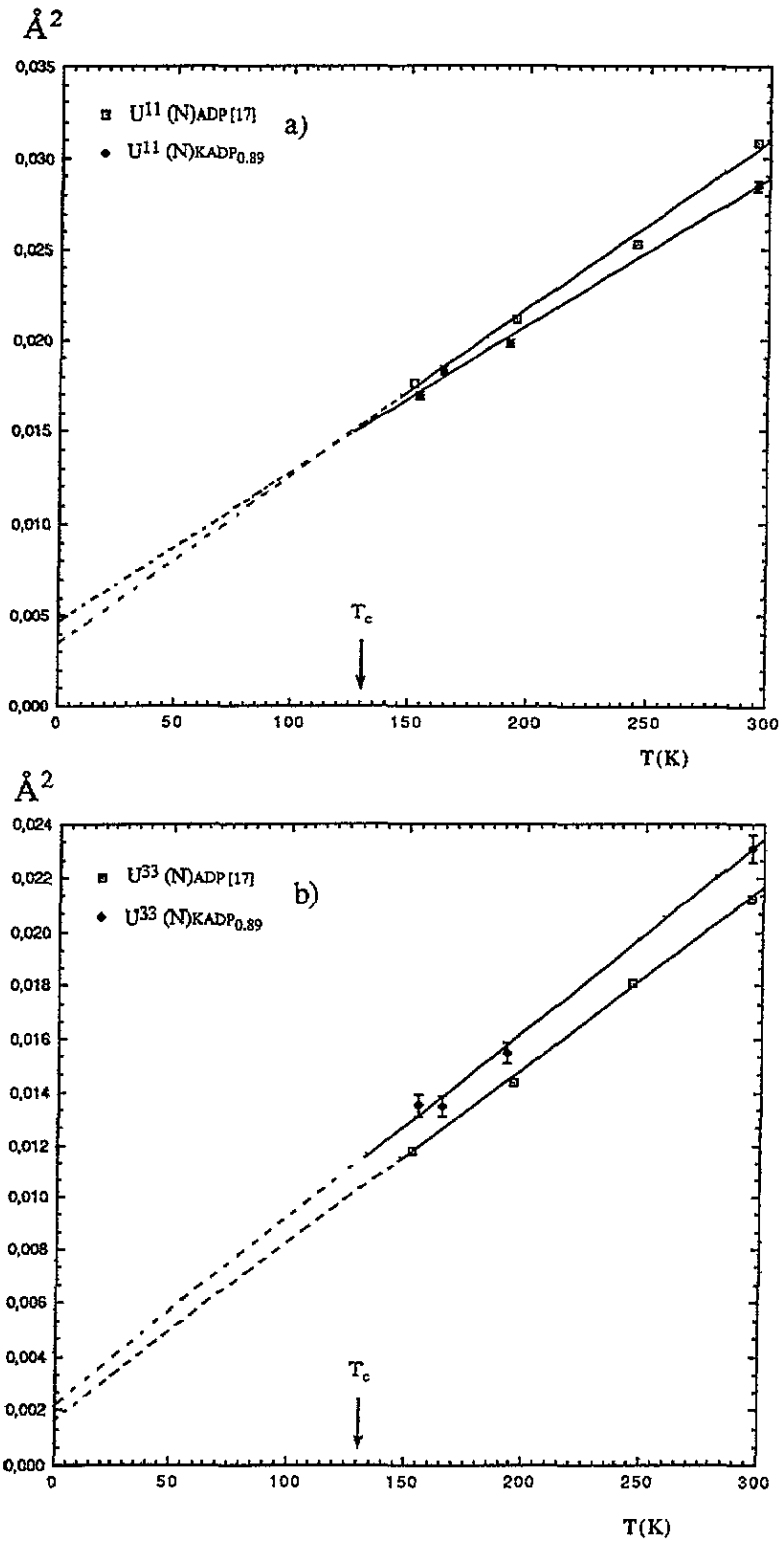


Figure 5. Anisotropic displacement parameters ( $\text{\AA}^2$ ):  $U^{11}$  (a),  $U^{33}$  (b) for the nitrogen atom as a function of temperature (K)

