

Review

Consistency checks on elastic properties of crystals

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Several methods are available for the determination of the bulk modulus of solids and single crystal elastic constants. Although high accuracy is claimed, cases exist where the values of the elastic properties reported by different workers using different or same methods show differences far beyond the claimed limits of experimental errors. More than two dozen cases are cited where the differences in the reported values of the bulk moduli are of the order of 20% or more; in some cases the differences are as much as a factor of 3–5. Similarly, nearly a dozen cases are cited where the single crystal elastic constants of a crystal from different sources differ by about 20% or more and in some cases by a factor of 3–15; in fact there are cases where the reported elastic constants even differ in sign. This paper discusses a number of consistency checks for elastic properties of solids which help in sifting acceptable values from out of a wide range of reported values.

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Nomenclature

A	Mean atomic weight
α_M	Madelung constant
a	Lattice constant
α	Linear coefficient of thermal expansion
B	Bulk modulus
C_{ij}	Elastic constants
C_V	Specific heat at constant volume
e	Electronic charge
ϵ_0	Static dielectric constant
f_i	Phillips ionicity
γ	Grüneisen constant
H	Hardness
k	Interatomic force constant
N_0	Avogadro number
G	Shear modulus
m	Mass
μ	Reduced mass
n	Refractive index
θ	Debye temperature
r	Interatomic distance
P	Pressure
ρ	density
S_{ij}	Elastic compliances
σ_P	Poisson's ratio
σ	Surface energy
u	Volume per ion pair
u_p	Particle velocity
u_{fs}	Free surface velocity
v, v_{ij}	Velocities of sound waves

U	Cohesive energy
U_S	Shock wave velocity
V	Molar volume
V_c	Unit cell volume
V_a	Atomic volume
ω_w	Transverse angular frequency
ψ	Compressibility
Y	Young's modulus
z	Valence
Z	Atomic number

1. Introduction

The elastic properties of solids have a two-fold importance. Firstly, they are indicators of mechanical strength which is a matter of great practical significance. Secondly, on the scientific side, the elastic properties are inputs for determination of interatomic potential parameters and lattice dynamical calculations. When measured at high pressures, they provide information regarding the anharmonicity of the lattice. In view of this importance, a vast amount of information is now available on the elastic properties of solids. This information is scattered in various scientific journals. Exclusive compilations of data on elastic properties of solids have also been published [1–7].

Several experimental techniques are available for the determination of elastic properties. Some commonly employed techniques will be discussed in Section 2 along with a mention of their limitations and uncertainties in the results obtained from them. Some of the

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techniques yield isothermal data whereas others yield adiabatic values. The isothermal and adiabatic values are mutually convertible by a thermodynamic correction. The difference between the two is in the range 0.5–2%. The uncertainties claimed in the reported elastic properties are generally about 5% but sometimes as much as 10%.

In Table I, we include values of bulk moduli at zero (or atmospheric) pressure. It can be seen that in several cases the differences in bulk moduli are of the order of 20% or more and in some cases they are as much as a factor of 3–5. In Tables II–IV, we quote data on single crystal elastic constants of some cubic, tetragonal, trigonal and hexagonal crystals. Here again the single crystal elastic constants differ by about 20% and in some cases by a factor of 3–15. In fact, there are cases where the elastic constants from different sources even differ in sign.

It may be mentioned that the list of crystals showing differences in reported elastic properties given in Tables I–IV is not an exhaustive list. Further such conflicting data have been included in some compilations without any comments. Thus Simmons and Wang [7] call their compilation ‘uncritical’ and mention the inclusion of ‘suspect elastic data’ leaving it to the reader to ‘choose the set which he believes better’.

These differences far exceed the admitted limits of uncertainty. When data differing so severely exist in literature, it becomes necessary to analyze them with a view to sifting the correct (or acceptable) data from the incorrect (or unacceptable). The purpose of this article is to review consistency checks for elastic properties of solids.

2. Experimental methods

For the sake of completeness, some of the commonly used experimental methods are briefly discussed in this section. For more details, reference may be made to the cited literature.

