

THE THERMAL EXPANSION OF CALCITE FROM ROOM TEMPERATURE UP TO 400° C.

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1. INTRODUCTION

A STUDY of the thermal expansion of calcite over a wide temperature range is of interest for the following reasons. Calcite belongs to the trigonal system and hence possesses two principal expansion coefficients—one along the optic axis and the other at right angles to it. Also its anisotropy of thermal expansion is large as it is the general case for crystals of the type $M(XO_3)$ (Lonappan, 1955). Its expansion coefficient perpendicular to the axis is negative and small. Such a negative expansion coefficient is of rare occurrence. Also its Raman and infrared spectra are known in great detail (1945, 1953). The temperature variation of its Raman spectrum has been investigated by Narayanaswamy (1946). Bhagavantam and Venkatarayudu (1939) have calculated the frequencies of all the normal modes of the crystal lattice employing a valence force field. Yet it is definitely not known whether calcite is typically ionic or typically of the valence type. X-ray studies indicate the former type; while its intense Raman spectrum is what is to be expected from a crystal belonging to the latter type. Chapman, Topping and Morral (1926) and Lennard Jones and Dent (1927) assumed a heteropolar force field and derived its lattice constant and other properties. An attempt at explaining the thermal expansion data in terms of the Raman and infrared spectra will be very interesting. The elastic constants of calcite have been measured by Bhimasenachar (1945). The specific heat, dielectric constant and a host of other physical properties have all been determined for calcite.

2. PREVIOUS WORK

The thermal expansion of calcite has been measured near room temperature by Fizeau (1868) and Benoit (quoted in Weigle and Saini's paper) using the interference method. The expansion of calcite down to liquid hydrogen temperatures was measured by Adenstadt (1936) using the interference method.

The lattice expansion of calcite was measured by Megaw (1933) from room temperature to 100°C. She claims an accuracy of 10% and her

values are in good agreement with the macroscopic expansion values of Fizeau. Weigle and Saini (1934) determined the lattice constant and thermal expansion of calcite using its powder photograph taken with a Seeman-Bohlin camera. They used a crystal which was not very perfect as they felt that thermal expansion might not be affected by small impurities or lattice imperfections. They claim an accuracy of better than 1%. Yet their values for expansion between 0 to 100° C. are lower than those of Fizeau and Benoit. The discrepancy is large—about 20%. Yet they conclude that this should not be taken as evidence for any real difference between lattice and macroscopic expansion. Such a discrepancy might perhaps have been caused by the imperfections in the crystal. Recent experiments by Glover (1954) on the lattice expansion of pure and calcium-containing potassium chloride have definitely shown the influence of impurities to be negligible. In view of this finding, Weigle and Saini's data appear to be unexplainable.

No measurements of high temperature expansion are present and the present investigation was carried out to fill this lacuna.

3. EXPERIMENTAL DETAILS

The experimental arrangement employed was that set up by Press (1949). The method of measurement has already been described in a previous paper by the author (1955). Preliminary measurements of the expansion coefficients both parallel and perpendicular to the axis were made by Mr. A. K. Sridhar; but he obtained anomalous results, probably because the orientations of his specimens were incorrect. The same specimens were used in the present investigations the orientation having been corrected with a polarising microscope. The specimens used finally were correct to within a degree of the required orientation. Three specimens were cut with the optic axis parallel to their bases. These were used to measure α_{\perp} . Three others were cut with the optic axis perpendicular to their bases. These served to determine α_{\parallel} .

4. RESULTS AND DISCUSSION

The results of these measurements are given in Table I below. The curves showing the variation of α_{\parallel} and α_{\perp} with temperature are given in Fig. 1.

The pieces employed for determining α_{\perp} were only 0.312 cm. thick and as the expansion coefficient is very small, reliable measurements for the mean expansion coefficient over as much as 100° C. only could be obtained. Even then the accuracy of measurement is reduced and is about 5% in this case.

