hydroxy 1–5 naphtoquinone, conduit à envisager le cas où des forces de liaison intermoléculaire, même très faibles, mises en jeu dans le cristal, suffisent pour déformer la molécule. On peut ainsi prévoir que, si les différences d'énergie entre plusieurs configurations possibles d'une molécule sont de l'ordre des énergies de liaison intermoléculaire, la molécule tendra vers la configuration de plus haute symétrie pour former l'édifice cristallin le plus compact.

Ce travail a été effectué en grande partie à l'I.R. CH.A., dans le laboratoire de Monsieur J. Mering. L'auteur est particulièrement reconnaissant à Mademoiselle C. Stora, directeur du Laboratoire de Chimie Cristallographique, d'avoir mis à sa disposition le photosommateur de von Eller, et les crédits nécessaires au raffinement de la structure.

Références

Billy, C. (1955). *C. R. Acad. Sci., Paris*, **240**, 887.

Borgen, O. (1956). *Acta Chem. Scand.* **10**, 867.

Cochran, W. (1952). *Acta Cryst.* **5**, 634.

Eller, G. von (1955). *Bull. Soc. Franç. Min. Crist.* **78**, 157.

Lipson, H. & Cochran, W. (1953). *The Determination of Crystal Structure*, p. 288. London: Bell.

Pascard-Billy, C. (1960). Thèse Université Paris. Sous presse.

Zahn, K. & Ochweit, P. (1928). *Ann.* **462**, 72.

Acta Cryst. (1962). **15**, 528

Thermal Expansion of Magnesium Fluoride

By K. V. Krishna Rao, S. V. Nagender Naidu and P. L. N. Setty
Physics Department Osmania University Hyderabad-7 India

(*Received* 24 *August* 1961 *and in revised form* 28 *September* 1961)

A precision determination of the lattice constants of magnesium fluoride, in the temperature range 30 to 640 °C., has been made, using a Unicam 19 cm. high-temperature powder camera and Cohen's analytical method. From these data, the coefficients of thermal expansion, $\alpha_{\parallel}$ and $\alpha_{\perp}$ have been evaluated by a graphical method. Both the coefficients are found to show a parabolic variation with temperature.

Introduction

The thermal expansion of magnesium fluoride was studied by Klemm (1928) and Duncanson & Stevenson (1958) by the dilatometer method. No X-ray study of the thermal expansion of this substance seems to have been made so far. Though many investigators determined its cell constants, the accuracy of the values is not high. Hence, it is thought desirable to determine accurately the cell constants of magnesium fluoride at various temperatures and study the thermal expansion.

Experimental

The powder photographs at temperatures, ranging from 30 to 640 °C., were taken by a Unicam 19 cm. high-temperature powder camera, using Cu $K\alpha$ radiation from a Raymax 60 diffraction unit. To get sharp lines in the high-angle region, it was found necessary to pre-heat the powder to 900 °C. Temperature control to within 1 °C. was obtained with the use of a voltage stabiliser and a variac. Aluminium was used as a standard to estimate the specimen temperature. Fig. 1 shows the powder photographs of magnesium fluoride at various temperatures.

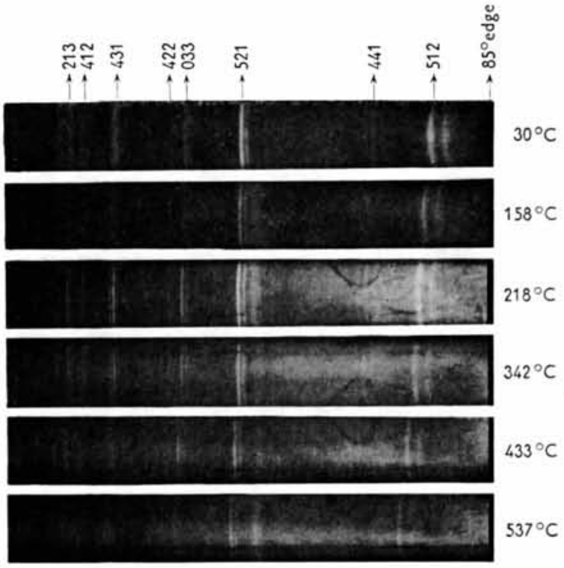

Fig. 1. Powder photographs of MgF_2 at various temperatures.

Evaluation of the cell constants

Eleven diffraction lines with Bragg angles ranging from 57° to 82° have been used to evaluate the cell constants applying Cohen's (1935) analytical method. The error equation, employed in these calculations, applicable to crystals of tetragonal system to which magnesium fluoride belongs, is

$$\sin^2 \theta_i = A\alpha_i + C\gamma_i + D\delta_i , \tag{1}$$

where

$$\begin{aligned} \alpha_i &= (h^2+k^2)_i , \\ \gamma_i &= l_i^2 , \\ \delta_i &= 10 \sin^2 2\theta_i , \\ A &= \lambda^2/4a^2, \\ C &= \lambda^2/4c^2, \end{aligned}$$

and D is the drift constant which takes care of the total systematic error involved in the determination. The cell constants at various temperatures are given in Table 1 and plotted in Figs. 2 and 3.