2.1. Piston displacement method

As the name suggests, in this method the sample is directly compressed by a piston or is enclosed in a medium which is compressed by a piston. The method was originally introduced by Bridgman [8, 9] and later developed by Weir [10], Stephens [11] and Vaidya and Kennedy [12] among others.

As a typical example, the arrangement used by Vaidya and Kennedy [12] is shown in Figs 1 and 2. Only the important parts are described here. *X* is the sample held between the piston *P* and a fixed tungsten carbide element *O*. The piston is driven by the hydraulic ram *M*. The pressure vessel *C* is made of tungsten carbide. The sample is covered by an indium sheath and the space between the sample and pressure vessel is filled with pyrophyllite. The compression seen as a relative displacement between the lever arms *W* and *H*, is measured by the dial gauges *G*.

The observed total compression has significant contributions from the compression of the press and the compression of the indium sheath. The ratio of these

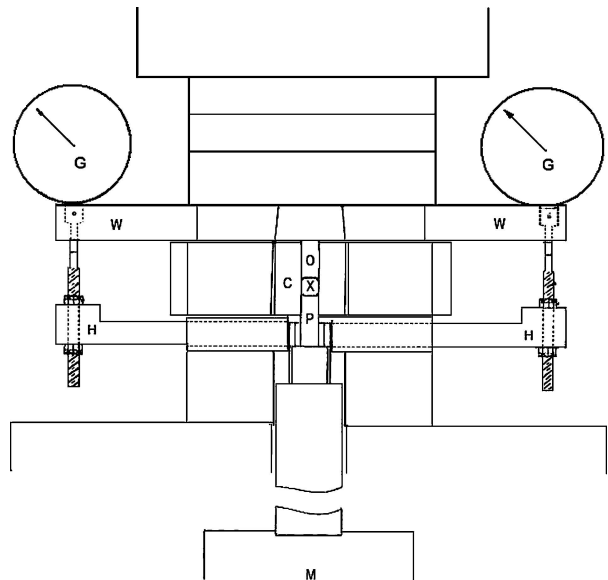


Figure 1 Schematic diagram of the piston displacement set-up.

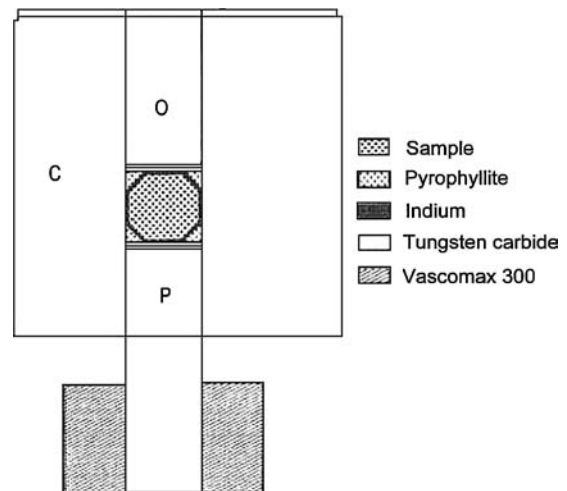


Figure 2 Details of the sample assembly in the piston displacement set-up.

contributions and the sample compression have to be optimized. In Bridgman’s experiments, the corrections were 75% of the total compression whereas they were reduced by half in the set-up of Vaidya and Kennedy [12]. Care has to be taken to minimize the effects of (i) distortion of the press (ii) horizontal fracture of the pressure vessel and (iii) friction between the piston and the pressure vessel walls.

This is a static method which gives isothermal values of the bulk moduli.

2.2. Shock wave method

In this method an explosive is detonated in an enclosed space. This results in the production of a shock wave. Either this shock wave is made to directly impinge on a sample or a projectile propelled by the shock wave is directed on to the sample. The shock wave velocity (U_s) and the particle velocity (u_p) are measured by recording the time of arrival of the waves at different designated points where electrical pin contactors are located. Whereas the shock wave velocity can be determined in a straight-forward way, the particle velocity

