

# ELASTIC PROPERTIES OF SINGLE CRYSTALS AND POLYCRYSTALLINE AGGREGATES

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## 1. INTRODUCTION

THE author and his collaborators have been engaged during the past ten years in studying the elastic properties of single crystals, polycrystalline aggregates, metals, rock sections, gels, plastics and so on, from different aspects using various ultrasonic methods. Amongst these, single crystals and artificially prepared polycrystalline aggregates are of importance from a fundamental point of view because of their relative simplicity. Experimental work relating thereto is briefly reviewed in the following pages. Work done in other laboratories is mentioned wherever necessary, but exhaustive references to literature are not included.

All solid bodies are characterised by their ability to carry longitudinal as well as transverse elastic waves. The velocities of propagation of these waves are different in different directions and are determined by the elastic constants of the solid. The number of elastic constants, in the simplest case of an isotropic substance is two. In the most general case of a single crystal belonging to the triclinic system, the number required to describe the elastic properties completely is twenty-one. This number gradually reduces as symmetry is introduced, finally becoming three for crystals of the cubic system. Isotropic substances and substances available as large specimens are the easiest to handle as far as experimental technique is concerned. Extension of the methods applicable to such substances to crystalline media and to small specimens presents difficulties. These difficulties have been successfully overcome and results of importance have been obtained for many single crystals. For understanding certain aspects of solid state physics, it is essential also to know how these elastic properties vary with temperature and special methods have been devised for studying this aspect. Some significant results of such a study are included in this review.

A study of the relations existing between the elastic properties of single crystals and those of polycrystalline aggregates and of the extent to which the latter can be determined from the former, is also of special interest. Extensive information is not available in the literature on this subject presumably due to difficulties in securing suitable polycrystalline specimens

and due to lack of proper experimental techniques. The elastic properties of the aggregates depend on the closeness of packing, size of particles and arrangement of the crystallites composing the aggregate. If they are distributed in a random manner in all possible orientations in space (having no preferred orientation), then the polycrystalline aggregates will be elastically isotropic and exhibit only two elastic constants which are independent of direction. Methods of calculation in such a case, based on the idea that the properties of polycrystalline aggregates are average values of the properties of the free crystals composing the aggregate, have appeared in a recent publication by Boas.<sup>1</sup> On the other hand, an ordered arrangement of the crystallites (preferred orientation) will result in a fibrous structure or something simulating it. Such a structure will be elastically anisotropic. A common example of the latter type is wood and there are several other naturally occurring minerals which merit a detailed study from this aspect. Further complications in dealing with some polycrystalline aggregates will arise due to the existence of foreign substances usually in the form of cementing material binding the various crystallites together. The elastic properties of these substances are very much influenced by the nature, quantity and distribution of this cementing material. Such studies have a bearing on the properties of rocks and other naturally occurring materials. Another factor which one has to take into account when studying the elastic properties of polycrystalline aggregates is the interaction between the crystals. This interaction arises due to the fact that a crystal embedded in a mass of other crystals does not behave in a manner similar to a free crystal. However, this interaction can be neglected under certain conditions.

## 2. EXPERIMENTAL METHODS

Almost all the early methods employed for the study of elastic properties were static ones, consisting of bending and twisting of specimens under investigation. Such static methods obviously limit the field of experimental investigation as they require large and faultless specimens and this is not always possible especially when we want to study single crystals. However, the advent of the piezo-resonator and the consequent development of piezoelectric techniques have resulted in the evolution of a number of dynamic methods. An excellent review of such methods has been given by Hearmon.<sup>2</sup>

Three different and distinct techniques have been employed in the work now being described. They are (a) the wedge method,<sup>3</sup> (b) the total internal reflection method<sup>4</sup>, and (c) the composite oscillator method.<sup>5, 6</sup> A brief description of these methods is given below;—

(a) *Wedge method.*—It is well known that a plane parallel plate of any piezoelectric crystal when used in an oscillator circuit acts as a generator of monochromatic sound waves. If the plate is shaped into a wedge of gradually varying thickness and the exciting frequency of the oscillator is varied, an appropriate portion of the wedge responds to the electrical frequency and generates an ultrasonic beam of the same frequency. Thus, a piezoelectric wedge acts as a source of ultrasonic waves of continuously varying frequency. The lower limit of the frequency range is determined by the maximum thickness of the wedge and the upper limit by the power of the oscillator, the sensitiveness of the detecting device and the breaking stress of the crystal employed. In all cases, we have used either a Z-cut tourmaline wedge or an X-cut quartz wedge with a frequency range of 1 to 12 Mc/S.

The wedge is placed on the crystal plate of known orientation under investigation with a drop of oil in between for securing good acoustical contact and the two are kept lightly pressed between two brass electrodes thus forming a parallel plate condenser, in parallel with the tuning condenser of a Hartley circuit. The arrangement is then lowered into a rectangular glass cell containing a transparent liquid like carbon tetrachloride such that the lower surface of the crystal plate just touches the liquid. The ultrasonic beam from the wedge passes through the crystal and then enters the liquid. The transmission maxima are detected using the Debye-Sears diffraction effects with the usual optical arrangement. Since the sound beam is best transmitted when the frequency of the wedge corresponds to either the fundamental or an overtone of one of the normal modes of the crystal plate, the Debye-Sears pattern will have a maximum intensity at such points. It has been found in practice that the setting for maximum transmission is very sharp and is capable of being reset to within 1 to 2 per cent. The transmission frequency is then measured with an accurate wave-meter.