Table 1. *Cell constants of* MgF$_2$ *at various temperatures*

Temperature	*a*	*c*
30 °C.	4·6218 Å	3·0534 Å
158	4·6275	3·0590
218	4·6308	3·0617
307	4·6355	3·0663
342	4·6375	3·0677
433	4·6430	3·0728
537	4·6505	3·0791
550	4·6515	3·0806
640	4·6587	3·0858

In evaluating the cell constants, independent measurements and calculations have been made by each of us and the deviations of the individual values from the mean have always been found to be less than ±0·0001 Å and ±0·0002 for *a* and *c* respectively.

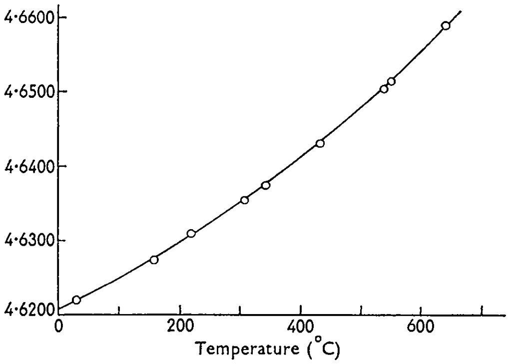

Fig. 2. Variation of *a* with temperature.

As the error due to refraction is much smaller than the experimental errors, refraction corrections were not applied. The cell constants at room temperature obtained in the present investigation, together with those reported by Baur (1956) and Duncanson & Stevenson (1958) are given in Table 2. All the values are reduced to 18 °C., using the coefficients of thermal expansion obtained by us.

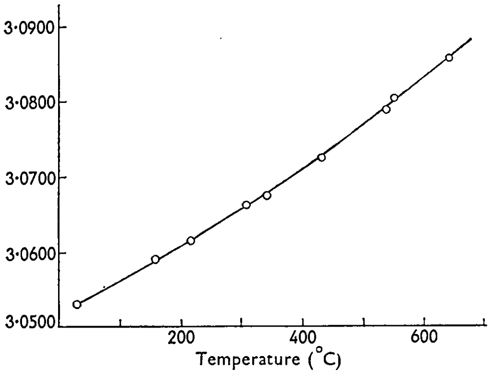

Fig. 3. Variation of *c* with temperature.

Table 2. *Cell constants of* MgF$_2$ *at room temperature*

	a (18 °C.)	*c* (18 °C.)
Duncanson & Stevenson	4·621 ±0·001 Å	3·050 ±0·001 Å
Baur	4·625 ±0·002	3·052 ±0·003
Authors	4·6213±0·0001	3·0519±0·0002

Coefficients of thermal expansion

A graphical method was used to evaluate the coefficients of thermal expansion at various temperatures. From a large scale graph drawn between the temperature and the cell constants given in Table 1, the change in the lattice constant *a* or *c* is read for 40° (Δt) temperature intervals. Then $\alpha_\perp$ and $\alpha_\parallel$ were evaluated using equations (2) and (3) respectively. The accuracy of the values, as estimated by the consistency of separate determinations, is of the order of 3%.

$$\alpha_\perp = (1/a_{30}).(\Delta a/\Delta t) . \tag{2}$$

$$\alpha_\parallel = (1/c_{30}).(\Delta c/\Delta t) . \tag{3}$$

Table 3. $\alpha_\perp$, $\alpha_\parallel$ *and* c/a *at different temperatures*

	$\alpha_\perp \times 10^6$		$\alpha_\parallel \times 10^6$		
Temperature	obs.	calc.	obs.	calc.	c/a
50 °C.	9·6	9·6	13·7	13·8	0·66069
90	10·0	9·9	14·2	14·1	0·66080
130	10·2	10·3	14·5	14·5	0·66092
170	10·5	10·7	15·1	15·0	0·66102
210	11·1	11·1	15·5	15·4	0·66115
250	11·8	11·6	15·9	15·9	0·66126
290	12·1	12·1	16·5	16·4	0·66137
330	12·6	12·7	17·0	17·0	0·66149
370	13·2	13·2	17·5	17·6	0·66160
410	13·7	13·8	18·0	18·2	0·66172
450	14·7	14·5	19·0	18·9	0·66183
490	15·3	15·2	19·6	19·6	0·66194
530	15·9	15·9	20·1	20·3	0·66206
570	16·6	16·7	21·1	21·1	0·66217
610	17·5	17·4	22·0	21·9	0·66229

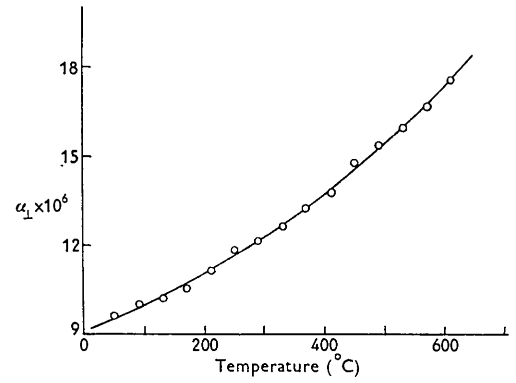

Fig. 4. Variation of $\alpha_\perp$ with temperature.