TABLE I Bulk moduli (B) of some solids

	Solid	Method	B (kbars)	Ref.
1.	C (Diamond)	(i) Ultrasonics	5800	Bhagavantam and Bhimasenachar [13]
		(ii) Doppler scattering	4170	Krishnan <i>et al.</i> [14]
		(iii) Ultrasonics	4430	McSkimin <i>et al.</i> [15]
2.	Si	(i) Piston displacement	3120	Int. Crit. Tables [16]
		(ii) Ultrasonics	971	Bolef [17]
		(iii) Piston displacement	814	Bridgman: data reanalysed by Kennedy [18]
		(iv) Piston displacement	1007	Vaidya and Kennedy [19]
3.	Iodine	(i) Piston displacement	87.03	Vaidya and Kennedy [19]
		(ii) Shockwave	98.04	Keeler [20]
		(iii) Piston displacement	76.92	Quoted by Gruneisen [21]
		(iv) X-ray diffraction	208.33	Lynch and Drickamer [22]
4.	Se (hex.)	(i) Piston displacement	92.7	Bridgman: quoted by Gschneidner [23]
		(ii) Piston displacement	79	Vaidya and Kennedy [19]
		(iii) Ultrasonics	174	Calculated by Sirdeshmukh and Subhadra [24] from Mort [25]
5.	Sb	(i) Piston displacement	369	Bridgman: data reanalysed by Kennedy [18]
		(ii) Piston displacement	404	Vaidya and Kennedy [19]
		(iii) Shockwave	255	Keeler [20]
		(iv) Ultrasonics	380	Epstein and Bretterville [26]
6.	Zr	(i) Piston displacement	755	Bridgman: data reanalysed by Kennedy [18]
		(ii) Piston displacement	1028	Vaidya and Kennedy [19]
		(iii) Shockwave	976	Keeler [20]
		(iv) Ultrasonics	945	Myers [27]
7.	Y	(i) Piston displacement	337	Bridgman: data reanalysed by Kennedy [18]
		(ii) Piston displacement	449	Vaidya and Kennedy [19]
		(iii) Shockwave	455	Keeler [20]
		(iv) Ultrasonics	491	Smith [28]
8.	LiH	(i) Piston displacement	270	Well and Lawson [29]
		(ii) Piston displacement	228	Voronov <i>et al.</i> [30]
		(iii) Piston displacement	357	Stephens and Lilley [31]
9.	LiI	(i) Piston displacement	168.3	Vaidya and Kennedy [32], Murnaghan Equation
		(ii) Piston displacement	135.4	Vaidya and Kennedy [32]; Modified Murnaghan Equation
		(iii) Shockwave	333	Keeler [20]
		(iv) Ultrasonics	171	Quoted in Sirdeshmukh <i>et al.</i> [33]
10.	NaI	(i) Piston displacement	156	Bridgman: data reanalysed by Kennedy [18]
		(ii) Piston displacement	151	Vaidya and Kennedy [32]
		(iii) Shockwave	200	Keeler [20]
		(iv) Ultrasonics	151	Quoted in Sirdeshmukh <i>et al.</i> [33]
11.	CsBr	(i) Piston displacement	144	Vaidya and Kennedy [32]
		(ii) Shockwave	221.8	Keeler [20]
		(iii) Ultrasonics	145.0	Barsch and Chang [34]
12.	AgI	(i) Piston displacement	20.1	Bridgman: data reanalysed by Kennedy [18]
		(ii) Piston displacement	28.5	Vaidya and Kennedy [32]
13.	CaO	(i) Piston displacement	218	Bridgman [35]
		(ii) Piston displacement	1120	Weir [10]
		(iii) X-ray	1120	Perez-Albuerne and Drickamer [36]
		(iv) Ultrasonics	1090	Hite and Kearney [37]
14.	CaS	(i) Piston displacement	357	Bridgman: quoted by Mathur <i>et al.</i> [38]
		(ii) X-ray	455	Perez-Albuerne and Drickamer [36]
		(iii) X-ray	699	Reanalysis of low pressure data in [36] by present authors
15.	SrO	(i) Piston displacement	1183	Weir [10]
		(ii) Ultrasonics	880	Son and Bartels [39]
16.	CeS	(i) Piston displacement	1300	Croft and Jayaraman [40]
		(ii) X-ray	820	Vedel <i>et al.</i> [41]
17.	SmS	(i) Piston displacement	151	Chatterjee <i>et al.</i> [42]
		(ii) X-ray	476	Kaldis and Wachter [43]
		(iii) Ultrasonics	503	Hailing <i>et al.</i> [44]
18.	ZnO	(i) Piston displacement	450	Cline and Stephens [45]
		(ii) Ultrasonics	1399	Soga and Anderson [46]
		(iii) Ultrasonics	1436	Bateman [47]
		(iv) Optical interferometry	1447	Montalvo and Langer [48]
19.	BeO	(i) Piston displacement	3704	Weir [10]
		(ii) Piston displacement	2433	Cline and Stephens [45]
		(iii) Ultrasonics	2198	Bentle [49]
		(iv) Ultrasonics	2140	Fryxell and Chandler [50]
20.	CdS	(i) Piston displacement	380	Cline and Stephens [45]
		(ii) Ultrasonics	615	Berlincourt <i>et al.</i> [51]
21.	CdSe	(i) Piston displacement	281	Cline and Stephens [45]
		(ii) Ultrasonics	532	Berlincourt <i>et al.</i> [51]

