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A crystallographic study of the acetates of potassium, rubidium and caesium.* By J. HATIBARUA† and G. S. PARRY,
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Crystal data for potassium, rubidium and caesium acetates are given. Potassium acetate has been found to undergo two phase transitions, at 75 and 155°C. The sequence of phases is monoclinic, monoclinic with an eightfold decrease in cell volume, orthorhombic. The orthorhombic phase is stable up to the melting point.

In the course of a study of the thermal behaviour of the acetates of potassium, rubidium and caesium by crystallographic and physical methods, the lattice parameters and space groups of these compounds have been obtained. A study of the thermal expansion of potassium acetate using a dilatometric method (Hazlewood, Rhodes & Ubbelohde, 1966) has established at least three solid state phase transitions. The present study has been undertaken to establish the structural basis of the transitions. The acetates of rubidium and caesium have been studied for comparison.

Room-temperature data were recorded on Weissenberg photographs; at higher temperatures, oscillation photographs recorded on a hemi-cylindrical film holder of 5.75 cm radius have been used. The thermostat was similar to that of Parry, Schuyff & Ubbelohde (1965). An electronic controller maintained the temperature within $\pm 0.1^\circ\text{C}$.

* Adapted from a part of the Ph. D. thesis of J. H., University of London, 1968.

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Single crystals were grown from the melt using dried polycrystalline commercial material: potassium acetate, 99% purity (M & B Reagent Grade); rubidium and caesium acetates, 98% purity (Alfa Inorganics).

It is concluded that potassium acetate has at least three polymorphs: one form exists from room temperature to a temperature of $\sim 75^\circ\text{C}$, when the weak layer lines with k odd disappear from b -axis photographs. This new phase transforms to a third at 155°C when there is an overall reduction in the number of reflexions. This third phase is stable up to the melting point: in particular, there is no evidence of any structural change at 230°C as reported by Hazlewood *et al.* (1966). It has been found that the structure above 155°C (form I) is orthorhombic, that from 155 to 75°C (form II) is monoclinic and that from 75°C to room temperature (form III) is monoclinic with an eightfold increase in cell volume. Monoclinic forms are twinned, the twinning plane being (100). The angle β has been found at higher temperatures by using the reflexions of the type $h0l$ and $h0\bar{l}$. These occur in pairs, one from each orientation

Table 1. Summary of the crystallographic data

| | $D(\text{obs.})$ (g.cm^{-3}) | $D_x(\text{calc})$ (g.cm^{-3}) | Z |
|-----------------------------------|--|--|-----|
| K acetate (III) | 1.55 (dilatometer data) | 1.58 | 16 |
| K acetate (I) | 1.52 (dilatometer data) | 1.45 | 2 |
| Rb acetate (24°C) | 2.19 (flotation) | 2.17 | 2 |
| Cs acetate (24°C) | 2.50 (flotation) | 2.42 | 6 |

Lattice parameters (accuracy $\pm 0.5\%$):

| | System | a | b | c | β |
|---------------------------------|--------------|---------|---------|--------|---------|
| K acetate | | | | | |
| form III (24°C) | monoclinic | 18.21 Å | 23.30 Å | 4.05 Å | 100.8° |
| form II (75°C) | monoclinic | 9.31 | 5.82 | 4.03 | 99.2 |
| form I (155°C) | orthorhombic | 9.74 | 5.76 | 3.99 | — |
| Rb acetate: | monoclinic | 8.69 | 6.18 | 4.26 | 104.4 |
| Cs acetate: | hexagonal | 13.08 | | 3.98 | — |

Reflexion conditions

K acetate (III):
 hkl present only for $h+k=2n$
($0k0$ present only for $k=8n$
 hkl absent when $k=4n+2$)

K acetate (II):
 $0k0$ present only for $k=2n$

K acetate (I):
 $0kl$ present only for $k+l=2n$

Rb acetate:
 $0k0$ present only for $k=2n$

Cs acetate:
No restrictions: reflexion intensities
indicate Laue symmetry to be $6/m$

Possible space groups

$Cm, C2/m, C2$

$P2_1, P2_1/m$

$Pnmm, Pn2_1m, Pnm2_1$

$P2_1, P2_1/m$

$P6, P6/m, P\bar{6}$

of the twin, which move towards each other with increasing temperature and coalesce at 155°C.

No thermal transformation has been detected in the acetates of rubidium and caesium between room temperature and the melting point.

All the crystallographic data are presented in Table 1.

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Gitterkonstanten von InNbO₄ und InTaO₄. Von J. LIEBERTZ, *Institut für Kristallographie der Universität zu Köln, 5 Köln, Deutschland (BRD)*

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The cell data of InNbO₄ and InTaO₄ have been determined. Both compounds are isostructural with wolframite.

Zur Darstellung der Verbindungen InNbO₄ und InTaO₄ wurden die entsprechenden Oxide (reinst) sorgfältig gemischt und in lockerer Schüttung 48 Stunden an Luft bei 1100°C gesintert. Die so erhaltenen Pulver sind rein weiss und völlig einphasig. Die Gitterkonstanten wurden aus Diffraktometer-Aufnahmen mit Cu-K α -Strahlung bestimmt.

