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X-ray Determination of the Thermal Expansion of Ammonium Dihydrogen Phosphate

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The lattice parameters of ammonium dihydrogen phosphate (ADP) have been measured accurately at different temperatures between 24 and 134 °C. Within the accuracy of measurements both the parameters change linearly with temperature, the respective variations being given by the expressions

$$a_t = 7\cdot4991 + 29\cdot45 \times 10^{-5}(t-20)$$
$$c_t = 7\cdot5493 + \ 1\cdot44 \times 10^{-5}(t-20)\ .$$

Here a_t and c_t are expressed in Å and the temperature t in °C. It is found that the coefficient of expansion perpendicular to the c axis ($\alpha_\perp$) is greater than the coefficient parallel to this direction ($\alpha_{\parallel}$), their values being $\alpha_\perp = 39\cdot3 \times 10^{-6}$ °C^{-1} and $\alpha_{\parallel} = 1\cdot9 \times 10^{-6}$ °C^{-1}. These coefficients are compared with those of potassium dihydrogen phosphate in which $\alpha_\perp < \alpha_{\parallel}$. It is suggested that this difference in the thermal expansion of the two isomorphous crystals may be due to the removal, from the ADP lattice, of the constraints produced by large NH_4 ions when the temperature of ADP is increased.

Introduction

Although ammonium dihydrogen phosphate (ADP) is isomorphous with the tetragonal dihydrogen phosphates of potassium (KDP) and rubidium (RDP), yet it has some properties which are qualitatively different from those of the two latter. The low-temperature transitions are antiferroelectric and ferroelectric respectively. At room temperature the elastic stiffness constants c_{11} and c_{33} of ADP are in the ratio of 2:1 whereas they are almost equal for KDP. The axial ratio of ADP, at room temperature, is greater than unity and those of KDP and RDP are less than unity. The most interesting difference is that between the principal coefficients of thermal expansion. In KDP the coefficient along the c axis is greater than that in a perpendicular plane. In ADP the reverse is true (Mason, 1946). X-ray measurements of the cell dimensions and their temperature variation for KDP have been reported by De Quervain (1944) and Ubbelohde & Woodward (1947). For ADP, apart from the values at room temperature and 5 °C above and below the transition point (Keeling & Pepinsky, 1955), no other data are available. A systematic study is therefore planned for the determination of the lattice parameters of ADP at various temperatures. This paper gives the results for elevated temperatures.

Experimental and results

Ten powder photographs of AR grade salt were taken at different temperatures between 24 and 134 °C, with two cameras, a flat-plate back-reflexion camera (A) and a symmetrically focusing back-reflexion camera (B). Details about the evaluation of the lattice parameters are the same as given in Deshpande & Mudholker (1960) and Deshpande & Sirdeshmukh (1961, 1962). All the powder lines used had their $\sin^2\theta$ values greater than 0·89. Only lines which could be unambiguously indexed were used. The number of lines measured varied from film to film, depending on the measurability of the lines. Cohen's method (1935) was used with appropriate error functions. For one film, taken at room temperature, standard errors in the lattice parameters were evaluated by the procedure given by Jette & Foote (1935). These were found to be ±0·00038 Å (0·005%) and ±0·0012 Å (0·016%) in the a and c parameters respectively. The larger error in the c value was due to the unfavourable l-indices of the reflexions recorded by Cu $K\alpha$ radiation. As the number of lines used at higher temperatures was slightly smaller the corresponding values of the parameters will be less accurate.

