THERMAL EXPANSION OF POTASSIUM NITRATE

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Introduction

In a previous report (Lonappan, 1955) was described an investigation of the thermal expansion of potassium chlorate by an X-ray method. For this monoclinic crystal two of the principal expansion coefficients were small, of the order of 30 to 40×10^{-6}, while the third one was much larger, about 130×10^{-6}. The direction of the latter was almost perpendicular to the plane of the O_3 groups of the chlorate ions, all of which are parallel in the structure of the crystal. It was thought worthwhile to extend the study to other crystals having similar O_3 groups, but having a different symmetry. Studies have been made with potassium nitrate (KNO_3) which is orthorhombic and orthoboric acid (H_3BO_3) which is triclinic. The results with potassium nitrate are reported here; those with boric acid will be discussed in a separate paper.

Potassium nitrate crystallizes in the class *mmm* and belongs to the space group $V_h^{16} - Pmcn$. The unit cell dimensions are $a = 5 \cdot 43$ Å; $b = 9 \cdot 17$ Å; $c = 6 \cdot 45$ Å and there are four molecules per unit cell (Edwards, 1931). Since the crystal is orthorhombic the principal axes of the ellipsoid of expansion coincide with the crystallographic axes. The present study of thermal expansion has been made with a good degree of accuracy for a range of temperature 30 to 100° C. The study could not be extended for higher ranges of temperature, as in the case of potassium chlorate, since potassium nitrate undergoes a transformation at about 128° C., the crystal changing over to the rhombohedral form (Groth, 1910; Kracek, Barth and Kosanda, 1932) and the crystal, though retaining its external shape, gets broken into fine crystallites (Leonhardt and Borchert, 1936) as exhibited by the powder lines appearing in the rotation photograph above this temperature. The complete ellipsoid of expansion could be determined by finding the variations in the spacings of the various reflections in [100] and [001] zones using appropriate crystals.

2. EXPERIMENTAL DETAILS

Rotation photographs of the zero layer were taken for [100] and [001] zones using the 19 cm. camera (Unicam) and the spacings of the high angle reflections at the two temperatures were accurately determined using the 85° fiducial mark in the camera, as described earlier (Lonappan, 1955). The overlap of reflections was avoided by the use of the 'tilted crystal method'. The indices of the reflections determined by the reciprocal lattice diagram were confirmed by taking Weissenberg photographs of the crystal. The thermal expansion perpendicular to a number of crystallographic planes in a particular zone were thus determined. From these the principal expansion coefficients were calculated. Only reflections having a θ-value $> 62°$ were used for the calculation of thermal expansion. Five such high-angle reflections were obtained in each zone.

From a knowledge of the indices of the planes, the values of the inclination ϕ of their normals to a chosen direction (b-axis) in the zone can be calculated. Then the relation between a_ϕ, the thermal expansion along any direction and the inclination ϕ of the direction concerned with b-axis takes the following form

For the [100] zone, $\quad a_\phi = a_b + \sin^2\phi\,(a_c - a_b)$ \hfill (1)

For the [001] zone, $\quad a_{\phi'} = a_b + \sin^2\phi'\,(a_a - a_b)$ \hfill (2)

There are five equations of type (1) and five equations of type (2) from which a_a, a_b and a_c are to be determined. Considering a as a function of ϕ and ϕ' three normal equations were formed using the ten equations, giving suitable weights to the a values according to their proximity to 90°. The probable errors were calculated using standard methods (Whittaker and Robinson, 1944).

As mentioned earlier, potassium nitrate undergoes a transformation at about 128° C. On heating single crystals of potassium nitrate above this temperature in the camera, the crystal became polycrystalline even when heated very slowly through the transition temperature and consequently the present method could not be used to study the thermal expansion for higher temperatures. The powder lines which appeared in the rotation photographs about the [100] and [001] axes taken at 200° C. were measured and could be indexed on the basis of the rhombohedral unit cell of KNO_3 (I), $a = 4\cdot50$ Å; $\quad a = 73°30'$ (Kracek, Barth and Kosanda, 1932). In both cases the crystals were found to give only powder lines when slowly cooled to room temperature and these corresponded to those given by the normal orthorhombic structure KNO_3 (II). The third modification of potassium

nitrate KNO_3 (III) reported to occur when KNO_3 is quenched from a high temperature was not observed in these experiments.