TABLE I
 Values of α_{\parallel} and α_{\perp} for calcite at various temperatures

Range of Temp. $\Delta T^{\circ} \text{C.}$	Mean Temp. $T^{\circ} \text{C.}$	$\alpha_{\parallel} \times 10^6$	Range of Temp. $\Delta T^{\circ} \text{C.}$	Mean Temp. $T^{\circ} \text{C.}$	$\alpha_{\perp} \times 10^6$
64-85	74.5	27.2	45-115	80	-5.78
85-105	94.9	28.2	70-150	100	-5.00
124-143	133.4	29.2	99-187	143	-4.57
179-198	188.9	29.9	143-241	192	-4.09
217-235	225.6	31.2	187-289	238	-4.09
250-268	259.3	31.4	241-347	294	-4.04
296-314	304.9	32.4	310-420	365	-3.83
330-348	338.5	33.0			
363-381	371.8	33.7			

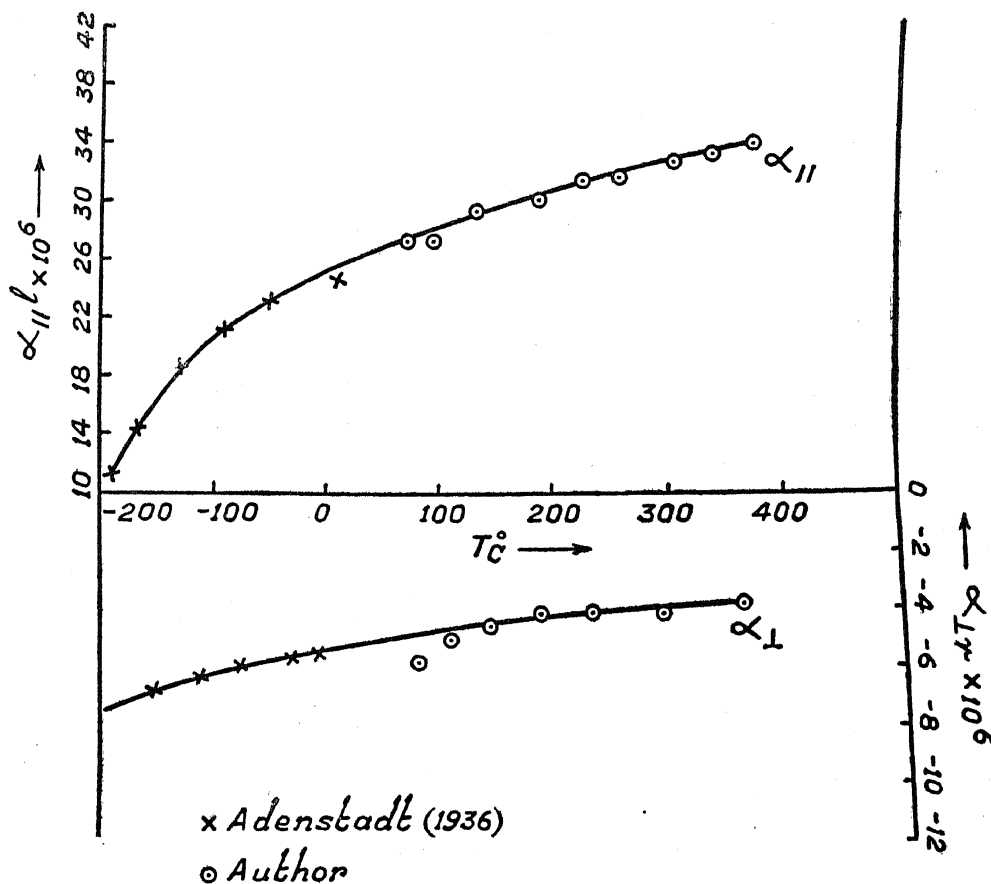


FIG. 1. Thermal Expansion of Calcite \parallel and \perp to the Axis.

