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Neutron diffraction study of the paraelectric phase of ammonium dihydrogen phosphate (ADP): hydrogen bonding of NH_4^+

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Abstract. We report on a neutron diffraction study of ammonium dihydrogen phosphate in the paraelectric phase at 158 K, i.e. slightly above the transition temperature to the antiferroelectric phase. The data have been refined in the space group $I42d$ using both an ordered model including the anharmonic motion of the protons and a disordered model in which the protons are distributed over two sites. The limited resolution of the experiment, $((\sin \theta)/\lambda)_{\max} \approx 1 \text{ \AA}^{-1}$, prevents us from drawing definite conclusions. The rotation of the NH_4^+ ion is hindered by bifurcated hydrogen bonds.

1. Introduction

At room temperature, potassium dihydrogen phosphate, KH_2PO_4 (KDP), and ammonium dihydrogen phosphate, $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP), are non-centrosymmetric isostructural compounds, and are well known for their non-linear optical and piezoelectric properties [1, 2]. These hydrogen-bonded compounds undergo different phase transitions at low temperature, from paraelectric to ferroelectric at 123 K for KDP, and from paraelectric to antiferroelectric at 148 K for ADP. The phase transition of KDP, which has been widely studied, is considered as a canonical order–disorder transition. The 50% occupation of the two symmetric sites for the proton at high temperature, and its freezing in one of the Slater configurations [3] at low temperature have been proved to occur by high-resolution neutron diffraction experiments [4]. A rather simple model proposed by Blinc and Žekš in 1960 gives a good account of the transition dynamics [5]. The two sites of the proton are represented by an Ising spin, and an exchange interaction between the pseudo-spins yields the energy of the different configurations. The coupling of the pseudo-spins with a transverse field takes into account the tunnelling of the proton between the two sites. For completeness, one should mention that the relevance of the tunnelling model has been questioned, however [6]. Very surprisingly, the phase transition of ADP has received much less attention. On the other hand, the solid solutions of the ferroelectric and antiferroelectric compounds ($\text{K}_x\text{A}_{1-x}\text{DP}$) exhibit a complicated glassy behaviour with the suppression of the structural phase transition for $0.3 < x < 0.8$ [7]. The glassy behaviour is expected to result from frustration effects,

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and two different models have been suggested to explain these effects. Blinc and co-workers considered the model used for KDP, and introduced frustrated random bonds [8]. Courtens, Cowley and co-workers considered that the tunnelling of the acid protons is not strongly relevant in the glassy phase, but they introduced a random-field effect on the pseudo-spin in addition to the random bond [9, 10]. The model was based on the observed displacements of the ammonium ions at the phase transition of ADP.

We think that a better understanding of the glassy phase requires a good knowledge of the interactions in the pure ADP. The experimental determination of the electron density and of the electrostatic potential may provide a good insight into the interaction of the NH_4^+ ions with their surroundings. Preliminary studies have been previously made [11, 12], but they may suffer from a lack of information concerning the hydrogen atoms, being based just on x-ray diffraction experiments. Hence, in ADP, half of the atoms are hydrogens located in general positions or low-symmetry sites. The correct location of the protons, and the knowledge of their thermal motion, including the anharmonic motion, are required for a reliable determination of the electron density. In addition, an approach to the dynamics, even with a model as simple as the Debye–Waller model, may be useful for the understanding of the phase transition. Thus, we have performed a neutron diffraction experiment at 158 K, i.e. slightly above the transition temperature. To our knowledge, the only previous neutron diffraction experiment on ADP single crystal was carried out at room temperature by Tenzer *et al* in 1958 [13].

2. Experimental procedure

The ADP crystals are grown from aqueous solution by slow evaporation. The specimen used for the neutron diffraction experiment was cut into a parallelepiped shape ($4 \times 5 \times 2.5 \text{ mm}^3$ along the *a*-, *b*-, and *c*-axes, respectively). The experiment was carried out at 158 K on the four-circle diffractometer 5C2 at the ORPHEE reactor (Saclay). The wavelength used is 0.8308 Å, and the data were collected up to $(\sin \theta)/\lambda = 1 \text{ \AA}^{-1}$. The absorption coefficient has been measured using a crystal with a known thickness. ADP crystallizes in the $I\bar{4}2d$ space group; the refined cell parameters are $a = b = 7.46(1) \text{ \AA}$ and $c = 7.55(1) \text{ \AA}$. 707 reflections were measured, and corrected for absorption effects, but only 654 with $I > 3\sigma(I)$, were used in the structural refinements. Among these, 338 are unique, but equivalent reflections have different intensities because of the strong extinction effects. This has been taken into account with the Becker–Coppens [14] anisotropic extinction model, type I, with a Lorentzian mosaic spread.