(Continued.)

TABLE I Continued.

	Solid	Method	B (kbars)	Ref.
21.	CdSe	(i) Piston displacement	281	Cline and Stephens [45]
		(ii) Ultrasonics	532	Berlincourt <i>et al.</i> [51]
22.	MnF ₂	(i) Piston displacement	184	Stevenson [52]
		(ii) Ultrasonics	883	Haussuhl [53]
23.	GeO ₂ (Rutile)	(i) Ultrasonics	1950	Soga [54]
		(ii) Ultrasonics	2576	Wang and Simmons [55]
24.	Stishovite (SiO ₂ , rutile)	(i) Piston displacement	3600	Arhens <i>et al.</i> [56]
		(ii) Piston displacement	3000	Arhens <i>et al.</i> [57]
25.	Magnetite	(i) Piston displacement	1830	Bridgman [58]
		(ii) Ultrasonics	1590	Doraiswamy [59]
		(iii) Ultrasonics	1390	Simmons and England [60]
		(iv) X-ray	1830	Mao <i>et al.</i> [61]
26.	Benzil	(i) Piston displacement	30.7	Bridgman [62]
		(ii) Piston displacement	66.5	Vaidya and Kennedy [63]

TABLE II Elastic constants (C_{ij} in kbar), bulk modulus B (kbar) and Poisson's ratio (σ) of some cubic crystals

S. no.	Crystal	C_{11}	C_{12}	C_{44}	B	σ	Source
1.	FeS ₂ (Pyrite)	(i) 3585	-529	1035	842	-0.17	Hearmon [2]
		(ii) 3818	310	1094	1479	0.07	Simmons and Birch [64]
2.	Sodium chlorate	(i) 618.2	-208.3	119.6	67	-0.50	Hearmon [1]
		(ii) 509	155	118	273	0.23	Alexandrov and Ryzhova [6]
3.	PbTe	(i) 1040	-44	130	317	-0.04	Chudinov [65]
		(ii) 1080	80	130	413	0.07	Houston <i>et al.</i> [66]
4.	PbSe	(i) 4040	3190	162	3473	0.44	Chudinov [67]
		(ii) 1130	150	130	477	0.11	Rabi [68]
		(iii) 1240	190	160	540	0.13	Lippmann <i>et al.</i> [69]

TABLE III Elastic constants (C_{ij} in kbar) and bulk modulus B (kbar) for some tetragonal crystals

S. no	Crystal	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	C_{16}	B	Source
1.	Zircon (ZrSiO ₄)	(i) 570	250	50	460	140	320		190	Bhimasenachar and Venkataratnam [70]
		(ii) 3300	1075	1540	3805	733	397		2040	Rhyzova <i>et al.</i> [71]
		(iii) 4230	703	1490	4900	1136	485		2030	Ozkan <i>et al.</i> [72]
2.	ADP	(i) 676	59	199	336	87	66		2820	Adhav [73]
		(ii) 758	-243	133	296	87	61		2060	Huntington [5]
3.	KDP	(i) 714	-49	129	562	127	63		2680	Huntington [5]
		(ii) 785	320	387	763	123	61		5020	Huntington [5]
4.	SrMoO ₄	(i) 1275	886	501	1034	347	213	40		Chung and Li [74]
			213	-2400				1275	-40	
			665	-490				823	+527	
			823	-989				665	-527	
		(ii) 1154	599	444	1042	350	475	121		James [75]
		(iii) 1190	620	480	1040	349	420	-120		Farley <i>et al.</i> [76]