Transmission maxima thus recorded have to be sorted out and assigned to their appropriate modes. Among these maxima, the strong ones usually correspond to the thickness longitudinal mode. The weaker maxima correspond to the transverse and quasi-transverse modes. They can be transmitted to the liquid medium only as longitudinal vibrations consequential to some sort of a coupling effect. Hence, the diffraction pattern due to these modes will be of low intensity. This difference in intensity furnishes a rough criterion by which the maxima can be sorted out and associated with their corresponding modes. Each of these frequencies corresponds either to the fundamental or one or the other of the higher harmonics of the crystal plate under investigation. The fundamental frequency can then be

determined from the intervals between successive frequencies showing maxima of same intensity.

Knowing the fundamental frequencies of the crystal plate of known orientation, the velocities are calculated from which the appropriate elastic constants are obtained. The detailed mathematical formulæ and the method of calculating the different elastic constants are omitted here as they have been published from time to time.<sup>7</sup>

This method has been successfully applied to several crystals belonging to different crystal systems from the cubic to the monoclinic. It has been subsequently extended to polycrystalline aggregates of alkali halides<sup>8</sup> by making suitable modifications in the experimental technique. The specimens of polycrystalline aggregates are obtained in the following way: pure and dry substances are finely powdered and passed through a 200-mesh sieve. These powders are compressed in a steel mould between two steel cylinders of 1" diameter at a pressure of about 60,000 lb./in.<sup>2</sup> The compressed cakes are then ground to uniform thickness on very fine emery cloth. Thus a uniformity of 1 to 2 in 100 is obtained. An X-ray study of these tabloids has revealed that the micro-crystals composing the polycrystalline aggregate are oriented in a perfectly random manner as a result of such a compression.

The density of each one of the compressed cakes is determined to an accuracy of 1 to 2 per cent. directly by evaluating the volume of the circular tabloid and determining its weight in air. While determining the characteristic frequencies of the tabloids, special care is taken to see that the tabloids do not come into direct contact with the liquid in the cell. Otherwise, the liquid gets into the pores of the specimens and vitiates the experimental results. For this purpose, the conventional design of the crystal holder is slightly modified. The lower annular brass electrode on which the specimen under investigation rests, is now replaced by a cup-like vessel, the central hole of which is covered by a thin aluminium foil. The rest of the experimental set-up is just the same as that used for single crystals. The characteristic frequencies of the compressed specimens are determined in the usual way in the frequency range 2 to 10 Mc/S.

The wedge method just described is simple, elegant and requires only small specimens. This last mentioned advantage has made it possible to determine the elastic constants of diamond<sup>9</sup> for the first time. The method has the additional advantage that inclusions or minute crevices in the crystal do not affect the results appreciably. The method is, on the whole, capable of giving elastic constants accurate to about 5 per cent.

In spite of all the abovementioned advantages, the wedge method has certain limitations of its own. As the specimen under investigation comes into contact with the liquid in the observation cell, the method is not quite suitable for porous substances like wood. Further, extension of the method to high temperatures is rather difficult as the liquid has to be heated along with the specimen. Consequently, the diffraction maxima appear blurred owing to convection currents set up in the liquid thus making it difficult to detect the transmission maxima. The method is also not suited to study substances like granites which highly attenuate the ultrasonic beam. In such cases, it becomes particularly difficult to locate the torsional maxima.

(b) *Total internal reflection method.*—In an attempt to overcome the abovementioned difficulties, a different technique based on a principle originally used by Bez-Bardili<sup>10</sup> has been adopted by us. Sound velocities in solids are usually much higher than in liquids, so that when an ultrasonic beam passes from a liquid to a solid, the phenomenon of total internal reflection will occur beyond a critical angle of incidence, as in optics. If this critical angle is determined, the ultrasonic velocity in one medium relative to that in the other can be calculated. In the method of Bez-Bardili, a plate of the material is placed in the path of the ultrasonic beam in a liquid and rotated. The emergent beam is detected by the Debye-Sears diffraction method. More recently, Schneider and Burton<sup>11</sup> employed a second piezoelectric crystal to detect the transmitted beam. In our investigation,<sup>4</sup> the pulse technique of Pellam and Galt<sup>12</sup> is adapted to work on this principle.

A pulsed ultrasonic beam is generated by oscillating one crystal and received by another identical crystal, the intervening space being filled with a liquid. The two crystals are ground flat to the same thickness, their fundamental frequency being 1.15 Mc/S and the third harmonic is used throughout the investigation. The specimen in the form of a rectangular plate is interposed in the path of the ultrasonic beam and rotated, thereby changing the angle of incidence of the beam on the plate. The intensity of the transmitted pulse, as indicated by the pattern on the oscilloscope, changes with variation in the angle of incidence. The transmitted beam first exhibits a sharp dip in intensity at the longitudinal critical angle and completely vanishes a little later at the torsional critical angle. The longitudinal and torsional velocities corresponding to these critical angles are calculated assuming the ultrasonic velocity in the liquid. The error in the determination of the longitudinal velocities will be in the range of half to one per cent. The torsional velocities can be determined even with greater accuracy as the angles involved are much larger.