3. Structural refinements

In this paper, for $I\bar{4}2d$ we use the setting given by the *International Tables for Crystallography*, while most of the previous work used an interchange of *x* and *y*.

We know from previous studies that the phosphorus and nitrogen atoms occupy the special 4a and 4b positions, while the oxygen and the hydrogen H_N of the ammonium group occupy the general 16e positions. For the acid proton H_O , one may choose either the special 8d position, which is midway between two oxygen atoms, or split the atom into two twofold-related positions. This latter hypothesis has been validated by Nelmes [4] for KDP, where neutron data show that the protons are randomly distributed at a general position populated by half a proton. Consequently, we have fitted the ADP data with these two different structural models. All of the refinements were performed with the Molly

program [15]; the neutron scattering lengths are $b_H = -0.374$, $b_N = 0.926$, $b_P = 0.543$, and $b_O = 0.581$ (in units of 10^{-12} cm).

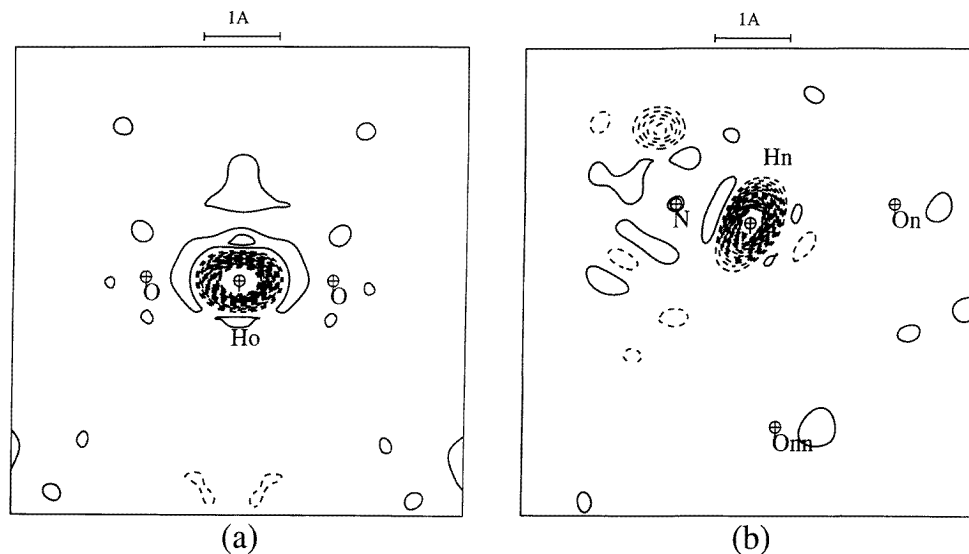


Figure 1. The Fourier synthesis of the p.d.f. of the protons, $\Delta\rho = V^{-1} \sum_H (|F_o| \exp(i\phi_0) - |F'| \exp(i\phi')) \exp(-2i\pi \mathbf{H} \cdot \mathbf{r})$ with F_o the modulus of the experimental structure factors, and ϕ_0 the calculated phase. F' and ϕ' refer to the calculated modulus and phase without the contribution of the proton. (a) H_O . (b) H_N . The crosses give the equilibrium positions of the nucleus.

3.1. Model I: H_O in the special $8d$ position

In the first stage of the refinement, the thermal motion of all of the atoms was taken into account by a harmonic anisotropic model. After the refinement of all of the parameters x , y , z , and U_{ij} , we have calculated the Fourier synthesis of the probability density function (p.d.f.) of the H_O and H_N protons (figure 1). It is clear that the protons have a rather large motion, and that the p.d.f. differs from a gaussian distribution. We then considered an anharmonic model for the thermal motion of the protons. The results of the refinement are reported in table 1. An anharmonic model for the heavy atoms was also tested, but it was rejected because it did not improve the quality of the fit significantly. We have fitted the second-rank thermal motion tensor of the ammonium ions with the TLS model [16, 17]. The corresponding residual factor $R_w = 0.04$ shows that the ammonium ion has mainly a rigid-body motion. The elements of the tensors \mathbf{T} and \mathbf{L} are isotropic in the ab -plane (table 2). The correction of the N–H distance for libration amounts to 0.027 Å. A refinement including those reflections with $I < 3\sigma$ leads to the same parameters within 0.2 esd.