The curves for α_{\parallel} and α_{\perp} as determined by the author are shown in Fig. 1. The low temperature expansion values of Adenstadt (1936) are plotted as crosses in the same figure. It is seen that the low temperature values of Adenstadt and the high temperature values of the author lie on a single curve for both α_{\parallel} and α_{\perp} .

The values of α_{\parallel} and α_{\perp} as determined from the graph at 50° C. are compared with the values in literature.

$$\alpha_{\parallel} \text{ at } 50^{\circ} \text{ C.} = 26.6 \times 10^{-6}$$

$$\alpha_{\perp} \text{ at } 50^{\circ} \text{ C.} = -5.2 \times 10^{-6}$$

The values in the literature are

$$\left. \begin{array}{l} \alpha_{\parallel} = 26.2 \times 10^{-6} \\ \alpha_{\perp} = -5.40 \times 10^{-6} \end{array} \right\} \text{Fizeau} \quad \left. \begin{array}{l} \alpha_{\parallel} = 25.3 \pm 1.5 \times 10^{-6} \\ \alpha_{\perp} = -5.2 \pm 0.7 \times 10^{-6} \end{array} \right\} \text{Megaw}$$

$$\left. \begin{array}{l} \alpha_{\parallel} = 25.7 \times 10^{-6} \\ \alpha_{\perp} = -5.50 \times 10^{-6} \end{array} \right\} \text{Benoit} \quad \left. \begin{array}{l} \alpha_{\parallel} = 21.0 \times 10^{-6} \\ \alpha_{\perp} = -3.8 \times 10^{-6} \end{array} \right\} \text{Weigle and Saini}$$

The agreement with the values of Fizeau, Benoit and Megaw is very good. The values of Weigle and Saini are too low presumably because of the imperfect crystal they employed.

In the following table are collected the thermal expansion values α_{\parallel} and α_{\perp} at various temperatures, the volume expansion coefficient β , the specific heat per gram c_p and the Gruneisen constant γ . The values of c_p have been taken from *International Critical Tables*; the value of the compressibility χ is taken as 15.4×10^{-13} sq.cm./dyne from Bhimasenachar (1945).

TABLE II

The linear expansion coefficients α_{\parallel} and α_{\perp} , the volume expansion coefficient β , the specific heat and the Gruneisen constants for calcite at different temperatures

$$\text{Compressibility } \chi = 1.54 \times 10^{-12}$$

$$\text{Molar Volume } V = 34.2 \text{ c.c.}$$

T° C.	$\alpha_{\parallel} \times 10^6$	$\alpha_{\perp} \times 10^6$	$\beta \times 10^6$	c_p joules/gm.	Gruneisen Const. γ
-150	16.4	-6.8	2.8	0.452	0.14
-100	20.6	-6.3	8.0	0.590	0.30
0	25.0	-5.4	14.2	0.763	0.41
100	28.1	-4.9	18.3	0.870	0.47
200	30.8	-4.2	22.4	0.962	0.52
300	32.8	-3.9	25.0	1.046	0.53

As usual the Gruneisen constant decreases with decreasing temperatures. The small value of the Grunesien constant is noteworthy as it is typical for a valence crystal. The intense Raman spectrum of calcite and its dielectric polarisation also point to such a type of binding in the crystal.

The author is indebted to Prof. R. S. Krishnan who suggested this problem and provided the specimens. He is also thankful to Dr. Vedam for his help in determining the orientation of the specimens.

5. SUMMARY

The thermal expansion of calcite along and perpendicular to the optic axis were measured from room temperature up to 400° C. $\alpha_{||}$ increased with increasing temperature, while α_{\perp} , which is negative, decreases in magnitude with increasing temperatures. The high temperature curves join up well with the low temperature curves of Adenstadt. The Gruneisen constant is shown to vary with temperature in the usual manner. Its small value points to a valence type of binding in the crystal—a fact supported by the intense Raman effect and dielectric polarisability of calcite.

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