Die indizierten Netzebenenabstände sind in Tabelle 1 aufgeführt. Hieraus errechnen sich die Gitterkonstanten zu:

| InNbO ₄ | InTaO ₄ |
|-----------------------------------|-----------------------------------|
| $a = 4,843 \pm 0,002 \text{ \AA}$ | $a = 4,833 \pm 0,002 \text{ \AA}$ |
| $b = 5,773 \pm 0,002$ | $b = 5,778 \pm 0,002$ |
| $c = 5,147 \pm 0,002$ | $c = 5,157 \pm 0,002$ |
| $\beta = 91^\circ 14'$ | $\beta = 91^\circ 23'$ |
| $V = 143,87 \text{ \AA}^3$ | $V = 144,01 \text{ \AA}^3$ |
| $Z = 2$ | $Z = 2$ |

Wie die Daten erkennen lassen, ist mit dem Übergang vom Niobat zum Tantalat eine geringe Verkleinerung von a und Vergrößerung von b und c verbunden, wobei das Volumen der Elementarzelle nahezu konstant bleibt.

Ein Vergleich mit den Gitterkonstanten von Wolframit und isotypen Verbindungen (Wyckoff, 1965) berechtigt zu der Annahme, dass InNbO₄ und InTaO₄ diesem Gittertyp angehören. Diese Vermutung wird bestärkt durch den ähnlichen Intensitätsverlauf bei den hier untersuchten Verbindungen einerseits und Verbindungen des Wolframit-Typs andererseits (vgl. z.B. ScNbO₄, ASTM-Karte Nr. 15-112, und CdWO₄, ASTM-Karte Nr. 13-514). Eine weitere Stütze ergibt sich daraus, dass $h0l$ -Reflexe nur mit $l=2n$ vorkommen, wie es die Raumgruppe des Wolframits C_{2h}^2-P2/c verlangt.

Verständlicherweise stimmt die Metrik am besten mit der von ScNbO₄ ($a=4,808$, $b=5,668$, $c=5,102 \text{ \AA}$, $\beta=91^\circ 20'$; $V=139,00 \text{ \AA}^3$) und ScTaO₄ (Schröcke, 1960; Rooksby & White, 1963) überein. Entsprechend dem etwas grösseren Ionenradius von In³⁺ sind die Gitterkonstanten der Indium-Verbindungen leicht erhöht.

Tabelle 1. Netzebenenabstände von InNbO₄ und InTaO₄

| InNbO ₄ | | | InTaO ₄ | | |
|--------------------|-----|--------------|--------------------|-----|--------------|
| d | l | hkl | d | l | hkl |
| 4,849 | 4 | 100 | 5,782 | 5 | 010 |
| 3,844 | 5 | 011 | 4,836 | 8 | 100 |
| 3,711 | 52 | 110 | 3,854 | 9 | 011 |
| 3,031 | 100 | 11 $\bar{1}$ | 3,708 | 54 | 110 |
| 2,985 | 94 | 111 | 3,039 | 100 | 11 $\bar{1}$ |
| 2,888 | 22 | 020 | 2,986 | 90 | 111 |
| 2,574 | 31 | 002 | 2,889 | 21 | 020 |
| 2,517 | 29 | 021 | 2,580 | 32 | 002 |
| 2,421 | 18 | 200 | 2,523 | 36 | 021 |
| 2,244 | 9 | 12 $\bar{1}$ | 2,416 | 20 | 200 |
| 2,224 | 4 | 121 | 2,298 | 6 | 10 $\bar{2}$ |
| 2,130 | 8 | 11 $\bar{2}$ | 2,224 | 8 | 121 |
| 2,098 | 8 | 112 | 2,134 | 9 | 11 $\bar{2}$ |
| 1,921 | 15 | 022 | 2,098 | 9 | 112 |
| 1,855 | 14 | 220 | 1,924 | 13 | 022 |
| 1,788 | 25 | 130 | 1,853 | 12 | 220 |
| 1,783 | 27 | 20 $\bar{2}$ | 1,790 | 30 | 130 |
| 1,754 | 16 | 22 $\bar{1}$ | 1,786 | 32 | 20 $\bar{2}$ |
| 1,745 | 17 | 202 | 1,755 | 18 | 22 $\bar{1}$ |
| 1,736 | 20 | 221 | 1,743 | 15 | 202 |
| 1,567 | 16 | 11 $\bar{3}$ | 1,734 | 20 | 221 |
| 1,554 | 5 | 310 | 1,571 | 12 | 11 $\bar{3}$ |
| 1,547 | 12 | 113 | 1,549 | 12 | 113 |
| 1,516 | 6 | 22 $\bar{2}$ | 1,518 | 6 | 22 $\bar{2}$ |
| 1,496 | 11 | 31 $\bar{1}$ | 1,495 | 11 | 31 $\bar{1}$ |
| 1,493 | 11 | 222 | 1,492 | 12 | 222 |

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