This method has been successfully employed for a study of the elastic properties of many Indian rocks<sup>4</sup> and certain gels,<sup>13</sup> the results of which do not find a place in the present review. The ease and accuracy with which the longitudinal and torsional velocities can be determined make this method superior to other methods in some respects. It has been mentioned that the torsional velocities in certain inhomogeneous rocks like granites could not be determined by the wedge method due to the high attenuation of the sound beam. In such cases, the total internal reflection method is found to be quite successful. However, the method has the disadvantage that it requires comparatively larger specimens and cannot readily be applied to crystalline media. Furthermore, the original difficulty of the specimen coming into contact with the liquid is not eliminated. As such it is not quite suitable for high temperature work.

(c) *Composite Oscillator method.*—The composite oscillator method originally developed by Balamuth<sup>5</sup> and Rose<sup>6</sup> is free from the abovementioned difficulties. As such, this method has been set up and adapted by us for a study of crystal elasticity. In this method, a suitably cut quartz rod is cemented to the crystal specimen end to end, both of them having the same cross-section. The quartz rod is provided with silver electrodes to which an alternating potential of constant amplitude is applied. The piezoelectric effect in the quartz rod sets up the required vibrations in the composite oscillator. The resonant frequency is found by observing the variation with frequency of the electrical impedance between the electrodes. The elastic constant of the specimen can then be found from the resonant frequency, the dimensions of the crystal specimen, and certain constants of the quartz rod. For longitudinal vibration, X-cut quartz bars of square cross-section are convenient while torsional vibrations are excited by a Y-cut quartz rod of circular cross-section with four electrodes. It is essential that each specimen under investigation is tried with different quartz rods, until a composite cylinder, whose frequency falls within 5 per cent. of the frequency of the quartz and the specimen, separately, is found. The composite oscillator can conveniently be placed at the centre of an electric furnace and high temperature measurements made with the least difficulty.

This method has been successfully applied to single crystals and polycrystalline aggregates in the author's laboratory both at room temperature and at higher temperatures. Young's modulus  $Y$  and rigidity modulus  $n$  along (100) direction are directly obtained in this method by the use of cylinders whose length lies along (100). The elastic modulus  $s_{11}$  is simply the reciprocal of  $Y_{(100)}$  while  $s_{44}$  is the reciprocal of  $n_{(100)}$ . The range of frequencies employed in this method is 90 to 230 Kc/S. The elastic moduli

$s_{11}$  and  $s_{44}$  can be determined to an accuracy of one per cent. while the uncertainty in  $s_{12}$  varies from 2 to 3 per cent. over the temperature range.

### 3. RESULTS AT ROOM TEMPERATURE

(a) *Cubic crystals*.—Table I gives the elastic constants of cubic crystals determined by employing one or the other of the techniques described in Section 2. Only those values which we consider as final are given. All the  $c$ 's in this and subsequent tables are in units of  $10^{11}$  dynes/cm.<sup>2</sup>

TABLE I  
*Elastic constants of cubic crystals*

No.	Substance	$c_{11}$	$c_{12}$	$c_{44}$
1	Sodium chloride .. ..	4.97	1.27	1.27
2	Sodium bromide .. ..	3.87	0.97	0.97
3	Lithium fluoride .. ..	11.9	5.38	5.34
4	Ammonium chloride .. ..	3.90	0.72	0.68
5	Ammonium bromide .. ..	2.96	0.59	0.53
6	Sodium chlorate .. ..	5.09	1.55	1.18
7	Sodium bromate .. ..	5.45	1.91	1.50
8	Lead nitrate .. ..	4.56	3.09	1.37
9	Barium nitrate .. ..	6.02	1.86	1.21
10	Strontium nitrate .. ..	4.73	2.18	1.46
11	Ammonium alum .. ..	2.50	1.06	0.80
12	Potassium alum .. ..	2.56	1.07	0.86
13	Chromium alum .. ..	2.37	0.93	0.77
14	Thallium alum .. ..	2.9	1.3	0.87
15	Iron pyrites .. ..	36.2	-4.64	10.52
16	Zinc blende .. ..	10.79	7.22	4.12
17	Galena .. ..	12.70	2.98	2.48
18	Diamond .. ..	95.0	39.0	43.0
19	Fluorite .. ..	16.44	5.02	3.47
20	Magnetite .. ..	27.3	10.6	9.71
21	Magnesium oxide .. ..	28.6	8.70	14.80

All the alkali halides including lithium fluoride, being ionic cubic crystals, satisfy Cauchy's relation  $c_{12} = c_{44}$ . The elastic constants of sodium bromide differ from those of Bridgman<sup>14</sup> whose values are given in Table II.  $r_0$  is the interionic distance in Ångstroms as given by Slater.<sup>15</sup>

TABLE II  
Elastic constants of alkali halides

Substance	$r_0$	$c_{11}$	$c_{12}$	$c_{44}$
Lithium fluoride .. ..	2.01	11.9	5.38	5.34
Sodium chloride .. ..	2.81	4.97	1.27	1.27
Sodium bromide <sup>14</sup> .. ..	2.98	3.26	1.31	1.33
Sodium bromide .. ..	2.98	3.87	0.97	0.97
Potassium chloride <sup>14</sup> .. ..	3.14	3.69	0.81	0.79
Potassium bromide <sup>14</sup> .. ..	3.29	3.33	0.58	0.62
Potassium iodide <sup>14</sup> .. ..	3.53	2.67	0.43	0.42

