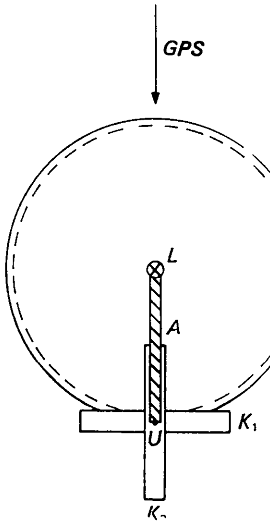

Fig. 1

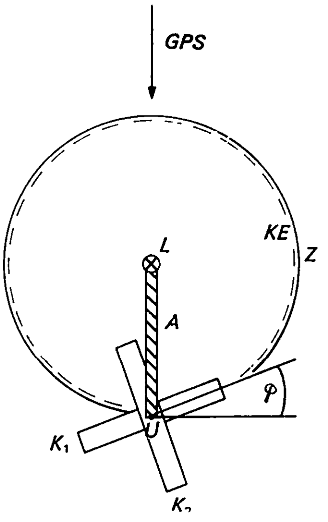

Fig. 2

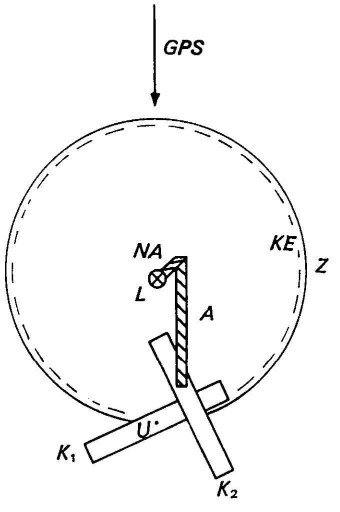

Fig. 3

Fig. 1. Normal position of the measuring device of the crystal setter (arcs K_1, K_2 and the special device A, NA, KE, L inside the transparent cylinder Z). Plane of paper is perpendicular to the axis of the cylinder. The axes of the two arcs K_1 and K_2 intersect at point U on the surface of the cylinder. *GPS* denotes the imagined X-ray beam.

Fig. 2. Crossed arcs turned by an angle φ from the normal position. Setting angles on crossed arcs equal zero.

Fig. 3. Crossed arcs as in Fig. 2 (turned by angle φ from normal position). Setting angles on crossed arcs different from zero.

obtain the arc corrections from an oscillation photograph with the crystal setter as described earlier (Kulpe, 1963) the lower arc of the goniometer has to be perpendicular to the X-ray beam.

However, this limitation is unnecessary. In a new instrument the two crossed arcs of the measuring device of the crystal setter may be turned around a vertical axis going through point U (Figs. 1,2 and Fig. 2 of Kulpe, 1963). Before turning, the arm A (carrying NA, KE and L) has to be disconnected from the crossed arcs K_1 and K_2 and held in its original position (Fig. 1). After turning the arcs (Fig. 2), arm A is again connected to them. With this device the setting angles for both arcs may be obtained for a goniometer head in any position relative to the X-ray beam during exposure. This is shown schematically in Figs. 1,2 and 3.

However, if by chance no attention was paid to the position of the crossed arcs in taking the oscillation photograph or if the particular shape of the crystal and its mounting makes it difficult or impossible to take the oscillation photograph in the normal position the modified crystal setter described here may be of real value.

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X-ray determination of the thermal expansion of potassium dihydrogen arsenate.

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Introduction

Potassium dihydrogen arsenate (KDA) crystallizes, at room temperature, in the space group $I\bar{4}2d$ of the tetragonal system and is isomorphous with the room-temperature form of potassium dihydrogen phosphate (KDP). The temperature variation of the lattice parameters and of the coefficients of thermal expansion of KDP at elevated temperatures has recently been studied in this laboratory (Sirdeshmukh, 1963). However, the lattice parameters of KDA have been determined only at room temperature (Helmholtz & Levine, 1942; Dickson & Ubbelohde, 1950) and no data are available on the temperature variation of these parameters either at low or at high temperatures. This paper gives the results of a systematic measurement in the high-temperature region.

Experimental and results

KDA was prepared by neutralizing an aqueous solution of pure potassium carbonate with an aqueous solution of pure arsenic pentoxide. The neutralized solution was slowly evaporated and needle-shaped crystals of KDA were obtained.

