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Thermo-Elastic Behaviour of Calcite

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The thermo-elastic behaviour of calcite has been studied in the temperature range 0 to 300 °C. The experimental technique employed is a composite piezo-electric oscillator method. The elastic moduli show a linear increase with temperature, with a sudden change in the gradient at 200 °C.

1. Introduction

Calcite belongs to the D_{3d} class and therefore its elastic behaviour is characterized by 6 independent elastic moduli S_{11}, S_{33}, S_{44}, S_{12}, S_{13} and S_{14}. These elastic moduli have been determined by Voigt (1928) and Bhimasenachar (1945). The temperature dependence of these elastic moduli have been studied and reported here.

2. Experimental

The composite piezo-electric oscillator method (Subrahmanyam, 1954) has been employed in the present investigation. Rectangular quartz bars are used to excite longitudinal oscillations and cylindrical rods for torsional oscillations. The effective longitudinal and torsional elastic moduli, S'_{33} and $2(S'_{44}+S'_{55})$ respectively are given by

$$S'_{33}=S_{11}(1-\alpha_{33}^2)^2+S_{33}\,.\,\alpha_{33}^4+(4S_{44}+2S_{13})\,.\,\alpha_{33}^2\,.\,(1-\alpha_{33}^2)+4S_{44}\,.\,\alpha_{23}\,.\,\alpha_{33}\,.\,(3\alpha_{13}^2-\alpha_{23}^2)$$

and

$$2(S'_{44}+S'_{55})=2\{S_{44}+\tfrac{1}{2}(S_{11}-S_{12})+[S_{44}-\tfrac{1}{2}(S_{11}-S_{12})]\,.\,\alpha_{33}^2+(S_{11}+S_{33}-4S_{44}-2S_{13})\,.\,\alpha_{33}^2\,.\,(1-\alpha_{33}^2)-4S_{14}\,.\,\alpha_{23}\,.\,\alpha_{33}\,.\,(3\alpha_{13}^2-\alpha_{23}^2)\}\,,$$

where α_{13}, α_{23} and α_{33} are the direction-cosines of the length of the bar or the rod. Two rectangular bars and four cylindrical rods of suitable orientation have been used to evaluate all the six elastic moduli. The orientations of such bars and rods are shown in Table 1.

The first two rods and bars in Table 1 give the diagonal terms of the elasticity tensor and the next two give the non-diagonal terms. A rod described by $X\,45°\,Z$ is cut so that its length makes angles of 45° with the X- and Z-axes and is perpendicular to the Y-axis. Similarly the length of the rod $Y\,135°\,Z$ makes 135° and 45° with the Y- and Z-axes respectively and is perpendicular to the X-axis.

To study the temperature variation of the elastic moduli, the composite oscillator with its holder is placed in an electrical furnace, the temperature of which can be controlled to within ±1 °C. at the required temperature, and can be raised to 350 °C. For investigations below room temperature, the composite bar or rod with its holder is sealed in a small container which is placed in a Dewar flask filled with a suitable freezing mixture. The temperatures are measured with a mercury-in-glass thermometer capable of reading to 0·1 °C. The resonant frequency of the composite rod is determined at each temperature and the data thus obtained are used to calculate the elastic moduli at various temperatures.

Very clear specimens of calcite free from twinning are used in the present investigation. The required number of rods and bars were cut from three independent pieces as the specimens available were not appreciable in size. For fixing the orientations of the rods and the bars, the system of reference axes used by Bhimasenachar (1945) has been adopted. The densities are determined separately for each section by the hydrostatic method. The lengths are measured to an accuracy of 0·01 mm. Densities and lengths at higher temperatures are computed making use of the thermal expansion data of Srinivasan (1955).

3. Results

The elastic moduli determined at room temperature are compared with those obtained by previous workers

Table 1. *Orientations of bars and rods and their effective elastic moduli*

No.	Direction of the bar or the rod	Direction-cosines α_{13}	α_{23}	α_{33}	Effective longitudinal constant S'_{33}	Effective torsional constant $2(S'_{44}+S'_{55})$
1	Y	0	1	0	S_{11}	$2[S_{44}+\frac{1}{2}(S_{11}-S_{12})]$
2	Z	0	0	1	S_{33}	$4S_{44}$
3	X 45° Z	$\sqrt{\frac{1}{2}}$	0	$\sqrt{\frac{1}{2}}$	—	$[S_{44}+S_{11}-\frac{1}{2}S_{12}+\frac{1}{2}S_{33}]-S_{13}$
4	Y 135° Z	0	$-\sqrt{\frac{1}{2}}$	$\sqrt{\frac{1}{2}}$	—	$[(S_{44}+S_{11}-\frac{1}{2}S_{12}+\frac{1}{2}S_{33}-S_{13})-2S_{14}]$