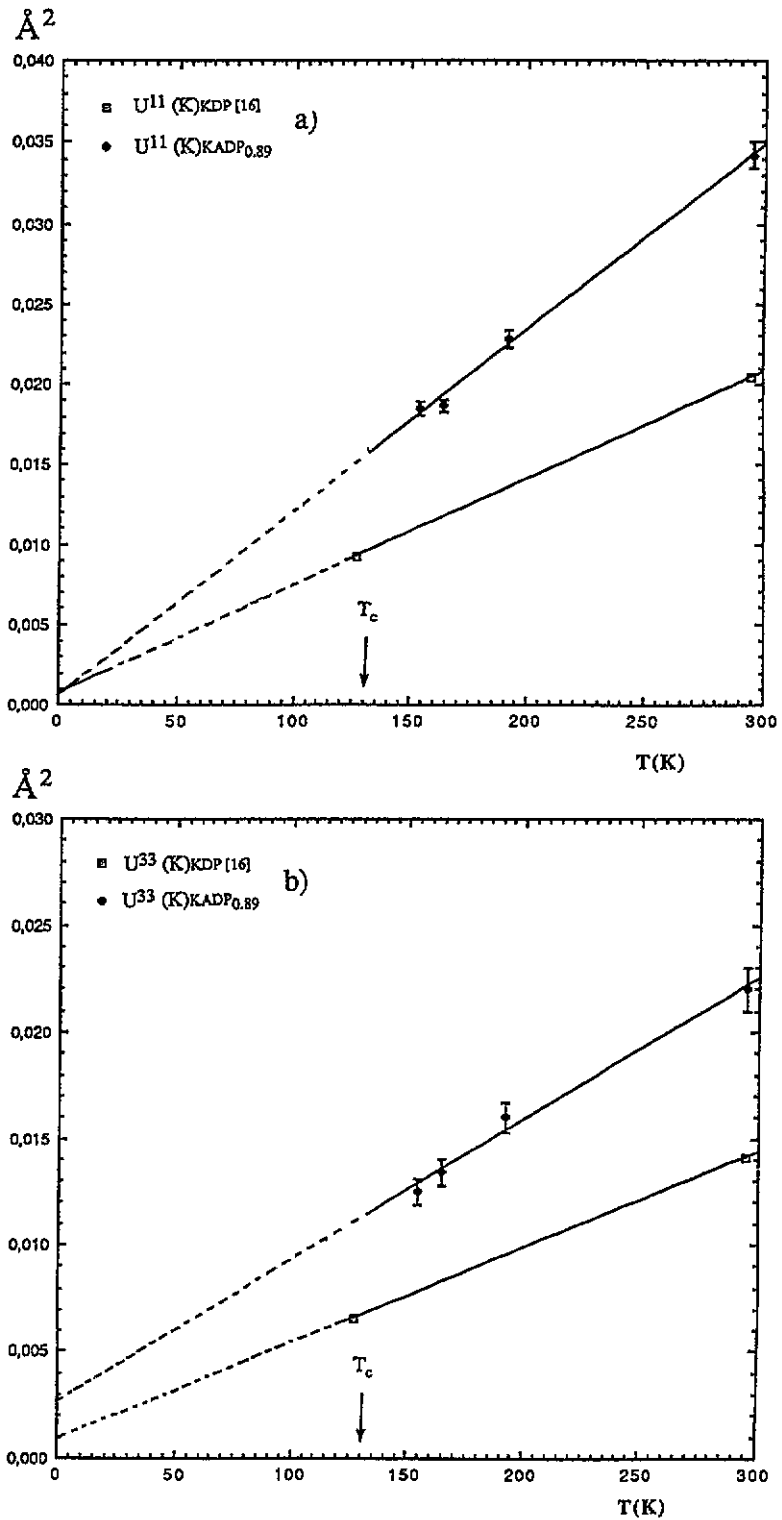


Figure 6. Anisotropic displacement parameters ( $\text{\AA}^2$ ):  $U^{11}$  (a),  $U^{33}$  (b) for the potassium atom as a function of temperature (K).

Table 8. Electron density parameters for the atoms N, P and H.

| T (K)     | N         |           |           |           | P         |           |           |           |
|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
|           | 154       | 164       | 192       | 295       | 154       | 164       | 192       | 295       |
| $P_v$     | 1.114(13) | 1.175(14) | 1.119(9)  | 1.267(11) | 1.161(18) | 1.162(20) | 1.218(13) | 1.122(16) |
| $\kappa$  | 0.982(6)  | 0.974(6)  | 0.987(4)  | 0.964(5)  | 1.016(9)  | 1.016(10) | 1.000(7)  | 1.047(8)  |
| $\kappa'$ | 1.008(41) | 1.026(38) | 0.990(42) | 0.979(43) | 1.266(19) | 1.275(17) | 1.216(18) | 1.186(25) |
| ZZ        | 0.076(5)  | 0.083(6)  | 0.074(5)  | 0.085(6)  | 0.049(8)  | 0.047(9)  | 0.034(7)  | 0.033(8)  |
| XX - YY   | 0.029(7)  | 0.039(8)  | 0.030(7)  | 0.032(8)  | 0.065(9)  | 0.059(10) | 0.079(8)  | 0.070(9)  |
| XYZ       | 0.054(22) | 0.048(23) | 0.046(18) | 0.002(20) | 0.150(36) | 0.166(37) | 0.190(26) | 0.117(25) |
| Z4        |           |           |           |           | -0.186(9) | -0.216(9) | -0.180(8) | -0.149(8) |
| X4 + Y4   |           |           |           |           | -0.019(7) | -0.022(8) | -0.019(7) | -0.021(7) |
| X3Y       |           |           |           |           | 0.022(9)  | 0.025(9)  | 0.017(8)  | 0.021(10) |