3.2. Model II: H_O in the general position

Harmonic motion was considered for all of the atoms except H_N , which was given an anharmonic motion. The results are reported in table 1. In order to compare the hydrogen bond O–H...O in ADP and KDP, we characterize the bond as in reference [4]. The distances between the oxygens and between the two sites of the proton are 2.471(4) Å and 0.377(5) Å

Table 1. Fractional coordinates and non-vanishing elements of the thermal motion tensors for models I, II, and III according to: $T(H) = \exp(-2\pi^2 h_i h_j U^{ij} a_i^* a_j^*)$; $R(F) = \sum ||F_o| - K|F_c|| / \sum |F_o|$; $R_w(F) = \sum w(|F_o| - K|F_c|)^2 / \sum w|F_o|^2$; $GOF = [\sum w(|F_o| - K|F_c|)^2 / N_{obs} - N_v]^{1/2}$; N_{obs} : data; N_v : parameters.

		Model I	Model II	Model III
N	U_{11}	0.0172(3)	0.0172(3)	0.0171(3)
	U_{33}	0.0100(4)	0.0100(4)	0.0096(4)
P	U_{11}	0.0072(3)	0.0073(3)	0.0072(3)
	U_{33}	0.0114(6)	0.0112(6)	0.0113(7)
O	x	0.1477(1)	0.1477(1)	0.1477(1)
	y	0.0847(1)	0.0847(1)	0.0847(1)
	z	0.1150(1)	0.1150(1)	0.1150(1)
	U_{11}	0.0116(3)	0.0114(3)	0.0114(3)
	U_{22}	0.0096(3)	0.0100(3)	0.0099(3)
	U_{33}	0.0159(3)	0.0158(4)	0.0157(4)
	U_{12}	0.0017(3)	0.0017(3)	0.0018(3)
	U_{13}	-0.0057(3)	-0.0057(3)	-0.0057(3)
	U_{23}	-0.0034(3)	-0.0034(3)	-0.0035(3)
H _O	x	0.1443(4)	0.1445(4)	0.1445(4)
	y	0.2500	0.2253(4)	0.2254(4)
	z	0.125	0.120(1)	0.120(1)
	Occupation	1	0.5	0.5
	U_{11}	0.023(1)	0.023(1)	0.023(1)
	U_{22}	0.040(2)	0.011(2)	0.011(2)
	U_{33}	0.023(1)	0.021(1)	0.021(1)
	U_{12}		-0.000(1)	-0.0003(9)
	U_{13}		-0.005(2)	-0.004(2)
	U_{23}	0.001(1)	-0.002(2)	-0.003(2)
	c_{123}	0.021(6)		
	d_{2222}	-0.016(1)		
d_{2223}	-0.021(3)			

respectively. The angle ϕ between the O...O bond and the xy -plane is $3.51(4)^\circ$, and the corresponding angle ψ for the line joining the two sites of the proton is $12(2)^\circ$. As in KDP [4] and ADP at room temperature [13], the main feature of the hydrogen bond is that the sites of the proton are not on the O–O bond.

3.3. Model III

The eigenvalues of the harmonic part of the thermal vibration tensor of the protons determined with model I are reported in table 3. As also shown in figure 1, table 3 shows that the motion of H_N is as large as that of H_O. In addition to the two-sites model for H_O, one may therefore consider that the location of H_N is disordered over two positions as well. As these positions are not related by symmetry operations of the space group, both the positions and their occupancies can be refined. Only harmonic motion is considered for all of the atoms. The results of the refinement are reported in table 1. They show two positions for H_N distant by $0.27(4)$ Å, and with relative occupancies of $0.6(1)$ and $0.4(1)$ respectively. As expected from the standard deviation, the quality of the refinement does not change if both sites are equally populated. In both positions, the NH₄ ion suffers

Table 1. (Continued)