Table 1. *Lattice parameters of ammonium dihydrogen phosphate at different temperatures*

t (°C)	Camera	a_t(obs.) (Å)	a_t(calc.) (Å)	c_t(obs.) (Å)	c_t(calc.) (Å)
24·5	*A*	7·4997	7·5004	7·5502	7·5494
25·0	*B*	7·5013	7·5006	7·5485	7·5494
33·0	*B*	7·5025	7·5029	7·5495	7·5495
37·5	*A*	7·5040	7·5043	7·5499	7·5496
66·0	*A*	7·5136	7·5127	7·5499	7·5500
79·0	*B*	7·5161	7·5165	7·5492	7·5502
97·0	*B*	7·5219	7·5218	7·5499	7·5504
101·0	*A*	7·5238	7·5230	7·5514	7·5505
123·0	*B*	7·5292	7·5294	7·5509	7·5508
134·0	*B*	7·5321	7·5327	7·5510	7·5509
$q = 0\cdot674\ \sqrt{(\Sigma \varrho_i^2/(N-K))}$			0·00043		0·00045

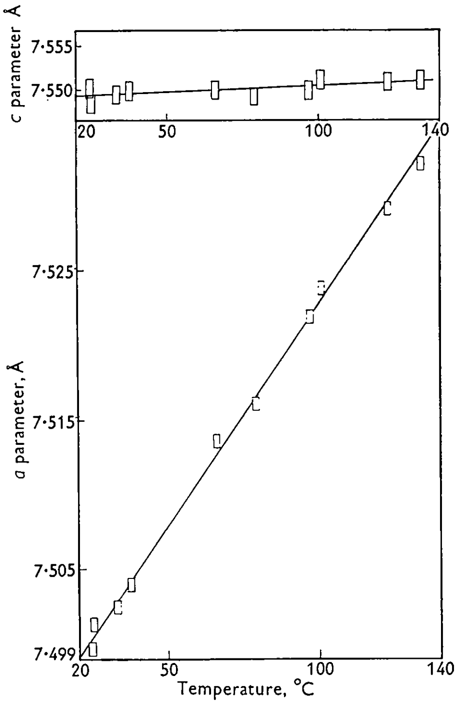

Fig. 1. Temperature variation of the lattice parameters of ammonium dihydrogen phosphate.

Table 1 gives the observed values of the cell dimensions at different temperatures. Temperature-parameter plots (Fig. 1) indicated that both the parameters increased linearly with temperature, within the experimental accuracy. Least-squares treatment gave the following equations for the variation of the two parameters with temperature:

$$\left.\begin{aligned} a_t &= 7{\cdot}4991 + 29{\cdot}45\times10^{-5}(t-20) \\ c_t &= 7{\cdot}5493 + 1{\cdot}44\times10^{-5}(t-20) \end{aligned}\right\} \qquad (1)$$

where a_t and c_t are expressed in Å and t in °C. The relatively large error in the evaluation of the c parameter combined with the very small coefficient of expansion in that direction makes the observed c values appear rather confusing. However, as Fig. 1 shows, the least-squares fitting gives a correct form of the temperature variation. The goodness of fit of both the straight lines has been computed with the help of the quantity $q = 0{\cdot}674\sqrt{(\Sigma\varrho_i^2/(N-K))}$, where ϱ_i are the residuals of the observed and calculated values of the parameters, N is the number of lines used and $K=2$ is the number of constants to be evaluated (Livingston, 1957). The values of the parameters calculated from (1) and the measure of the goodness of fit are given in Table 1. The cell dimensions at 20 °C obtained are found to be in good agreement with the values reported in the ASTM cards. The two principal coefficients of thermal expansion, defined by

$$\alpha = \frac{1}{l_{20}}\cdot\frac{dl}{dt},\ (l = a \text{ or } c)$$

come out as $\alpha_\perp = 39{\cdot}3\times10^{-6}$ deg.C^{-1} and $\alpha_\parallel = 1{\cdot}9\times10^{-6}$ deg.C^{-1}.

Discussion

As already mentioned, there are some interesting differences between the thermal expansions, elastic constants and the axial ratios of KDP and ADP. These properties are summarized in Table 2 for the sake of comparison. As KDP and RDP are isomorphous, packing considerations suggest that the replacement of K$^+$ ion by Rb$^+$ ion would expand the lattice in both a and c directions. This is also what has been observed experimentally. However, the expansion is not the same in the two directions. Structural studies of KDP have shown that all the O–H · · · O bonds in this crystal lie almost in the X–Y plane (Kanzig, 1957). It is likely that in RDP these bonds are inclined to this plane resulting in an elongation of the cell in the c direction, over and above the expansion produced by the larger size of the Rb$^+$ ion.