The X-ray diffraction work was done on a flat-plate back-reflexion camera with Cu $K\alpha$ radiation (Deshpande & Mudholker, 1960). The camera recorded reflexions from eight different planes but only six of these could be indexed unambiguously. The $\sin^2\theta$ values of these reflexions were greater than 0·880. Cohen's (1935) analytical method was used for the evaluation of the lattice parameters. Standard errors in the values of the parameters were calculated for one film taken at 27 °C, by the method of Jette & Foote (1935). The values of the two parameters obtained from this film were

$$a = 7{\cdot}6300 \pm 0{\cdot}0004, \quad c = 7{\cdot}1630 \pm 0{\cdot}0009 \text{ Å}.$$

No attempt was made to calculate the errors for films taken at higher temperatures. However, it is likely that because of the fall in the intensities of the diffraction lines at these temperatures and consequent decrease in the number of measurable lines, the errors will be larger than those given above.

Table 1 gives the observed values of the lattice parameters at different temperatures. The coefficients of expansion along the two principal directions were evaluated at different temperatures by the procedure given by Deshpande & Mudholker (1960). Least-squares fitting of the resulting data then gave the following equations for the two principal coefficients.

$$\alpha_\perp = 15{\cdot}87 \times 10^{-6} + 10{\cdot}93 \times 10^{-8} \times t - 0{\cdot}87 \times 10^{-10} \times t^2 \text{ per°C}$$

$$\alpha_\parallel = 30{\cdot}56 \times 10^{-6} + 6{\cdot}54 \times 10^{-8} \times t + 14{\cdot}65 \times 10^{-10} \times t^2 \text{ per°C}$$

Here $\alpha_\perp$ and $\alpha_\parallel$ are the coefficients of expansion along the a and c axes respectively and t is the temperature in °C.

Table 1. *Lattice parameters of potassium dihydrogen arsenate at different temperatures*

t	*a*	*c*	*c*/*a*
27 °C	7·6300 Å	7·1630 Å	0·9388
29	7·6299	7·1637	0·9389
54	7·6344	7·1699	0·9392
55	7·6340	7·1703	0·9393
90	7·6410	7·1811	0·9398
117	7·6453	7·1921	0·9407
129	7·6492	7·1976	0·9410
134	7·6502	7·1994	0·9411
147	7·6524	7·2049	0·9415

Discussion

The values of the lattice parameters of KDA at 18 °C, obtained by extrapolation of the temperature–lattice parameter curves, are $a = 7{\cdot}6287$ and $c = 7{\cdot}1612$ Å. These are in satisfactory agreement with the values given by Dickson & Ubbelohde (1950).

The average values of the two principal coefficients and the coefficient of volume expansion over the whole range of temperature are $\alpha_\perp = 24{\cdot}9 \times 10^{-6}$, $\alpha_\parallel = 50{\cdot}0 \times 10^{-6}$ and $\alpha_v = 99{\cdot}8 \times 10^{-6}$ per °C respectively. The corresponding quantities for KDP are $26{\cdot}9 \times 10^{-6}$, $46{\cdot}6 \times 10^{-6}$ and $100{\cdot}4 \times 10^{-6}$ (Sirdeshmukh, 1963). It can be seen from Fig. 1 that in KDA $\alpha_\parallel$ is greater than $\alpha_\perp$ over the whole range of temperature, suggesting that the binding along the c direction in this lattice is weaker than in the perpendicular plane. Sirdeshmukh's data on KDP reveal the same behaviour. This common property of the two crystals can be explained in terms of the orientations of the hydrogen bonds in the respective unit cells. In KDP these bonds are known to lie almost at right angles to the c axis (Kanzig, 1957). Calculations based on the oxygen atom parameters in KDA, given by Helmholtz & Levine (1942), show that the proton-bond vectors in this crystal are inclined at about 6° to the ab plane and hence have their major components perpendicular to the c axis. Thus in both the crystals the orientation of the hydrogen bonds appears to make the binding stronger along directions normal to the c axis than parallel to it.

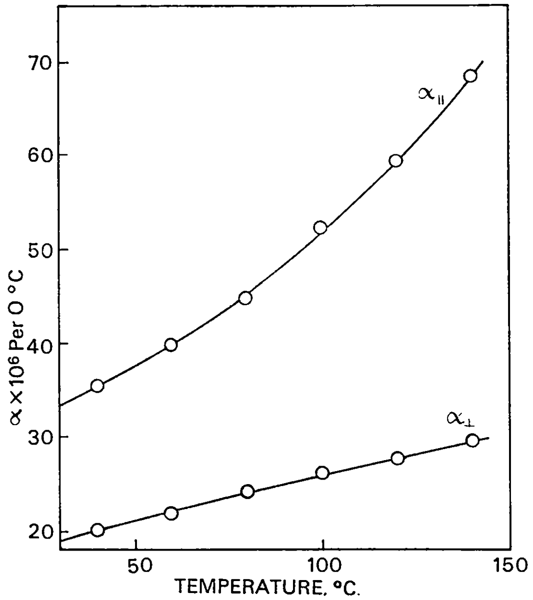

Fig. 1. Temperature variation of the principal coefficients of thermal expansion of KDA

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