The ions of the alkali halides all have completed outer shells of electrons of the rare gas configuration and as such there should be some sort of a regularity in their elastic properties.<sup>16</sup> As the interionic distance increases, the elastic resistance of the crystal decreases, that is, the elastic constant decreases. This fact is borne out by all the alkali halides excepting Bridgman's values for sodium bromide. However, with the values obtained in this laboratory in the place of Bridgman's values, the alkali halides show a regular gradation. Furthermore, these values are in better agreement with the theoretical values of Krishnan and Roy<sup>17</sup> ( $c_{11}=4.3$ ;  $c_{12}=1.0$  and  $c_{44}=1.0$ ). Also, sodium bromide and galena figure as exceptions in a paper by Kathleen Lonsdale<sup>18</sup> dealing with the vibration amplitudes of atoms in cubic crystals. For the rocksalt type of compounds it is observed that the largest amplitudes for pure longitudinal waves are associated with the cube diagonal which is also the direction of the largest atomic separation. This condition is satisfied by all NaCl type compounds except NaBr and PbS. However, the values obtained in this laboratory for both NaBr and PbS give largest amplitudes along the cube diagonal showing that these two substances do not behave in an exceptional manner. A similar conclusion is reached by a consideration of the amplitudes for transverse waves also.

The elastic constants of diamond<sup>9</sup> are of special interest and have been the subject-matter of much subsequent discussion. Voigt reported a negative value for  $c_{12}$  (negative Poisson's ratio) in the case of sodium chlorate and iron pyrites. Mason's<sup>19</sup> finding that this constant is positive for sodium



chlorate has been confirmed by us while the Poisson's ratio for iron pyrites is found to be negative. Two series of isomorphous substances have been studied, the nitrates of lead, barium and strontium and some alums. No definite conclusions are possible unless a larger number of isomorphous substances is studied. Although magnesium oxide is an ionic cubic crystal, it still remains as an extreme example for the breakdown of Cauchy's relation ( $c_{44}$  is nearly twice  $c_{12}$ ).

The elastic constants of mixed alums (Table III) show a regular gradation as the percentage composition of one of the components is varied. It can be seen that the bulk modulus  $K$  equal to  $(c_{11} + 2c_{12})/3$  decreases as the density increases.

TABLE III  
*Elastic constants of mixed alums*

Substance	Percentage in gm. of Pot. alum	Density	$c_{11}$	$c_{12}$	$c_{44}$	$K$
Potassium alum ..	100	1.760	2.56	1.07	0.86	1.567
Mixed alum ..	86.5	1.772	2.52	1.05	0.81	1.540
Do. ..	60	1.796	2.47	1.01	0.78	1.497
Do. ..	54.5	1.802	2.44	1.00	0.78	1.480
Chromium alum ..	0	1.845	2.37	0.93	0.77	1.410

Another type of mixed crystals studied is a set of naturally occurring garnets. Seven different specimens of garnets obtained from different sources in India have been studied and the results are given in Table IV.

It is seen from Table IV that the individual constants do not vary regularly with composition, but the bulk modulus varies more or less linearly with the ferrous content, which in almost all the cases happens to be the total iron content.

(b) *Other crystals.*—The elastic constants of crystals other than cubic are given in Tables V, VI and VII.

Dealing with physical properties and atomic arrangements in crystals, Wooster<sup>20</sup> has written a section on elastic properties and atomic arrangements in crystals. He has drawn up a table consisting of  $c_{11}$  and the hardness of

TABLE IV  
*Elastic constants of garnets*

No.	Density	Ferrous iron (in percentage)	$c_{11}$	$c_{12}$	$c_{44}$	K
1	3.759	21.8	19.7	9.0	5.7	12.6
2	3.673	22.7	19.2	9.9	5.9	13.0
3	3.630	23.6	21.0	10.3	6.7	13.9
4	3.670	23.0	22.2	10.4	7.0	14.3
5	3.750	26.2	22.6	12.6	6.2	16.0
6	4.130	28.7	27.3	15.7	6.8	19.6
7	4.320	33.5	32.7	12.4	8.9	19.2

TABLE V  
*Elastic constants of hexagonal and trigonal crystals*

No.	Substance	$c_{11}$	$c_{33}$	$c_{44}$	$c_{12}$	$c_{13}$	$c_{14}$
1	Calcite .. ..	13.74	8.01	3.42	4.40	4.50	-2.03
2	Sodium nitrate ..	8.67	3.74	2.13	1.63	1.60	0.82
3	Apatite .. ..	16.67	13.96	6.63	1.31	6.55	..
4	Quartz .. ..	8.69	10.68	5.76	0.69	1.56	1.74
5	Beryl (Spotted green)	27.81	24.8	6.61	10.01	6.77	..
6	Beryl (Sea green) ..	29.71	26.50	7.54	10.26	7.39	..
7	Alumina .. ..	46.6	50.6	23.5	12.7	11.7	9.4
8	Tourmaline (1) ..	26.3	15.1	5.95	6.1	4.9	-0.9
9	Tourmaline (2) ..	30.4	17.6	6.5	8.8	3.5	-0.4