The effective ionic radius of the ammonium ion is the same as that of Rb$^+$, yet there is a significant difference in the cell dimensions of RDP and ADP. The a parameter of ADP shows a considerable decrease while the c parameter shows an increase over the corresponding parameters of RDP. This difference is obviously due to the role of NH_4^+ ions and their ability to form hydrogen bonds. X-ray and neutron-diffraction studies (Ueda, 1948; Keeling & Pepinsky, 1955; and Tenzer, Frazer & Pepinsky, 1958) have shown that there are two systems of hydrogen bonds in ADP. One of these is similar to that found in KDP and connects each PO_4 group to four neighbouring PO_4 groups. However, in ADP because of the size of the cation the O–H · · · O bonds are inclined to the X–Y plane. The other H-bond system, peculiar to ADP, is such that it links every N atom with four

Table 2. *Comparison of the properties of* KDP, RDP *and* ADP

	a (Å)	c (Å)	c/a	Cationic radius (Å)	$c_{11}\times10^{-10}$ (dyn.cm^{-2})	$c_{33}\times10^{-10}$ (dyn.cm^{-2})	$\alpha_\perp\times10^6$ (°C^{-1})	$\alpha_\parallel\times10^6$ (°C^{-1})
KDP	7·434(1)	6·945(1)	0·934	1·33(2)	78·5(3)	76·3(3)	21·6(1)	34·3(1)
RDP	7·58(4)	7·28(4)	0·960	1·48(2)	—	—	—	—
ADP	7·500(5)	7·550(5)	1·008	1·48(2)	66·9(6)	32·8(6)	39·3(5)	1·9(5)

(1) Ubbelohde & Woodward (1947). (2) Wells (1950). (3) Huntington (1958).
(4) Magyar (1948). (5) Present work. (6) Joel & Wooster (1960).

oxygens of neighbouring PO_4 groups and forms a flat tetrahedron (Megaw, 1957). This flatness is with respect to the *c* axis. Thus in ADP the H-bond vectors of both the systems have larger components in the X–Y plane. This feature makes the ADP structure more firmly bound in this plane than the KDP and RDP lattices are and hence is responsible for the decrease in the *a* parameter and a consequent elongation along the *c* direction. This picture is also consistent with the relative values of the elastic stiffness constants c_{11} and c_{33}. However, it leads to a difficulty in understanding the difference in thermal expansion. One expects, in a general way, a small coefficient of expansion in a direction along which the elastic constant is large and *vice versa*. This expectation is not satisfied in ADP. An explanation of this behaviour is suggested below.

Tenzer *et al.* (1958) have pointed out that the angle between the P–O and O–H ··· O bonds in ADP is 116° 42′, whereas it is only 113° 15′ in KDP. They have attributed this difference to the *c*-direction packing. They have also noticed a difference in ADP between the above angle and the angle P–O–H_0. This, according to these authors is suggestive of a tendency of the ADP lattice to assume for the angle P–O_H–O a value more nearly equal to that in KDP. This means that if the constraints due the size of the NH_4^+ ions are removed the O–H ··· O bonds would fall in the X–Y plane and thereby reduce the length of the cell along *c* direction. This is probably what takes place when the temperature is increased. With increasing temperature there is an expansion of the lattice, accompanied by a general loosening of the structure. The constraints due to the ammonium ions are reduced, the angle P–O_H–O gradually assumes a value equal to that in KDP and the O–H ··· O bonds progressively fall in the X–Y plane. This would result in a small but progressive collapse of the lattice along the *c* direction, which will be superposed on the usual thermal expansion. The obvious result will be a reduced coefficient of expansion perpendicular to the X–Y plane, contrary to expectation. It is rather difficult to make any quantitative estimate of the two opposing effects. An accurate structural study at high temperatures is likely to give evidence about the changes of the angles discussed above. Work of this nature is being planned in this laboratory.

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