		Model I	Model II	Model III	
				H _{N1}	H _{N2}
H _N	<i>x</i>	0.1085(8)	0.1085(8)	0.103(4)	0.123(3)
	<i>y</i>	0.0161(4)	0.0146(7)	0.011(3)	0.021(3)
	<i>z</i>	0.5768(4)	0.5769(4)	0.587(4)	0.558(5)
	Occupation	1	1	0.6(1)	0.4(1)
	<i>U</i> ₁₁	0.054(2)	0.055(2)	0.064(6)	0.023(7)
	<i>U</i> ₂₂	0.034(1)	0.034(1)	0.038(4)	0.024(5)
	<i>U</i> ₃₃	0.041(1)	0.041(1)	0.029(5)	0.030(7)
	<i>U</i> ₁₂	0.004(1)	0.006(1)	0.007(4)	−0.002(3)
	<i>U</i> ₁₃	−0.023(2)	−0.023(2)	−0.021(4)	−0.020(4)
	<i>U</i> ₂₃	−0.004(2)	−0.002(2)	−0.004(3)	0.003(4)
	<i>c</i> ₁₁₁	−0.016(3)	−0.016(3)		
	<i>c</i> ₂₂₂		−0.005(2)		
	<i>c</i> ₁₂₂	−0.011(3)	−0.011(3)		
	<i>c</i> ₁₁₃	0.016(4)	0.017(4)		
	<i>c</i> ₁₂₃	0.011(5)	0.008(5)		
	<i>d</i> ₁₁₁₃	0.019(5)	0.019(5)		
	<i>d</i> ₁₂₃₃	−0.016(7)			
<i>d</i> ₂₂₂₃	0.005(3)	0.007(3)			
Agreement factors	GOF	2.28	2.29	2.34	
	<i>R</i> (<i>F</i>)	3.51%	3.52%	3.54%	
	<i>R</i> _w (<i>F</i>)	3.55%	3.57%	3.63%	

Table 2. Elements of the tensors **T** and **L**. \parallel and \perp mean parallel and perpendicular to the *c*-axis, respectively.

$$\begin{array}{ll}
 T_{\parallel} = 0.015(2) \text{ \AA}^2 & T_{\perp} = 0.022(2) \text{ \AA}^2 \\
 L_{\parallel} = 70(20) \text{ deg}^2 & L_{\perp} = 126(14) \text{ deg}^2
 \end{array}$$

Table 3. The eigenvalues of the tensor of the harmonic thermal motion of the protons.

		H _O	H _N	Eigenvalue ratio
Eigenvalues	λ_1	0.0206	0.0174	0.845
	λ_2	0.0208	0.0323	1.553
	λ_3	0.0620	0.0782	1.261

from strong tetragonal distortions with $c/a = 1.2(1)$ and $c/a = 0.67(7)$, respectively, and this throws some doubt on the physical meaning of the results. A more realistic model would be to consider a more rigid NH_4^+ ion, and then the disordering over two sites would imply the relaxation of the nitrogen position from the $\bar{4}$ symmetry site. The interpretation of the Raman scattering spectra suggests a twofold symmetry for NH_4^+ in the paraelectric phase [18]. This relies on a correct assignment of the bands of the crystal which is not unambiguous, since the crystal may not only lift the degeneracy of the molecular modes, but also mix different modes of the same molecule or modes of different molecules. We have not tried a refinement with such a model, for reasons that will be given below.

3.4. Comparison between the different models

While the statistical agreement factors (table 1) favour model I, the other models cannot be disregarded. In fact, our data do not allow us to distinguish between a disordered model and anharmonic thermal motion. That was to be expected, since the distances between the sites of the disordered models are much smaller than the resolution of the experiment (0.5 Å). A better understanding of the structure would require a high-resolution diffraction experiment with $(\sin \theta)/\lambda$ as high as 2 \AA^{-1} .

4. Discussion

Our discussion is based on the results obtained with model I—and we use the N–H_N distance of 1.003(5) Å (not corrected for libration effects). We shall first compare our results with those obtained by Tenzer *et al* at room temperature (R.T.) [13]. Although, the lattice parameters depend on the temperature, the *c/a* ratios being 1.006 and 1.012 at R.T. and 158 K respectively, the tetragonal distortion of the PO₄ tetrahedron remains the same at both temperatures, the OPO angles being 111.2 and 111.3(1)° at R.T. and 158 K respectively. The orientations of the tetrahedron, with respect to the crystal axis, are almost the same at the two temperatures; the rotation of its principal axis around the *c*-axis is 0.4° between R.T. and 158 K. While the NH₄⁺ tetrahedron is flattened along the *c*-axis at R.T., the H–N–H angle being 113.43°, it has a cubic $\bar{4}3m$ symmetry at 158 K within the accuracy of the data, the H–N–H angle being 109.3(5)° (109.47° for $\bar{4}3m$ symmetry). This comparison needs to be considered with great care, however. In fact, the room temperature data have been refined with a harmonic model for the hydrogens, and we have found that the harmonic approximation of model I yields a tetragonal distortion of the NH₄⁺ ions with a H–N–H angle of 111.6(4)°. Our result is consistent with NMR experiments, which show a non-tetragonally distorted ammonium ion at high temperature [19]. The orientations of the NH₄⁺ tetrahedron with respect to the crystal axis are different for the two experiments; a rotation of 7.3° around the *c*-axis is observed between R.T. and 158 K. Once again, this may result from the difference between the two models.