TABLE VI  
*Elastic constants of orthorhombic crystals*

No.	Substance	$c_{11}$	$c_{22}$	$c_{33}$	$c_{44}$	$c_{55}$	$c_{66}$	$c_{12}$	$c_{13}$	$c_{23}$
1	Sodium tartrate	4.61	5.47	6.65	1.24	0.31	0.98	3.34	3.52	3.50
2	Rochelle salt ..	4.06	5.20	6.40	1.22	0.30	0.95	2.61	3.27	3.05
3	MgSO <sub>4</sub> ·7H <sub>2</sub> O	6.98	5.29	8.22	1.07	2.33	2.22	3.90	2.82	2.83
4	ZnSO <sub>4</sub> ·7H <sub>2</sub> O	4.00	3.22	5.45	0.50	1.70	1.81	1.32	1.08	1.19
5	Sulphur ..	2.40	2.05	4.83	0.43	0.87	0.76	1.33	1.71	1.59
6	Barytes ..	8.62	9.17	10.84	1.20	2.87	2.74	5.23	3.41	3.56
7	Celestite ..	10.44	10.61	12.86	1.35	2.79	2.66	7.73	6.05	6.19

TABLE VII  
*Elastic constants of a monoclinic crystal (Sodium Thiosulphate)*

$c_{11}=4.57$	$c_{44}=0.60$	$c_{12}=1.84$	$c_{16}=-0.69$
$c_{22}=3.31$	$c_{55}=0.57$	$c_{13}=1.68$	$c_{26}=0.25$
$c_{33}=3.02$	$c_{66}=1.11$	$c_{23}=1.83$	$c_{36}=1.04$
$c_{45}=-0.27$			

the corresponding crystal in order to obtain a rough idea of its variation. The crystals are arranged in the order of decreasing elastic constant and it is found that there is a rough correspondence between  $c_{11}$  of a crystal and its hardness. We can say that this general correspondence is true for all the crystals given in the above tables. He further goes on to explain that the value of  $c_{11}$  is determined by the tightness of the bonding between neighbouring atoms and the rate of variation with position of the atoms of the forces of attraction and repulsion between them. On the basis of this, he has given a qualitative interpretation for the magnitude of  $c_{11}$  for typical crystals like diamond, sulphur, iron pyrites and so on. Further, from a survey of the elastic properties another generalization he made is that where the atomic binding parallel to an axial direction is strong, the corresponding elastic constant is large. He has given a satisfactory explanation of the

relative magnitudes of  $c_{11}$  and  $c_{33}$  in terms of the structure of the crystals. It is obvious that while such qualitative observations are significant in their own way, there is much room here for quantitative theoretical work.

(c) *Polycrystalline aggregates*.—Table VIII shows the elastic constants of some artificially prepared polycrystalline aggregates.

TABLE VIII  
*Elastic constants of polycrystalline aggregates*

No.	Substance	$\rho_{crystal}$	$\rho_{tabloid}$	$(c'_{11})$		$(c'_{44})$	
				Mean	Av. calc.	Mean	Av. calc.
1	Potassium chloride	1.984	1.96	3.08	3.18	1.03	1.05
2	Sodium chloride ..	2.168	2.12	4.42	4.51	1.47	1.50
3	Ammonium chloride	1.527	1.50	3.09	3.17	1.01	1.04
4	Potassium bromide ..	2.756	2.67	2.43	2.73	0.81	0.92
5	Potassium iodide ..	3.127	2.95	1.64	2.11	0.57	0.70

In the case of the first three substances whose densities ( $\rho_{tabloid}$ ) lie within about 2 per cent. of the crystal density ( $\rho_{crystal}$ ), the measured average values of  $c'_{11}$  and  $c'_{44}$  are also lower than those calculated from single crystal constants by only about 2 to 3 per cent. In such cases, we may extrapolate the density and obtain the ideal elastic constant if required. On the other hand, in the case of potassium bromide and iodide where the densities are lower than the crystal densities by more than 3 per cent., the deviations in the average values of the elastic constants are disproportionately larger. In other words, the compressibility of a pressed specimen increases rapidly and out of proportion to the decrease in density, if we depart appreciably from the ideal densities. These results are in general agreement with those of Bridgman<sup>21</sup> and others.

#### 4. TEMPERATURE VARIATION OF ELASTIC MODULI

(a) *Single crystals*.—The composite oscillator method already described has been extensively employed in recent years by the author and his co-workers for studying the temperature variation of elastic moduli of single crystals. Nearly a dozen substances including some alkali halides have been

studied so far but only a few typical cases are being cited here. Full details will be published separately. The values of  $s$ 's are given in units of  $10^{-13}$  cm.<sup>2</sup>/dyne in all the tables. Sodium chloride, chosen as the test case, has been experimented upon first and the values obtained are in good agreement with those of Hunter and Siegel.<sup>22</sup>

Experimental results obtained with alkali halides reveal the following points regarding their thermal behaviour.

(1) The variation of  $s_{11}$  with temperature is greater than that of  $s_{44}$  in the alkali halides of the NaCl type.

(2) Contrary is the case with ammonium chloride as the change in  $s_{44}$  is greater than that in  $s_{11}$  in this case. Ammonium chloride has a structure which is of the CsCl type.

(3)  $s_{12}$  decreases with increasing temperature in the NaCl type halides. It increases with temperature in the case of ammonium chloride.

(4) Elastic constants  $c_{11}$ ,  $c_{12}$  and  $c_{44}$  all decrease with increasing temperature in all the cases.

Tables IX, X and XI give the results in the three specially interesting cases of iron pyrites, magnetite and sodium chlorate respectively.