3. RESULTS OF THE INVESTIGATION

The measured values of the expansion coefficient perpendicular to various planes in the two zones studied are given in Table I. The principal expan-

TABLE I

Measured thermal expansion coefficients of reflections in the
[001] and [100] zones

Indices of reflection	Inclination with b^*-axis	$\sin^2 \phi$	Thermal expansion $\alpha_\phi \times 10^6$
6 6 0	59° 22′	0·7404	23·05
1 11 0	8° 44′	0·0230	21·37
5 7 0	50° 20′	0·5925	23·19
6 4 0	68° 27′	0·8651	23·34
2 10 0	18° 40′	0·1024	21·70
0 3 8	75° 14′	0·9350	171·73
0 8 6	46° 50′	0·5319	107·71
0 2 8	80° 2′	0·9700	177·85
0 10 4	29° 38′	0·2445	61·33
0 9 5	38° 18′	0·3841	84·52

sion coefficients along the three crystallographic axes, calculated from these data, are

$$\alpha_{11} \ (b\text{-axis}) = 22 \cdot 0 \pm 0 \cdot 3;$$

$$\alpha_{22} \ (a\text{-axis}) = 23 \cdot 5 \pm 0 \cdot 5;$$

$$\alpha_{33} \ (c\text{-axis}) = 182 \cdot 6 \pm 0 \cdot 2; \qquad \times 10^{-6}$$

Fig. 1 brings out the agreement between the observed values and those calculated from the constants of the ellipsoid of expansion. In Fig. 1, α is plotted against $\sin^2 \phi$ or $\sin^2 \phi'$ as the case may be. The observed values
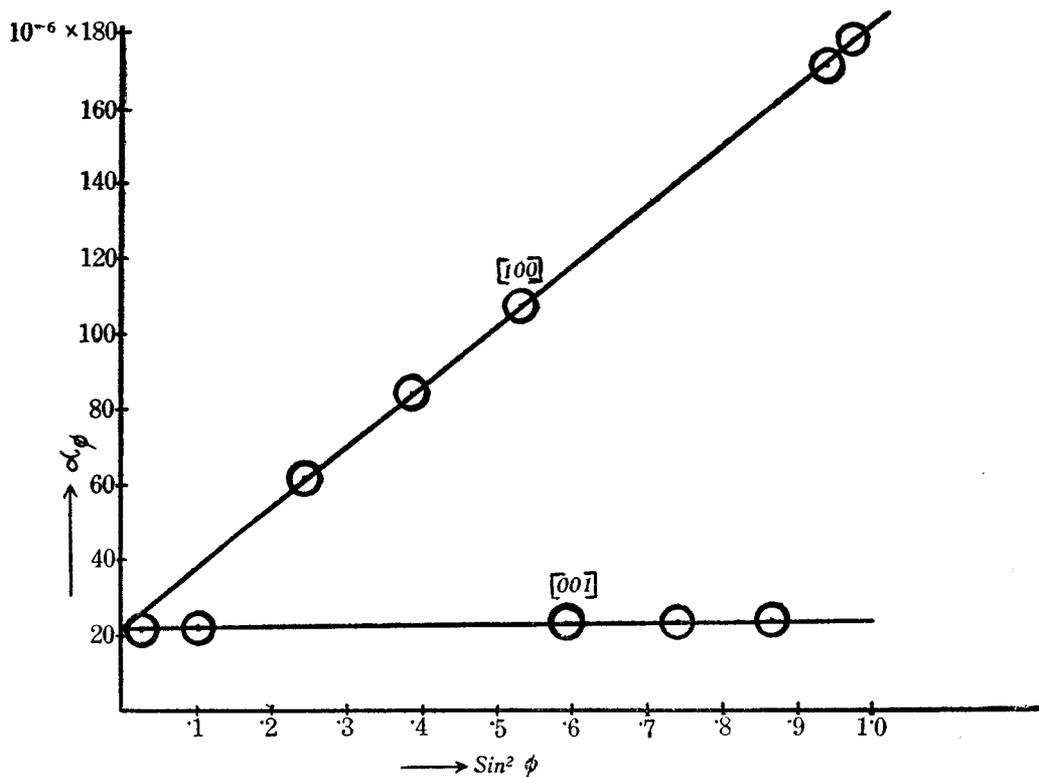
FIG. 1. Variation of expansion coefficient (30 to 100° C.) with $\sin^2 \phi$ in the two zones [100] and [001]. The circles represent the experimental values and the straight lines have been drawn using the calculated values of α_a, α_b and α_c.

should lie on two straight lines and they are found to be very close to the theoretical values.