Let us now consider the hydrogen bonding of the NH₄⁺ ion which is our main interest in the present study. The ammonium ion is surrounded by eight oxygen atoms, four of which (O_{*n*}) are nearest neighbours (the NO_{*n*} distance is 2.889(3) Å), while the remainder (O_{*m*}) are next-nearest neighbours (the NO_{*m*} distance is 3.172(4) Å). Only the N–H...O_{*n*} bonding has been considered so far [9, 10, 13]. We recall that the hydrogen bond is considered as optimal when the three atoms lie on a straight line; in ADP, the N–H...O_{*n*} angle is 156.8(3)°, however. The O_{*n*} tetrahedron is very much flattened along the *c*-axis (the O_{*n*}NO_{*n*} angle is 138.69(8)°). If the NH₄⁺ ion is considered as very rigid, the optimization of the hydrogen bond would be obtained when the principal axes of the NH₄⁺ and O_{*n*} tetrahedrons coincide; this implies a shortest HO_{*n*} distance of 1.934 Å, and a N–H...O_{*n*} angle of 158.12°. The observed angle between the corresponding principal axes in the (*a*, *b*) planes of the two tetrahedra is 5.06(1)°, and the corresponding H...O_{*n*} distance is 1.940(6) Å. The rotation of the NH₄⁺ ion is such that the distance HO_{*m*} (2.634(4) Å) is shorter than in the case where the principal axes of the tetrahedra coincide. This suggests that the O_{*m*} are also attractors for the protons. The sum of the three angles N–H...O_{*n*}, O_{*n*}...H...O_{*m*}, and O_{*m*}...H–N amounts to 359.6(2)°, and the distance of the proton from the N–O_{*n*}–O_{*m*} plane is 0.043(4) Å. This is characteristic of a three-centre or bifurcated hydrogen bond [20]. The hydrogen bonding of the ammonium ion in ADP is then strongly frustrated, and this is well demonstrated by the orientation of NH₄⁺ in the (*a*, *b*) plane, which is not simply related to

the crystal axis or to the principal axis of the O_n tetrahedron (see figure 1(b)).

An interesting feature of the dynamical behaviour, as shown in figure 1(b), is related to the bifurcated hydrogen bond. The proton performs a rather large motion in the NO_n-O_{nn} plane, favouring one hydrogen bond for some proton positions where the H...O distance decreases, while the other bond is favoured for other positions. Such a dynamical improvement of the hydrogen bonding has been previously suggested for perovskites [21]. Also, concerning the dynamics of the ammonium, the fact that it exhibits a nearly rigid motion allows the dynamics to be studied with rather simple models. The hindered rotational energy levels are those of a spherical top in a rotational potential function which has both the symmetry of the ion ($\bar{4}3m$) and the symmetry of the site ($\bar{4}$). The potential $V(\omega)$ can be expanded in terms of Wigner $D_{MK}^J(\omega)$ functions [22], ω being the Euler angle of the ions with respect to the crystal axis. For a given accuracy, the number of Wigner functions (the largest J) increases with the height of the potential barrier on going from the rotational to the librational limit. For the $\bar{4}$ site symmetry, there are 12 Wigner functions with $J \leq 7$, which do not have their extremum values at the same Euler angles [22], showing again the strong frustration of the NH_4^+ bonding in the crystal. As a strong frustration often results in metastable equilibrium positions, this gives theoretical support to a disordered model for the ammonium (model III). A tetragonal distortion of the NH_4^+ ion leading to the $\bar{4}2m$ symmetry of the ion would not modify the previous conclusions.

5. Conclusion

Despite the lack of resolution of our experiment, we have obtained a p.d.f. for the protons which allowed us to draw conclusions concerning the binding of the ammonium in the crystal not depending on the subtle details of the p.d.f. The latter may be only seen (if they are seen at all) in very high-resolution diffraction experiments that require deuterated samples, owing to the poor signal-to-noise ratio of protonated compounds, namely, ones with neutrons of very short wavelengths. An experimental study of the charge density using these results is under way.

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