TABLE IX

*Iron pyrites*

Temp. ° C.	$s_{11}$	$+s_{12}$	$s_{44}$
28	2.623	0.20	9.361
50	2.632	0.22	9.406
80	2.642	0.25	9.475
100	2.651	0.25	9.517
125	2.662	0.26	9.581
150	2.674	0.28	9.627
180	2.688	0.29	9.674
200	2.696	0.30	9.745
250	2.720	0.32	9.835
270	2.730	0.34	9.890
300	2.743	0.35	9.950

TABLE X

*Magnetite*Units =  $10^{11}$  dynes/cm.<sup>2</sup>

Temp. ° C.	$Y_{100}$	$n_{100}$
30	14.41	9.08
90	14.06	9.10
100	14.01	9.11
145	13.82	9.12
170	13.74	9.13
190	13.66	9.15
210	13.59	9.15
255	13.46	9.16

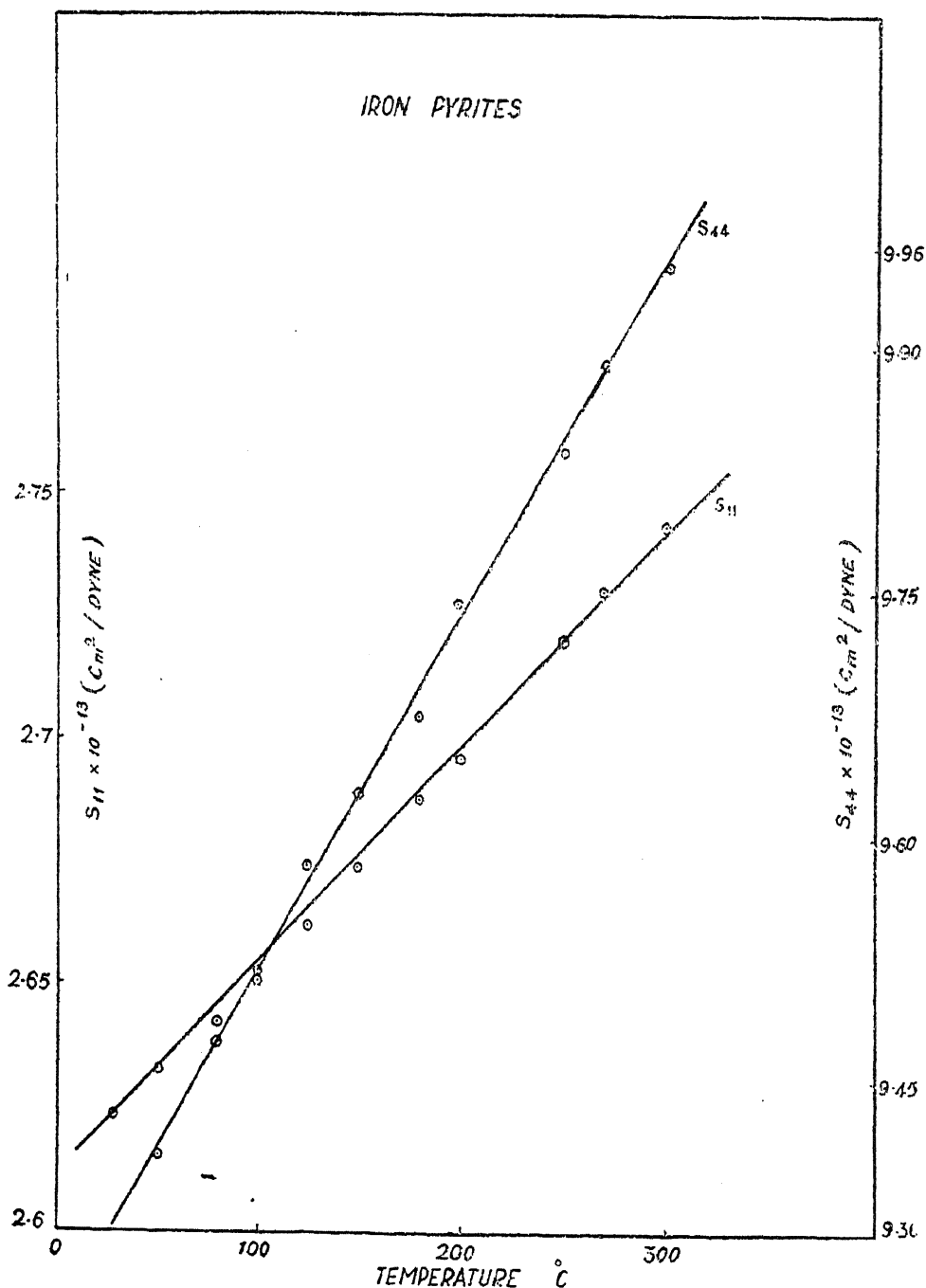
TABLE XI

*Sodium chlorate*

Temp. ° C.	$s_{11}$	$-s_{12}$	$s_{44}$
30	23.50	5.20	84.8
40	23.81	5.20	85.6
60	24.39	5.25	87.0
100	25.65	5.30	90.0
130	26.65	5.85	92.4
150	27.31	5.95	94.2
170	28.53	6.40	96.5
200	29.50	6.50	100.7
210	29.97	6.70	102.3
230	30.98	6.80	106.5
240	32.85	7.10	108.6
250	33.40	7.20	111.2

Iron pyrites is unique in exhibiting a negative Poisson's ratio (positive  $s_{12}$ ; see Table IX). The positive sign for  $s_{12}$  persists throughout the temperature range studied.  $s_{11}$  and  $s_{44}$  vary linearly with temperature (see Fig. 1) while  $s_{12}$  increases slightly. Rate of variation of the shear modulus  $s_{44}$  is larger than that of the bending modulus  $s_{11}$ .