It is interesting that α_a and α_b are found to be almost equal whereas α_c is very much higher. This is due to the fact that the planes of all the nitrate ions occurring in the crystal are parallel to one another. According to the structure determined by Edwards, the O_3 groups all lie in the c-plane. In the present study the maximum value of thermal expansion coefficient is obtained along the c-axis, which is perpendicular to the plane of the O_3 group, as it should be. The similarity between the morphology and structure of potassium nitrate and aragonite has already been pointed out by Miller (1840) and Edwards (1931). However the actual values of the thermal expansion coefficients for aragonite are 10, 16 and 33×10^{-6} while for KNO_3 they are 22, $23 \cdot 5$ and 183×10^{-6}. It will be noticed that the value of the largest coefficient is very different in the two cases. This is not surprising for a similar large difference occurs even between calcite and $NaNO_3$ (Table II) which

are closely related in structure. It appears that the coefficient normal to the plane of the ions is much larger with nitrates than with carbonates.

TABLE II

Thermal expansion of some crystals of the type ABO_3

Crystal	Thermal expansion $\times 10^6$		
	a_{11}	a_{22}	a_{33}*
Aragonite	10	16	33
Calcite	− 6	− 6	25
$NaNO_3$	11	11	120
$KClO_3$	30	39	134
KNO_3	22	23·5	183

* a_{33} always normal to plane of O_3 group.

Coefficient of *cubical expansion* calculated from the present data namely $a_{cub} = (a_{11} + a_{22} + a_{33}) = 228 \times 10^{-6}$ agrees with the directly measured value of 211×10^{-6} reported by Bellati and Finazzi (1910).

The value of cubical expansion coefficient may be used to verify the Grüneisen relation for potassium nitrate. The density of the crystal at room temperature is 2·098, from which the molar volume V_0 is calculated to be 48·2. The molar specific heat (C) as given in the *Landolt-Bornstein Tabellen* is 24·15. Unfortunately the value of the compressibility K_0 required in the relation

$$\gamma = V_0 a_{cub}/K_0 C_v$$

(where γ is the Grüneisen constant) is not available in the literature. However γ may be evaluated from the formula

$$\gamma = - \frac{\partial (\log \nu)}{\partial (\log V)} = - \frac{\frac{1}{\nu}\frac{\partial \nu}{\partial T}}{\frac{1}{V}\frac{\partial V}{\partial T}} = \frac{X_\nu}{a_{cub}}$$

Here X_ν is the proportional rate of change of frequency with temperature, as defined by Ramachandran (1947 *a*). The value of X_ν for potassium nitrate is not available, but the corresponding value of sodium nitrate may be calculated from the Raman Effect data for this crystal (Nedungadi, 1939).

The tilting and transverse oscillations of NO_3 group in sodium nitrate have X-values of 800 and 600×10^{-6} respectively (Ramachandran, 1947 b), the mean of which, namely 7×10^{-4} may be taken for our calculations. This yields the value 3·07 for the Grüneisen constant.

Putting this value of γ in the equation mentioned earlier, we get

$$K_0 = 35 \cdot 28 \times 10^{-13}$$

This value for compressibility is of the same order as for other nitrates, namely 31·2 for barium nitrate, 34·2 for strontium nitrate, $28 \cdot 2 \times 10^{-13}$ for lead nitrate, which indicates the approximate validity of Grüneisen's relation for the crystal.

SUMMARY

The principal coefficients of expansion have been determined for the orthorhombic crystal potassium nitrate for the range of temperature 30 to 100° C. by an X-ray method. The values are $a_{11}(b) = 22 \cdot 0$; $a_{22}(a) = 23 \cdot 5$; $a_{33}(c) = 182 \cdot 6 \times 10^{-6}$. The direction of the greatest expansion is perpendicular to the plane of the O_3 group and the expansion is nearly constant for all directions in the plane of the O_3 group. The approximate validity of the Grüneisen relation is tested by calculating the compressibility from a knowledge of the variation of the Raman frequency with temperature.

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