| T (K)    | H(O)      |           |           |           | H(N)    |           |           |           |
|----------|-----------|-----------|-----------|-----------|---------|-----------|-----------|-----------|
|          | 154       | 164       | 192       | 295       | 154     | 164       | 192       | 295       |
| $P_v$    | 0.377(17) | 0.410(20) | 0.341(13) | 0.304(16) | 0.700   | 0.657(22) | 0.668(16) | 0.461(14) |
| $\kappa$ | 1.171(30) | 1.158(33) | 1.199(28) | 1.263(46) | 1.16    | 1.16      | 1.16      | 1.16      |
| X        | 0.45(6)   | 0.89(14)  | 0.33(5)   | 0.24(6)   | 0.03(1) | 0.07(2)   | 0.05(1)   | 0.07(1)   |
| Y        | -0.22(10) | -0.45(11) | -0.27(7)  | -0.19(7)  | 0.08(1) | 0.07(2)   | 0.09(1)   | 0.07(1)   |
| Z        | 0.09(4)   | 0.16(7)   | 0.09(3)   | 0.12(3)   | 0.07(3) | 0.08(3)   | 0.06(3)   | -0.01(3)  |

Table 9. Electron density parameters for O.

| T (K)     | O          |            |            |            |
|-----------|------------|------------|------------|------------|
|           | 154        | 164        | 192        | 295        |
| $P_v$     | 6.397(18)  | 6.344(20)  | 6.402(13)  | 6.595(14)  |
| $\kappa$  | 0.970(1)   | 0.974(20)  | +0.969(2)  | 0.962(2)   |
| $\kappa'$ | 0.869(19)  | 0.876(19)  | 0.925(20)  | 1.014(30)  |
| X         | -0.011(12) | -0.020(12) | -0.028(9)  | 0.017(10)  |
| Y         | -0.043(12) | -0.044(13) | -0.051(9)  | -0.090(10) |
| Z         | -0.077(11) | -0.066(13) | -0.049(9)  | -0.034(9)  |
| ZZ        | -0.069(11) | -0.060(11) | -0.059(8)  | -0.032(10) |
| ZX        | -0.023(12) | -0.035(12) | -0.022(10) | -0.030(11) |
| ZY        | 0.007(14)  | 0.031(15)  | 0.008(11)  | -0.010(12) |
| XX - YY   | -0.065(15) | -0.063(15) | -0.081(12) | -0.021(13) |
| XY        | -0.235(11) | -0.252(11) | -0.222(9)  | -0.210(10) |
| ZZZ       | -0.001(15) | -0.011(15) | 0.009(13)  | 0.012(14)  |
| XZZ       | -0.050(19) | -0.035(20) | -0.044(15) | -0.040(15) |
| YZZ       | -0.000(25) | -0.010(26) | -0.042(19) | -0.039(20) |
| XX - YY   | -0.045(24) | 0.050(24)  | 0.060(19)  | 0.030(19)  |
| XYZ       | 0.006(16)  | -0.000(17) | -0.005(13) | 0.018(15)  |
| XXX       | 0.021(25)  | -0.023(25) | -0.026(19) | -0.001(20) |
| YYY       | 0.012(15)  | 0.022(16)  | 0.012(13)  | -0.015(15) |

#### 4. Conclusion

Multipole analysis of the electron density enables us to obtain unbiased thermal parameters for  $KADP_{0.89}$  from high-resolution x-ray diffraction data and multipole refinement. Thermal displacement amplitudes of the  $PO_4$  tetrahedron in  $KADP_{0.89}$  are very close to those observed for ADP in the (001) plane; along  $c$ , the P and O atoms are distributed on two sites distanced by 0.2 and 0.1 Å, respectively. The electrostatic properties calculated from the x-ray



multipole refinements of this mixed crystal will be described and compared with those of KDP and ADP in a future paper.

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