Elastic constants of magnetite vary with temperature in an unusual manner (Table X). Usually elastic constants of crystals decrease with increasing temperature, provided there is no change of state. As can be seen from Fig. 2, Young's modulus along (100) direction decreases with temperature as usual, while the rigidity in the same direction increases. The



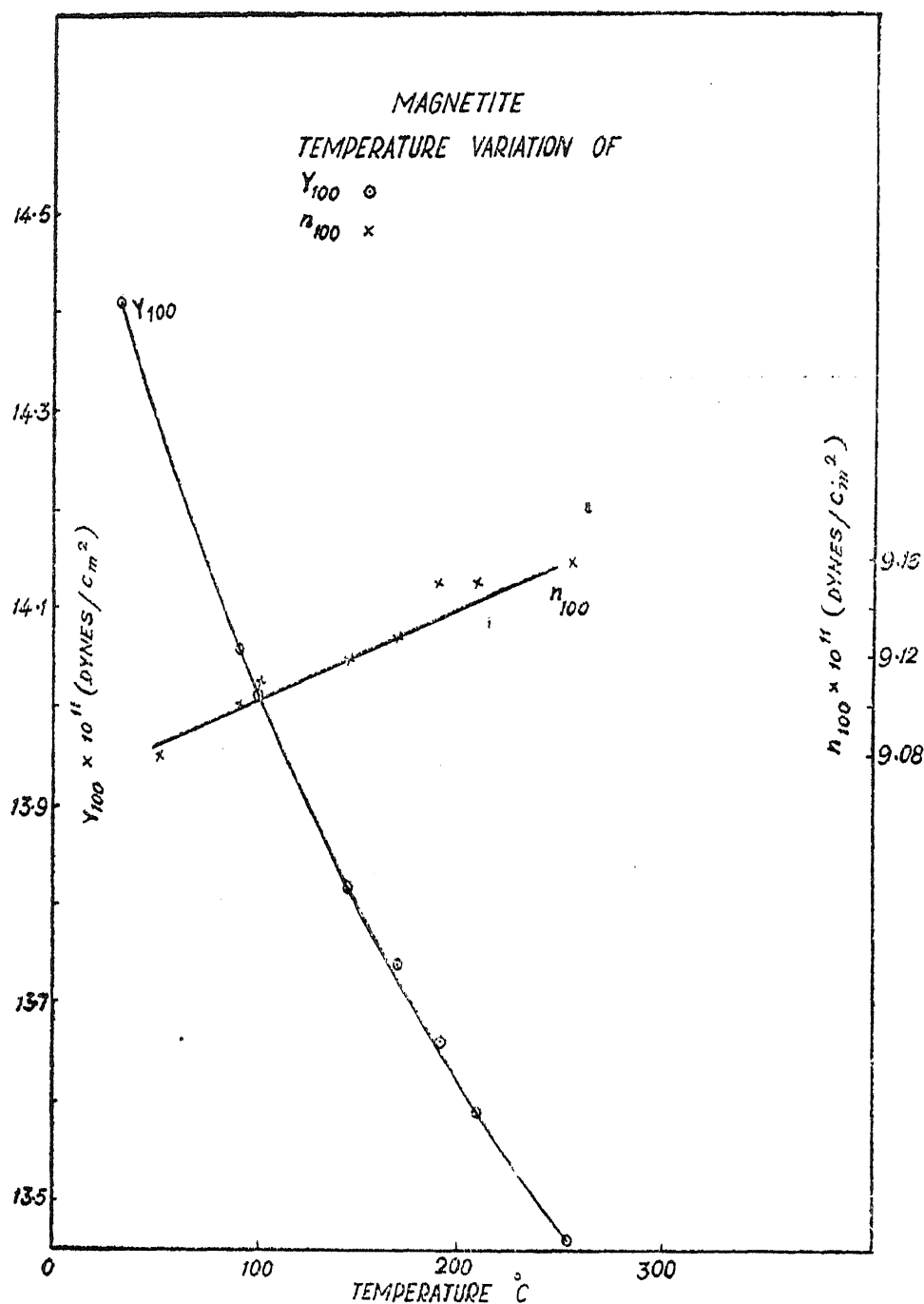


FIG. 2

increase is definite, though small. It has also been found that along (111) direction the behaviour is exactly the reverse. Rigidity decreases with temperature while the Young's modulus increases.\* Such an abnormal behaviour may be expected if the crystal undergoes some transition in the particular temperature range, but the region under study is far removed from its Curie point and the low temperature transition as well. Hence the results obtained are indeed likely to be of special significance.

\* Detailed results are not reproduced here.



