

THERMAL EXPANSION OF CRYSTALS AT LOW TEMPERATURES

Part II. Alums

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ABSTRACT

Expansion characteristics of two cubic crystals, potassium and ammonium alums have been investigated over a range of temperature from 0°C . to -170°C . Using the available values of specific heats and compressibilities, Gruneisen's constant has been calculated for both the crystals. The constant so obtained shows a marked variation with temperature.

1. INTRODUCTION

In continuation of the work on the thermal expansion of crystals at low temperatures, the author (Sreedhar, 1952) has now investigated the thermal behaviour of potassium and ammonium alums from room temperature down to liquid-air temperature. The alums are of special importance because the data regarding their specific heats, compressibility, etc., are already available in the literature. Spring (1884) measured the changes of density of the alums with temperature and calculated the coefficients of cubical expansion. His results are not reliable as they were vitiated by partial dehydration and by the possibility of dissociation of the hydrates with temperature. Alexander and Klug (1942) have measured the expansion of alums using the X-ray methods, in the limited temperature range of 20°C . to 50°C . No determinations have so far been made at temperatures below 20°C .

2. EXPERIMENTAL DETAILS

Single crystals of alums of fairly large size were crystallized from saturated aqueous solutions. They contain 12 molecules of water of crystallisation (according to the formulæ $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) and have low melting points and hence their expansion can only be studied at low temperatures. Since the crystal structure of alums belongs to the cubic system, measurements in any arbitrary direction will give the coefficient of expansion directly.

The experimental technique employed is described in Part I of the series (Sreedhar, 1952). The results obtained are tabulated below.

TABLE I
Potassium alum

Temp. (° K.)	C_p (Cals. deg. ⁻¹ mol. ⁻¹)	C_v	$\alpha \times 10^6$	$\gamma = \frac{3\alpha V_0}{\chi C_v}$
278.2	147.4	147.2	9.10	0.184
255.2	137.8	137.7	7.94	0.168
230.2	126.3	126.2	5.34	0.126
201.2	113.1	113.1	4.30	0.113
170.2	98.5	98.5	3.10	0.094
138.7	83.1	83.1	1.74	0.062
103.2	64.9	64.9	1.24	0.062

TABLE II
Ammonium alum

Temp. (° K.)	C_p (Calc. deg. ⁻¹ mol. ⁻¹)	C_r	$\alpha \times 10^6$	$\gamma = \frac{3\alpha V_0}{\chi C_r}$
273.2	152.2	152.1	6.65	0.135
253.2	143.4	143.3	6.13	0.132
233.2	133.9	133.8	5.00	0.115
213.2	124.4	124.4	3.75	0.093
193.2	114.2	114.2	2.84	0.077
173.2	103.8	103.8	2.13	0.064
153.2	92.9	92.9	1.50	0.050
133.2	81.9	81.9	1.13	0.043
113.2	70.3	70.3	0.86	0.038

The variation of the expansion coefficient with temperature is exhibited graphically in Fig. 1.