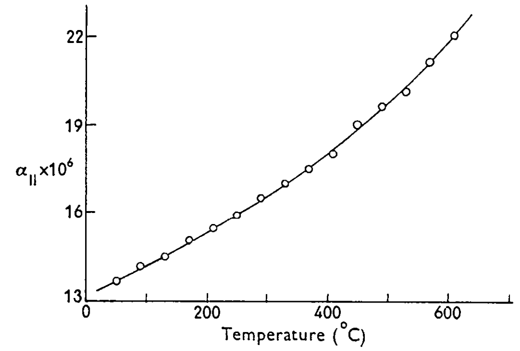

Fig. 5. Variation of $\alpha_\parallel$ with temperature.

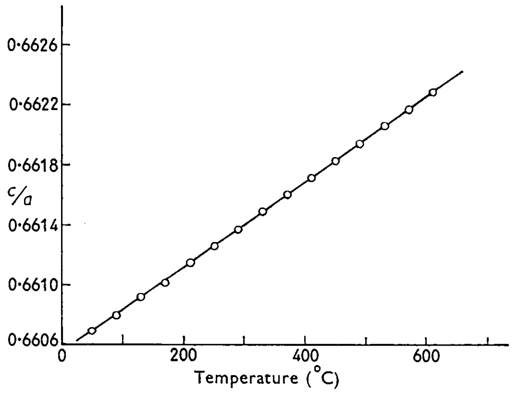

Fig. 6. Variation of c/a with temperature.

$\alpha_\perp$, $\alpha_\parallel$ and c/a at various temperatures are given in Table 3 and plotted in Figs. 4, 5 and 6. Both $\alpha_\perp$ and $\alpha_\parallel$ are found to show a parabolic variation with temperature. Equations (4) and (5) are obtained for the two coefficients by the usual methods.

$$\alpha_\perp = 9{\cdot}213 \times 10^{-6} + 6{\cdot}805 \times 10^{-9} t + 1{\cdot}097 \times 10^{-11} t^2. \quad (4)$$

$$\alpha_\parallel = 13{\cdot}390 \times 10^{-6} + 7{\cdot}416 \times 10^{-9} t + 1{\cdot}072 \times 10^{-11} t^2. \quad (5)$$

Discussion

The values of $\alpha_\perp$ and $\alpha_\parallel$ at 20 °C., from equations (4) and (5), are slightly higher than those reported by Duncanson & Stevenson (1958). The coefficient of cubical expansion i.e. $(2\alpha_\perp + \alpha_\parallel)$ at 20 °C. is found to be $32{\cdot}4 \times 10^{-6}$ deg.$^{-1}$, in good agreement with the value 32·0 obtained by Klemm (1928) by the dilatometer method.

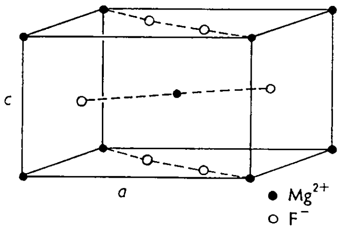

Fig. 7. Unit cell of MgF_2 showing the chains of –F–Mg–F–F–Mg–F–.

The crystal structure of magnesium fluoride is usually described in terms of an ionic model based on ions of Mg^{2+} and F^-. Each magnesium ion is surrounded by six fluorine ions, situated at the corners of a distorted octahedron; the fluorine ion is surrounded by three magnesium ions at the corners of an equilateral triangle (Fig. 7). Alternatively, the crystal structure may be visualized as chains of ions –F–Mg–F–F–Mg–F– in parallel layers normal to the c-axis. It is well known that, for layer structures, the thermal expansion normal to the layers is very large when compared to the expansion along the layers. In the case of magnesium fluoride, since the forces between the adjacent layers are Coulomb forces and are therefore not weak as in layer structures the coefficient of expansion normal to the layers is only slightly greater than the coefficient of expansion along the layers.

References

Baur, V. W. H. (1956). *Acta Cryst.* **9**, 515.

Cohen, M. U. (1935). *Rev. Sci. Instrum.* **6**, 68.

Duncanson, A. & Stevenson, R. W. H. (1958). *Proc. Phys. Soc. Lond.* **72**, 1001.

Klemm, W. (1928). *Z. Elektrochem.* **34**, 525.