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Crystal transition in diammonium hydrogen orthophosphate.

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A high-temperature polymorph of diammonium hydrogen orthophosphate is produced when diammonium phosphate is heated to a temperature above ~140°C (precautions being taken to prevent ammonia loss from the sample); reversion to the room-temperature form occurs at about 100°C. At 120°C the unit cell is orthorhombic, of dimensions $a=10{\cdot}78$, $b=14{\cdot}46$, $c=9{\cdot}06$ Å, and the probable space-group is primitive. The powder-diffraction pattern is given, and the relationship of this high-temperature form to the room-temperature form discussed.

Many ammonium salts have characteristic transition temperatures at which crystalline changes occur: for example, ammonium chloride and bromide both convert from the cubic lattice *Pm*3*m* to the cubic lattice *Fm*3*m* as their temperatures are raised through 184·3 and 137·8°C respectively, while ammonium dihydrogen orthophosphate changes from the orthorhombic lattice *Fdd*2 to the tetragonal lattice $I\bar{4}2d$ as its temperature is raised through −126°C. Solid diammonium hydrogen orthophosphate loses ammonia readily on heating, and for this reason it has been little studied at elevated temperatures. During a differential thermal analysis investigation on $(NH_4)_2HPO_4$ in sealed containers (Sherwin, 1964) an endothermic peak characteristic of a crystalline transition was observed.

The transition temperature appeared to be slightly influenced by the presence of water and by repeated cycling through the transition, but was little affected by the rate of heating and cooling, within the range 0·25–2·5°C per minute. In a substantially anhydrous sample the conversion $\beta \rightarrow \alpha$ (α and β are defined as the high and low temperature forms, respectively) took place at 145°C and the reverse change $\alpha \rightarrow \beta$ at 102°C; after 17 complete cycles the conversion temperatures were 126°C for $\beta \rightarrow \alpha$ and 98°C for $\alpha \rightarrow \beta$. In the case of a sample containing 5 wt.% water, the change $\beta \rightarrow \alpha$ occurred at 135°C on the first heating cycle, and $\alpha \rightarrow \beta$ at 93°C; after 34 cycles $\beta \rightarrow \alpha$ took place at 128°C and $\alpha \rightarrow \beta$ at 92°C. The repeated cycling caused only a small reduction in the transition temperature hysteresis.

The latent heat associated with the transition, calculated from the area of the thermal analysis peaks, was 5·5 cal.g^{-1}. (standard deviation 0·2 cal.g^{-1}.).

The conversion was studied by X-ray powder diffraction with the Geiger diffractometer (Coates & Woodard, 1963) and specimen-heating adaptation (Coates & Woodard, 1964) previously described. The $(NH_4)_2HPO_4$ (all through 300 B.S.S. to provide sufficient crystallite randomization) was pressed into a ½ in. diameter disc at a pressure of 10 tons.in^{-2}. To reduce ammonia evolution, the disc was enclosed in a fold of Kapton polyimide film (thickness 0·001 in.), the edges of the film being sealed with Evostik. A thermocouple element was attached to the irradiated surface of the disc using Evostik and the leads brought out of the packet through a sealed edge. At 120°C and for 30 minutes X-ray exposure time, the ammonia loss and consequent production of $NH_4H_2PO_4$ peaks in the diffraction pattern were insignificant. The disc used to obtain the measured diffraction pattern was heated as rapidly as possible to 145°C, and then immediately cooled to 120°C. This gave an $NH_4H_2PO_4$ content in the diffraction pattern of about 5%, which caused no interference with the α-$(NH_4)_2HPO_4$ peaks.

The X-ray powder-diffraction pattern for α-$(NH_4)_2HPO_4$ at 120°C is given in Table 1. Use of the Hesse–Lipson sorting method (Lipson, 1960) yielded an orthorhombic unit-cell: $a=10{\cdot}78$, $b=14{\cdot}46$, $c=9{\cdot}06$ Å. The indices of the lines are given in the table, together with a comparison between $\sin^2\theta_{\text{obs}}$ and $\sin^2\theta_{\text{calc}}$. The final column quotes the statistical error which can be expected in $(\sin^2\theta_{\text{obs}} - \sin^2\theta_{\text{calc}})$ for a unit cell of these dimensions, calculated according to the method of de Wolff (1961). All actual errors are smaller than those statistically expected, indicating a good probability that the derived unit cell is the correct one. The lack of systematic absences in *hkl* terms suggests

Table 1. *X-ray powder-diffraction pattern for* α-$(NH_4)_2HPO_4$ *at* 120°C

d(Å)	*I* rel.	$\sin^2\theta_{\text{obs}}$ $\times 10^4$	$\sin^2\theta_{\text{calc}}$ $\times 10^4$	*hkl*	Statistical error in $\sin^2\theta \times 10^4$ (de Wolff, 1961)
5·40	67	204	204	200	16
4·53	20	289	289	002	
3·83	100	405	402	022	13
3·29	26	548	544	032	
3·25		562	560	311	
3·12	3	609	606	222	
3·00	3	659	658	240	
2·92	15	696	701	103	
2·77	2	773	777	312	
2·70	2	814	815	123	
			816	400	
2·62	7	864	861	322	
2·48	7	965	968	223	10
2·25	3	1172	1168	350	
2·07	2	1385	1388	214	9
			1389	520	
			1390	070	
1·98	3	1514	1513	171	
			1514	262	
1·88	1	1678	1678	072	
			1678	522	
1·81	2	1811	1806	005	
			1814	244	8
			1815	080	
1·75	2	1937	1938	181	
			1938	611	
1·64	3	2206	2206	470	
1·58	2	2377	2379	325	
1·51	2	2602	2600	006	
			2600	623	7
			2601	711	

the cell is primitive, and there are no obvious systematic absences in $hk0$ or $0kl$ terms. There is only one $h0l$ term (in which $k+l=2n$), making no conclusion possible from these; in the cases where $0k0$ and $00l$ terms have k and l odd, acceptable duplicate indices are available, again making conclusions impossible.