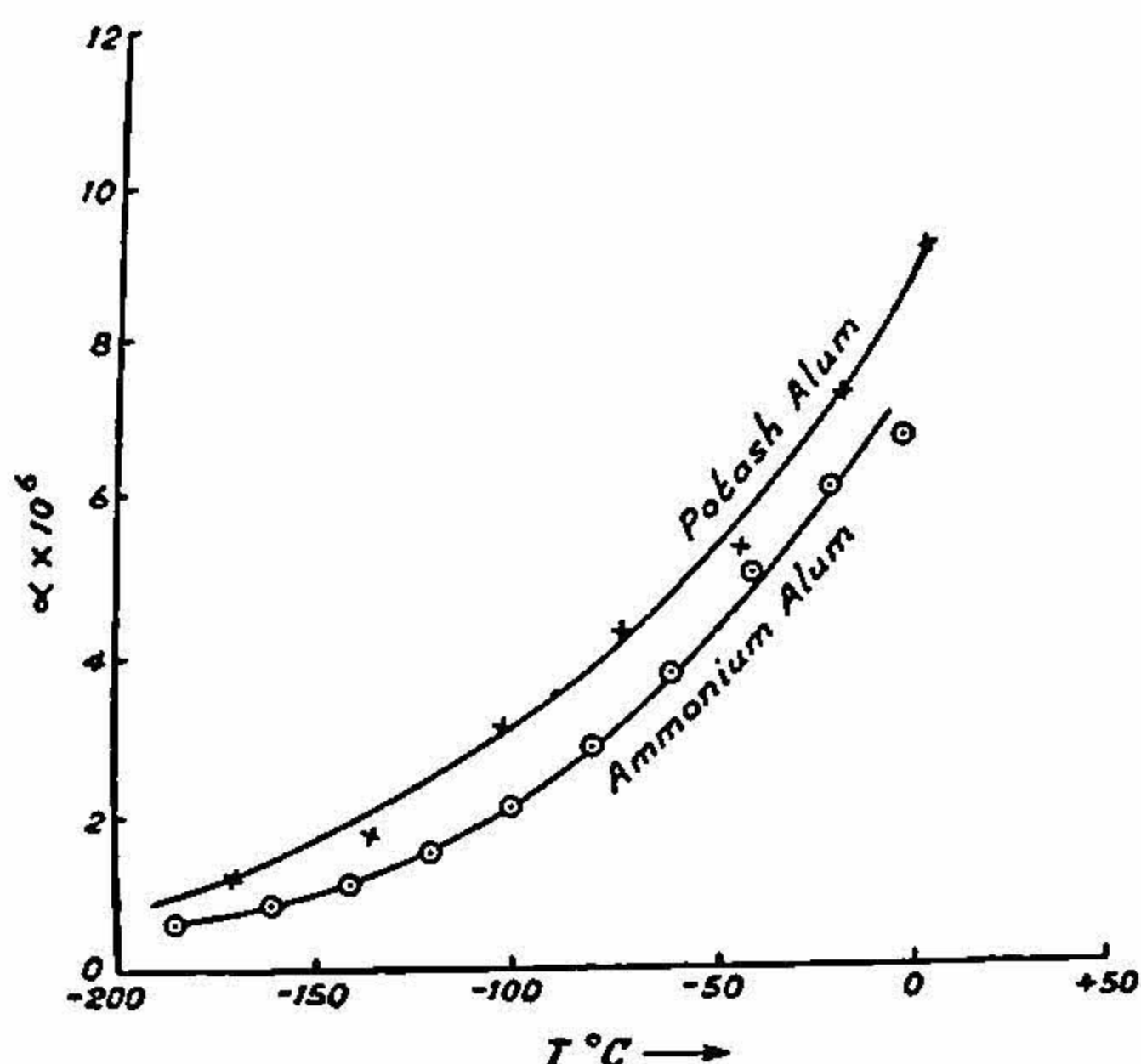


FIG. 1. Thermal Expansion of Alums.

3. DISCUSSION

The results show the comparatively low values of the expansion coefficient of the alums, especially at lower temperatures. The coefficient of expansion of ammonium alum is less than that of potash alum for the same temperature. This may be explained as due to greater inter-atomic forces in the former. Klug and Alexander give the following values for α at the mean temperature of 310.5°K .

$$\alpha_{\text{K alum}} = 11.0 \times 10^{-6}$$

$$\alpha_{\text{Am. alum}} = 9.5 \times 10^{-6}$$

also showing the higher expansion of potash alum.

The investigations of Shomate (1945) on the specific heats of alums at low temperatures show a transition in the structure of ammonium alum at 71°K and that in potash alum at 59.7°K . The expansions of the alums fall down to very low values at temperatures lower than 110°K . They may again show a change on the other side of the transition points.

To test the correctness of Gruneisen's Law specific heat data at various temperatures are necessary. Shomate *loc. cit.*, has measured specific heats from room temperature down to about 100°K in intervals of 10° . The values of C_p are obtained at the various temperatures at which α has been measured, by interpolation from his readings. The specific heat at constant

volume C_v is calculated using the thermodynamic relation $C_p - C_v = (9\alpha^2 V/\chi) T$, where V is the gram molecular volume and χ is the compressibility. The value for χ is taken from Sundara Rao's (1947-48) work on the elastic constants of alums. He gives for the bulk modulus $K = 1/\chi$ the values.

$$K_{\text{Pot. alum}} = 1.54 \times 10^{11} \text{ dynes/sq. cm.}$$

$$K_{\text{Am. alum}} = 1.57 \times 10^{11} \text{ dynes/sq. cm.}$$

These values are in close agreement with those of Bridgman and Voigt. It is found that on account of the low expansion and relatively high compressibility, C_v is almost equal to C_p .

The Gruneisen constant γ is given by $\gamma = \frac{3\alpha V_0}{\chi C_v}$, where $V_0 =$ gram molecular volume at 0°K and at zero external pressure and $\chi =$ compressibility under the same conditions. Since V and χ cannot be measured their values are taken at room temperature and at atmospheric pressure. This is justified since we are interested in the nature of variation of γ with temperature and not in its absolute magnitude.

$$\text{Pot. alum—}\chi = 6.486 \times 10^{-12} \text{ cm.}^2/\text{dyne}$$

$$\text{density} = 1.76 \text{ g.c.c., } V_0 = 269.6 \text{ c.c.}$$

$$\text{Ammonium alum—}\chi = 6.369 \times 10^{-12} \text{ cm.}^2/\text{dyne}$$

$$\text{density} = 1.65 \text{ g./c.c., } V_0 = 274.8 \text{ c.c.}$$

The calculated values of γ are given in Tables I and II. The results show clearly that for both the alums, γ exhibits a marked variation with temperature. This is because α varies more rapidly with temperature than does the specific heat.

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