A systematic study of the elastic properties of crystals in the vicinity of their melting points is bound to throw light on the mechanism of melting. The fact that sodium chlorate has no water of crystallisation together with the fact of its having a comparatively low melting point prompted a study of its elastic behaviour upto  $250^{\circ}\text{C}$ . (see Table XI).  $s_{11}$  varies linearly with temperature upto  $200^{\circ}\text{C}$ ., above which it varies rapidly and non-linearly (Fig. 3). The effect is more pronounced in the case of shear modulus,  $s_{44}$ , as one should expect it to

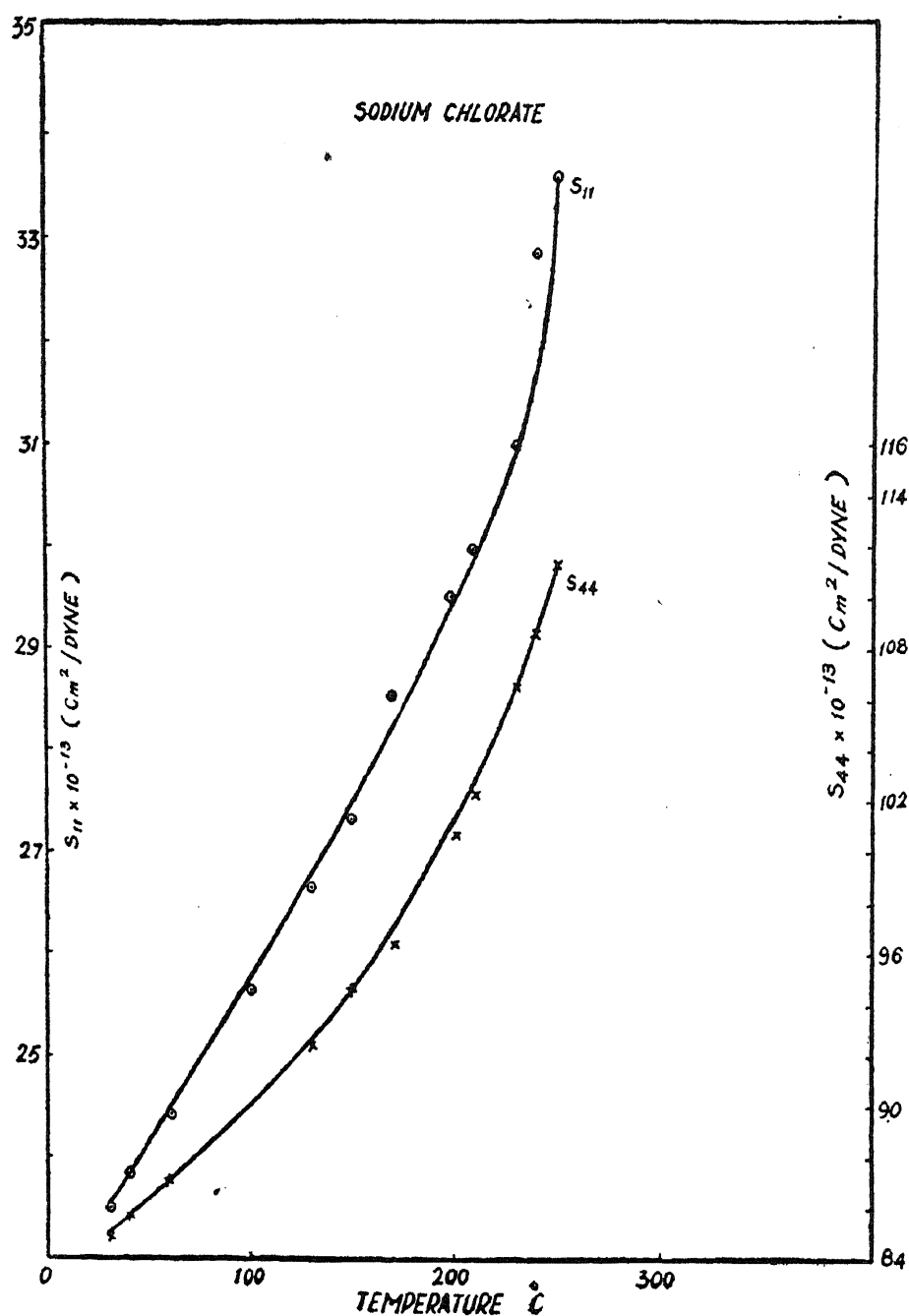


FIG. 3

be. These results afford confirmation of similar results reported earlier by Mason.<sup>19</sup>

(b) *Polycrystalline aggregates.*—The elastic properties of polycrystalline aggregates of a few alkali halides, namely, sodium chloride, potassium chloride, potassium bromide and ammonium chloride have also been studied at high temperatures. Results in one typical case are presented in Table XII.

TABLE XII  
*Polycrystalline sodium chloride*

Temp. ° C.	$(c'_{11})_{Av}$	
	Measured	Calculated
27	4.42	4.42
100	4.31	4.26
200	4.06	4.01
292	3.74	3.73

The measured values of  $(c'_{11})_{Av}$  compare well with those calculated from single crystal constants at different temperatures. In fact, in all the four cases studied, the thermal behaviour of the aggregate is in complete agreement with that calculated from the single crystal constants at different temperatures.

### 5. GENERAL REMARKS

From the standpoint of solid state physics with particular reference to the nature of interatomic and interionic forces in crystals, experimental studies of the elastic properties of single crystals do possess a great significance. Hitherto, though it has been possible to obtain data for quite a large number of single crystals at the room temperature, we have not had extensive work on their temperature variation reported in the literature. Methods developed and described in this article have enabled us to extend the investigations on elasticity into the region of higher temperatures and obtain useful and interesting results. Application of these methods to polycrystalline aggregates is expected to lead to a thorough understanding of the elastic behaviour of the rocks and the crust that constitute the earth at different depths thus possessing different temperatures. It is earnestly hoped that the data presented here as well as the results of the work that is still under progress will ultimately help in the construction of a full and coherent picture of the crystalline forces as well.

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