schemes were also different. We have found that a change of weighting scheme can alter bond-length values by 0·02 Å in a structure analysis not affected by disorder. It is hardly surprising that somewhat larger differences were found in this case. We should point out that the size of shift which can be neglected depends on the size of the smallest latent root of $D^{-1}A$, for the block-diagonal approximation, and this can be expected to be unusually small if atomic sites overlap because of disorder. For the azulene analysis the sizes of the final shifts were not stated.

Our main conclusion is that the block-diagonal approximation is a satisfactory substitute for full-matrix analysis in normal cases, but only provided that due care is exercised. The need for such care, and a desire for more precise estimates of error, are our main reasons for preferring the full-matrix method if a computer of sufficient size and speed is available.

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Variation with Temperature of the Elastic Compliances of Corundum

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The elastic compliances of a natural corundum are determined by the composite piezo-electric oscillator method. The variation of these six compliances with temperature has also been studied in the temperature range 0 to 300 °C. All the compliances increase with temperature, though the variations do not follow a linear law.

Introduction

Corundum, Al_2O_3, one of the important naturally occurring crystals, has industrial value as an abrasive since its hardness is next to that of diamond. It belongs to the 'hematite group', R_2O_3, crystallizing in the rhombohedral class. The crystals are usually rough and round, the (0001) plane being perfect and the $(11\bar{2}0)$ plane less distinct. Due to twinning, the $(10\bar{1}1)$ plane is also prominent.

As this crystal belongs to the D_{3d} class of the trigonal system, its elastic behaviour is defined by 6 independent elastic compliances, S_{11}, S_{33}, S_{44}, S_{12}, S_{13} and S_{14}. These have been determined by Sunder Rao (1949), using a synthetic specimen. Bhimasenachar (1949, 1950) has determined these constants using a naturally occurring crystal, employing the wedge method. A similar determination has been made by Mayer & Hiedemann (1958) for synthetic sapphire. Very recently Wachtman and others (1960) have redetermined the elastic constants by a resonance method, using synthetic specimens. In the present investigation, the elastic compliances of a natural crystal are determined at room temperature and also their variation with temperature between 0 and 300 °C.

Table 1. *Orientations of crystal bars and rods and the effective compliances*

No.	Direction of the bar	Direction-cosines α_{13}	α_{23}	α_{33}	Effective constants s_{33}'	$2(s_{44}'+s_{55}')$
1	X	1	0	0	s_{11}	$2[s_{44}+\frac{1}{2}(s_{11}-s_{12})]$
2	Z	0	0	1	s_{33}	$4s_{44}$
3	$X45°Z$	$\sqrt{\frac{1}{2}}$	0	$\sqrt{\frac{1}{2}}$	—	$(s_{44}+s_{11}-\frac{1}{2}s_{12}+\frac{1}{2}s_{33})-s_{13}$
4	$Y45°Z$	0	$\sqrt{\frac{1}{2}}$	$\sqrt{\frac{1}{2}}$	—	$(s_{44}+s_{11}-\frac{1}{2}s_{12}+\frac{1}{2}s_{33}-s_{13})+2s_{14}$

Experimental

The composite oscillator method (Subrahmanyam, 1954) has been employed in this investigation. The description of the crystal bars and rods employed to calculate all the 6 elastic compliances are presented in Table 1. The crystal bar $X45°Z$ indicates that the length of the bar makes 45° with X and Z axes and is perpendicular to Y-axis. Similar meaning is attached to the bar $Y45°Z$.

The effective constants, s_{33}' and $2(s_{44}'+s_{55}')$, given in the last two columns of Table 1, were evaluated from the general formulae given in a previous paper (Jayarama Reddy & Subrahmanyam, 1960). The two rectangular bars and the four cylindrical rods employed were cut from a single opaque and brownish crystal of natural corundum. Its basal plane (0001) and the faces (11$\bar{2}$0) were well formed. The bars and rods were cut to an accuracy of 1° of arc. The lengths and densities at room temperature were taken to hold good at the high temperatures also since its coefficient of thermal expansion is very small.

Results and discussion

The experimental results along with other relevant data are presented in Table 2. The measurements on the crystal bars 1, 3 and 4 give the direct values, $s_{11}=2{\cdot}67$, $s_{33}=2{\cdot}33$ and $4s_{44}=7{\cdot}51$. Observations on the bars 2, 5 and 6 give on substitution the compliances, s_{12}, s_{13} and $2s_{14}$. The complete set of elastic

Table 2

No.	Direction of the bar	Length in cm.	Frequency in kcyc./sec.	Mode	Effective elastic constant: Expression	Value
1	X	2·22	222·50	L	s_{11}	$2{\cdot}67\times10^{-13}$
2	X	2·22	129·33	T	$2[s_{44}+\frac{1}{2}(s_{11}-s_{12})]$	7·92
3	Z	2·26	234·19	L	s_{33}	2·33
4	Z	2·26	130·42	T	$4s_{44}$	7·51
5	$X45°Z$	2·12	141·41	T	$(s_{44}+s_{11}-\frac{1}{2}s_{12}+\frac{1}{2}s_{33})-s_{13}$	7·26
6	$Y45°Z$	2·14	135·70	T	$(s_{44}+s_{11}-\frac{1}{2}s_{12}+\frac{1}{2}s_{33}-s_{13})+2s_{14}$	7·74

(L: longitudinal; T: torsional).