Data for β-$(NH_4)_2HPO_4$ were given by Smith, Lehr & Brown (1957): $a=8{\cdot}03$, $b=6{\cdot}68$, $c=11{\cdot}02$ Å; $\beta=113°38'$; 4 molecules per unit-cell, calculated density 1·61 g.cm^{-3}. It is to be noted that $c \sin\beta = 10{\cdot}09$ Å, which compares with 10·78 Å for the a axis of the α form, suggesting that this direction may remain common to both forms, merely expanding slightly. If the α form had 8 molecules per unit cell, the calculated density would be 1·25 g.cm^{-3}. The ratio of low-temperature-form density to high temperature-form density is then 1·29, which compares with ratios of 1·24 and 1·20 for NH_4Br and NH_4Cl respectively.

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Effect of wavelength on the sign of the photo-elastic constant (P_{11}-P_{12}) of crystals of sodium-chloride structure.

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A new method is presented for calculating the reversal wavelength at which the strain optical constant $(P_{11}-P_{12})$ for alkali halides of sodium-chloride structure changes sign. Calculated absolute strain optical constants, their ratios and the strain polarizability constants of rubidium halides are given.

Bansigir & Iyengar (1961*a*) developed a theory of piezo-optic birefringence in cubic crystals of sodium chloride structure. The expressions obtained were:

$$(n^3/2)(P_{11}-P_{12})=3M-(1+\sigma)A \qquad (1)$$

$$(n^3/2)(P_{11}+2P_{12})=(3L-A)(1-2\sigma) \qquad (2)$$

and

$$(n^3/6)(P_{11}+2P_{12})=L(1-\lambda_0) \qquad (3)$$

where

$$\lambda_0 = 2\sigma + A(1-2\sigma)/3L$$

$$M=(n^2-1)^2(n^2+5)/45n,$$

$$L=(n^2-1)(n^2+2)/6n$$

and

$$A = \frac{(n^2+2)^2(n^2+5)}{54n}\left[1{\cdot}458 + 2{\cdot}9005\,\beta\left(\frac{1}{f_1}+\frac{1}{f_2}\right)\right]\times\theta^2 - \frac{(n^2-1)(n^2+2)(n^2+5)}{18n}\left[2{\cdot}916 + 4{\cdot}2083\,\frac{\beta}{f_1} + 7{\cdot}5927\,\frac{\beta}{f_2}\,\theta\right] + \frac{(n^2-1)^2(n^2+5)}{3n}\left[0{\cdot}2711 + 1{\cdot}6922\,\frac{\beta}{f_2}\right].$$

P_{11} and P_{12} are the strain-optical constants, n the refractive index, σ Poisson's ratio, β the number of valence electrons, f_1, f_2 the oscillator strengths, $\theta=\alpha_j/r^3$ (α_j is the polarizability of the jth ion and r is the interionic distance) and λ_0 is the strain polarizability constant.

Using these expressions, Bansigir & Iyengar (1961*b*) calculated the wavelengths at which the photo-elastic constant $(P_{11}-P_{12})$ changes sign for KCl, KBr and KI crystals. The method adopted is based on an empirical relation that α_j/α varies linearly with $1/\lambda^2$ in the visible region (α is the sum of the polarizabilities of the two types of ion and λ is the wavelength of light). If this empirical relation is used, one has to evaluate α_j/α for a large number of wavelengths from the observed photo-elastic constants $(P_{11}-P_{12})$.

In this note a new method is given by which one can calculate the reversal wavelength at which $(P_{11}-P_{12})$ changes sign, *i.e.* from a positive value to a negative value. In order to calculate the wavelength at which $(P_{11}-P_{12})$ is equal to zero, equations (1) and (2) can be expressed in the following form:

$$x^3+ax^2+bx+c=0 \qquad (3)$$

where

$$a=\frac{45}{2}\left(\frac{1+\sigma}{1-2\sigma}\right)P_{12}-\frac{15}{2}(1+\sigma)+3$$

$$b=-\frac{15}{2}(1+\sigma)+9$$

$$c=15\,(1+\sigma)+5$$

and $x=n^2$ (where n is the refractive index of the crystalline medium for which $(P_{11}-P_{12})$ is equal to zero).

Therefore x or n can be evaluated if we know the Poisson's ratio and the photo-elastic constant P_{12} for the wavelength at which $(P_{11}-P_{12})$ is equal to zero. For KCl, KBr and KI these wavelengths lie in the ultraviolet region (Srinivasan, 1959).

It is observed (Rahman & Iyengar 1966; Bansigir & Iyengar, 1961*b*) that the variation of the photo-elastic constant P_{12} is less than 5% for the entire wavelength range (from ultraviolet to the visible region). In view of this observation, one can evaluate the value of P_{12} approximately in the ultraviolet region from the observed value of P_{12} in the visible region. P_{12} of KCl, KBr, KI, RbCl, RbBr, and RbI in the ultraviolet region have been calculated by reducing the observed value at 5890 Å by 5%. Using these reduced values of P_{12}, refractive indices at the reversal wavelengths have been calculated and given in Table 1. Since dispersion data for KCl, KBr, KI and RbCl (Gyulai, 1927), RbBr and RbI (Kublitzky, 1932) are