CRYSTALLOGRAPHY

Thermal Expansion of Rubidium Dihydrogen Phosphate

A PROGRAMME of investigation into the temperature variation of the lattice parameters of tetragonal crystals, isomorphous with potassium dihydrogen phosphate, in the high-temperature region, has been undertaken in this laboratory. Results on potassium dihydrogen phosphate¹, ammonium dihydrogen phosphate² and potassium dihydrogen arsenate³ have already been published. This communication presents the results of the precision determination of the unit cell dimensions of rubidium dihydrogen phosphate at different temperatures between 29° C and 78° C and also the principal coefficients of its thermal expansion obtained from these data.

Crystals of rubidium dihydrogen phosphate were prepared by slow evaporation of an aqueous solution of rubidium carbonate neutralized with an aqueous solution of hypophosphoric acid. X-ray powder pictures were taken with a high-temperature, back-reflexion camera⁴ using copper K_α radiation. Six unambiguously indexed K_α doublets, with their $\sin^2 \theta$ values greater than 0.866, were employed in calculating the values of the *a* and *c* parameters, using the conventional least-squares technique. An error analysis made for a film taken at 35° C, by the method given by Jette and Foote⁵, gave the standard errors in the values of *a* and *c* as 0.013 per cent and 0.019 per cent, respectively. Standard errors in the values of the parameters at other temperatures were assumed to be of the same order.

Table 1 gives the values of the two parameters at different temperatures, and the following expressions were obtained for their temperature dependence by the usual statistical methods.

$$a_t = 7.6054 + 21.11 \times 10^{-5} (t-20) \\ c_t = 7.2989 + 37.95 \times 10^{-5} (t-20)$$

Here *a_t* and *c_t* are the values of the two parameters in Ångströms at *t*° C. Slight extrapolation of the present data gives the values of the parameters at 20° C as *a* = 7.6054 Å and *c* = 7.2989 Å and these are found to be in good agreement with the values reported by Magyar⁶.

Table 1. VALUES OF THE LATTICE PARAMETERS OF RUBIDIUM DIHYDROGEN PHOSPHATE AT DIFFERENT TEMPERATURES

<i>t</i> ° C	<i>a</i> (Å)	<i>c</i> (Å)
29.0	7.6078 ± 0.0009	7.3026 ± 0.0014
35.0	7.6080	7.3040
50.0	7.6114	7.3109
61.5	7.6150	7.3139
74.0	7.6168	7.3196
78.0	7.6174	7.3209

Within the accuracy of the measurements, both the parameters show a linear increase with temperature. The principal coefficients of thermal expansion, defined by the relation $\alpha = 1/L_{20}(dL/dt)$ (*L* = *a* or *c*), come out as $\alpha_a = 27.75 \times 10^{-6}/^\circ\text{C}$ and $\alpha_c = 52.0 \times 10^{-6}/^\circ\text{C}$. It is interesting to note that, like potassium dihydrogen phosphate and potassium dihydrogen arsenate, the coefficient of expansion of rubidium dihydrogen phosphate along the tetragonal axis is greater than that in any direction in a perpendicular plane. This feature is being discussed separately in terms of the structures of these crystals.

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¹ Sirdeshmukh, D. B., thesis (Osmania University, 1963).

² Deshpande, V. T., and Khan, A. A., *Acta Cryst.*, **18**, 936 (1963).

³ Deshpande, V. T., and Khan, A. A., *Acta Cryst.* (in the press).

⁴ Deshpande, V. T., and Mudholker, V. M., *Acta Cryst.*, **13**, 488 (1960).

⁵ Jette, E. R., and Foote, F., *J. Chem. Phys.*, **3**, 605 (1935).

⁶ Magyar, Hermann, Anzeiger und Osterr., *Akad. Wissen.*, **85**, 166 (1948).

CHEMISTRY

Contact Angles of Mercury on Low-energy Solids

THE recent theory of Fowkes¹⁻⁵ concerning the attractive forces at interfaces leads to the following relationship between cosine of contact angle (θ) and liquid surface tension (γ_L):

$$\cos \theta = -1 + 2 \sqrt{\gamma_s^d} \left(\frac{\sqrt{\gamma_L^d}}{\gamma_L} \right) \quad (1)$$

where γ_s^d , γ_L^d are the dispersion force contributions to the solid surface tension and liquid surface tension respectively.

A plot of $\cos \theta$ against $\sqrt{\gamma_L^d}/\gamma_L$ for the data of Zisman^{6,7} for four low-energy surfaces gives good agreement with equation (1). The range of surface tensions investigated was, however, not great. The only liquid investigated with a surface tension greater than water ($\gamma_L = 72$ dynes/cm) was mercury ($\gamma_L = 485$ dynes/cm), for which values were published only for the following surfaces: polytetrafluoroethylene, 150° (ref. 8); octadecylamine monolayer on platinum, 146° (ref. 9); perfluorodecanoic acid monolayer on platinum, 152° (ref. 10).

Fowkes⁵ quotes a value for paraffin wax $\cos \theta = -0.9$ ($\theta = 154^\circ$). These points do not fall on Fowkes's plot of $\cos \theta$ against $\sqrt{\gamma_L^d}/\gamma_L$. Fowkes⁵ comments: "It is possible that some wax spread on mercury resulting in a decrease of surface tension and therefore too high a contact angle".

Few measurements of contact angle of mercury on low-energy solids seem to have been made, and those made by Zisman consisted only of the mean of three measurements with no record of the scatter. The measurements in this communication are put forward in an attempt to increase the available facts.

Fowkes's theory might be expected to be particularly accurate for mercury on low-energy solids and the results should provide a sensitive confirmation of the validity of his theory.

Measurements have been made, therefore, of the contact angle of mercury on polytetrafluoroethylene, paraffin wax, and polyethylene.

Clean mercury was prepared according to the recommendation of Nicholas *et al.*¹¹. It was distilled, washed successively with dilute nitric acid and caustic soda solution, distilled again and then shaken, successively, with 50 per cent nitric acid, distilled water, acetone, ether and filter paper before being applied as small drops to the test surface by a clean hypodermic syringe with a polytetrafluoroethylene base. Measurements were made as rapidly as possible—usually within 1 min of application.

Paraffin and polyethylene surfaces were prepared by the methods of Fox and Zisman¹², freshly cut surfaces being melted against cleaned glass slides, which were removed immediately before use. Clean, flat surfaces of polytetrafluoroethylene were prepared by fine polishing on successive grades of powdered emery, final traces of abrasive being removed by lens tissues. Contact angle measurements were made using a horizontal microscope technique as described elsewhere¹³. The surfaces were mounted on the rotating stage when in a vertical plane and the advancing and receding angles obtained by rotating the stage until movement just ceased. A goniometer eyepiece was used to measure angles.

Results are given in Table 1. They include the 95 per cent confidence limits and the standard deviation on $\cos \theta$.

It will be noted that the values for polytetrafluoroethylene (151.7° advancing, 150.2° receding) are very close to the value of 152° reported by Fox and Zisman⁸. The values for paraffin wax, on the other hand (141.1° advancing, 140.9° receding), do not agree with the 154° reported by Fowkes⁵.