Table 2. *Elastic moduli of calcite at room temperature*

	S_{11}	S_{33}	$4S_{44}$	$-S_{12}$	$-S_{13}$	$2S_{14}$
Voigt	11·3	17·5	40·3	3·7	4·3	9·1
Bhimasenachar	11·0	17·3	39·4	3·4	4·3	8·6
Authors	11·0	17·0	38·2	3·0	5·2	10·2

(The elastic moduli are expressed in units of 10^{-13} cm.²/dyne).

in Table 2. The elastic moduli S_{11}, S_{33} and $4S_{44}$ were determined directly whereas the moduli S_{12}, S_{13} and $2S_{14}$ were obtained by solving complicated equations. Since torsional modes of oscillations were used in the present investigation in determining the moduli S_{13} and $2S_{14}$, the agreement with those of previous workers is regarded as good. Temperature variations of the elastic moduli are shown in Fig. 1. Curves corre-

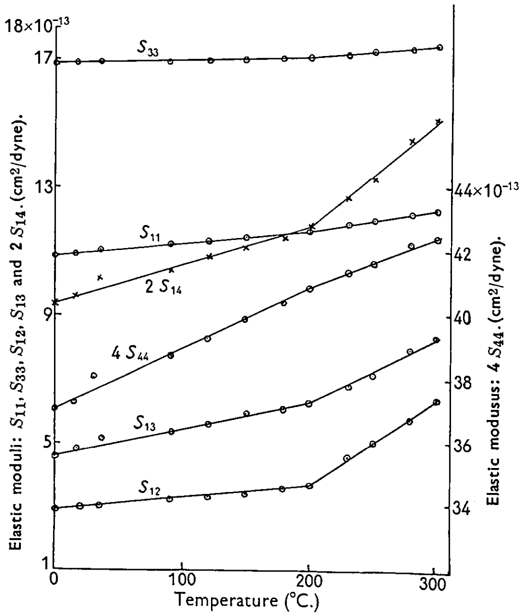

Fig. 1. Temperature variation of elastic moduli of calcite.

sponding to S_{11}, S_{33} and $4S_{44}$ were determined directly from measurements on bars Y and Z and rod Z respectively. The non-diagonal terms were calculated from observations on the remaining rods and then represented graphically. The moduli S_{12} and S_{13} are inherently negative and so their sign is reversed while plotting their temperature variation. The curves show that the numerical values of the moduli always increase linearly with temperature. At a temperature of 200 °C., the rate of increase suddenly rises considerably while a linear relationship with temperature is still maintained. From the curves, the rate of change of elastic modulus with temperature is calculated. This is expressed as a percentage of the value at 0 °C.—$[1/S\,(\partial s/\partial t)\times 100]$. There are two such constants associated with each curve—one for the region 0 to 200 °C. and the other 200 °C. and above. The numerical values of these coefficients are given in Table 3.

Table 3. *Temperature coefficients of elastic moduli*

No.	Temperature range	Temperature coefficient associated with modulus S_{11}	S_{33}	$4S_{44}$	$-S_{12}$	$-S_{13}$	$2S_{14}$
		$\times 10^2$	$\times 10^2$	$\times 10^2$	$\times 10^2$	$\times 10^2$	$\times 10^2$
1	0 to 200 °C.	3·7	0·59	5·1	13·8	20·0	12·2
2	200 to 300 °C.	5·6	1·80	4·3	93·1	44·4	36·2

From the thermal expansion data of Srinivasan (1955) the temperature variations of densities of rods used in this investigation have been calculated and are represented graphically in Fig. 2. These curves also

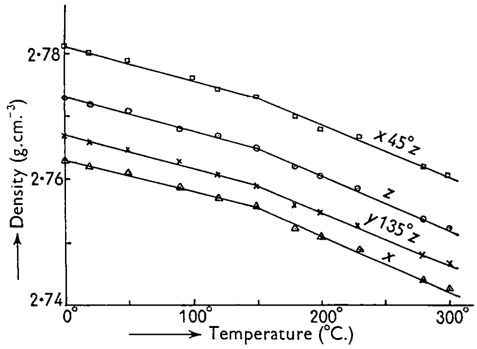

Fig. 2. Temperature variation of density of calcite cut in different orientations.

show a sudden change in their slopes at about 150 °C. Thus this temperature region of 150 to 200 °C. appears to be associated with some characteristic internal change in the crystal.

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