Table 3

		s_{11}	s_{33}	$4s_{44}$	s_{12}	s_{13}	$2s_{14}$
1	Sunder Rao	2·84	2·21	5·47	−0·95	−0·47	−1·52
2	Bhimasenachar	2·32	1·93	5·77	−1·05	−0·38	−1·71
3	Mayer & Heideman	2·18	2·02	5·04	−0·50	−0·16	−0·49
4	Wachtman and others	2·35	2·17	6·94	−0·78	−0·36	+0·49
5	Author	2·67	2·33	7·51	−1·50	−0·80	+0·47

(Expressed in units of 10^{-13} cm.^{2}/dyne).

Table 4. *Elastic compliances of corundum*

Temperature (°C.)	s_{11}	s_{33}	$4s_{44}$	$-s_{12}$	$-s_{13}$	$+2s_{14}$
0	2·66	2·32	7·49	1·49	0·80	0·47
30	2·67	2·33	7·51	1·50	0·80	0·48
60	2·68	2·34	7·55	1·51	0·81	0·48
100	2·69	2·36	7·63	1·54	0·82	0·48
150	2·71	2·38	7·74	1·61	0·81	0·53
180	2·73	2·40	7·82	1·66	0·83	0·54
230	2·76	2·43	7·93	1·72	0·83	0·67
270	2·78	2·47	8·02	1·77	0·87	0·78
300	2·80	2·50	8·10	1·80	0·87	0·88

(Unit: 10^{-13} cm.^{2}/dyne).

compliances is evaluated and presented in Table 3, along with results of previous workers for comparison. The first point to be noted in Table 3 is that the sign of s_{14} agrees with that of Wachtman and others, as the same coordinate system was used in this case also. There are variations in the values of the diagonal constants, especially $4s_{44}$, the difference amounting to 10%. Since the specimen used in the present investigation was a natural specimen and the cutting was done to an accuracy of 1° to 2° (contact goniometer), the agreement is to be considered good.

The variation of the effective compliances with temperature has been studied and the 6 independent compliances are calculated in the temperature region 0 to 300 °C. They are presented in Table 4. The variation of the diagonal constants with temperature is represented in Fig. 1 and that of the non-diagonal constants in Fig. 2. The signs of the negative constants s_{12} and s_{13} are reversed for plotting their variation with temperature. The curves show that the variations do not follow a linear law. There is a general increase with temperature.

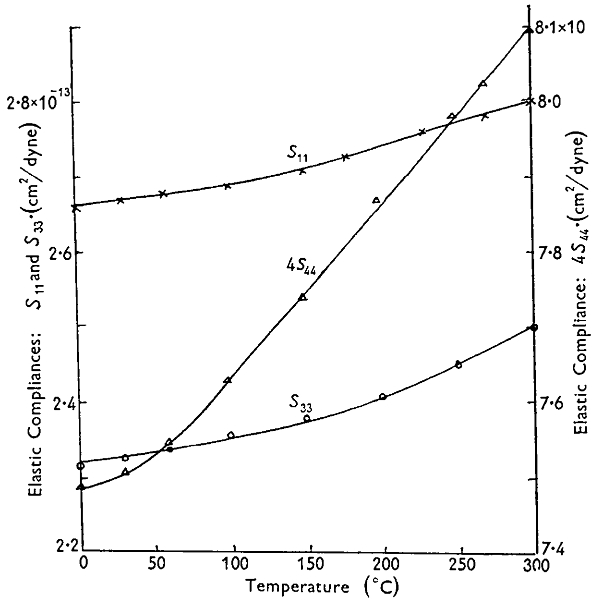

Fig. 1.

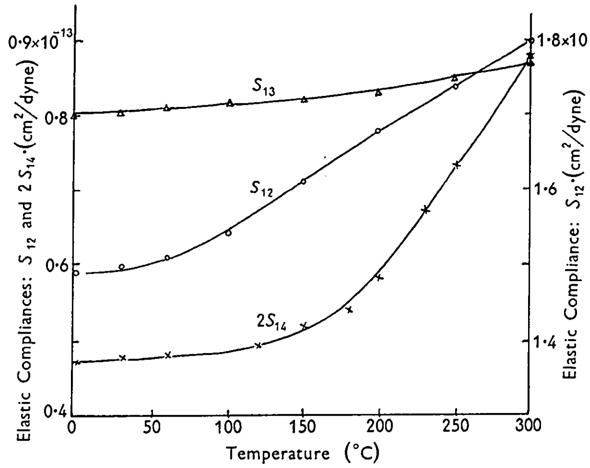

Fig. 2.

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