TABLE IV Elastic constants (C_{ij} in kbar), elastic compliances (S_{ij} in kbar⁻¹), bulk modulus B (kbar) and Debye temperature (θ K) for some hexagonal and trigonal crystals

S. no.	Crystal	S_{11}	$-S_{12}$	$-S_{13}$	$2S_{14}$	S_{33}	$4S_{44}$	B	θ	Source
1.	Calcite (trigonal)	(i) 0.00103	0.00035	0.00080	0.0012	0.00175	0.0038	-6300		Ramamurthy and Reddy [77]
		(ii) 0.00100	0.00038	0.00048	0.0009	0.00175	0.0041	700		Dandekar and Ruoff [78]
		C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	B	θ	Source
2.	BeO (hex.)	(i) 4700	1680	1190	4940	1530	1520	2495	1260	Bentle [49]
		(ii) 4606	1265	885	4916	1477	1670	2244	1280	Cline <i>et al.</i> [79]
3.	LaCl ₃ (hex.)	(i) 3065	1238	1653	3611	1677	913	2050	600	Stedman and Newman [80]
		(ii) 2585	1670	1517	3419	1731	458	1979	500	Stedman and Newman [80]
		(iii) 2952	1564	1607	3648	1742	694	2100	507	Stedman and Newman [80]
		(iv) 190	80	100	230	100	60	128	~150	Carlson <i>et al.</i> [81]

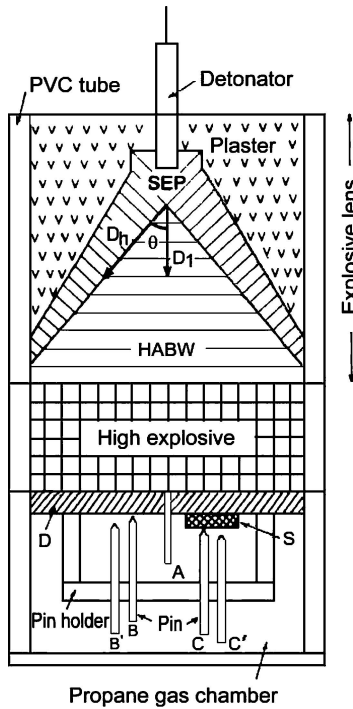


Figure 3 Schematic diagram of a shock-wave set-up.

has to be obtained from the free surface velocity (u_{fs}). A typical arrangement (Syono *et al.* [82]) is shown in Fig. 3, which is self-explanatory. The working equations are:

$$\rho_0 U_S = \rho_1 (U_S - u_p) \quad (1)$$

$$P_1 - P_0 = \rho_0 U_S u_p \quad (2)$$

where ρ is the density, P the pressure, U_S the shock velocity and u_p the particle velocity; $u_p = u_{fs}/2$ approximately. The subscripts 0 and 1 refer to the compression state ahead of the shock and the state immediately behind the shock front respectively. The procedure for transforming the experimental velocities to pressure-compression data is discussed in detail by Rice *et al.* [83]. The P - V plot thus obtained is called the ‘‘Hugoniot’’; from the Hugoniot, the bulk modulus can be calculated. Further details are given by Goranson *et al.* [84]; Mallory [85], Rice *et al.* [83] and Syono *et al.* [82].

This method is capable of, by far, the greatest pressure range, up to 2 Mbar (Drickamer *et al.* [86]). It is a dynamic method. It is found that, in general, the compatibility of static (piston displacement) and shock wave results is good (Rice *et al.* [83]; Vaidya and Kennedy [12]). The method yields essentially isothermal values.

2.3. X-ray diffraction method

When the X-ray diffraction pattern is recorded at different pressures, the Bragg angles change. From this, the changes in lattice parameters can be calculated. This information, in turn, leads to the evaluation of the linear compressibilities and finally to the bulk modulus. The method yields isothermal values of elastic properties.

The pressure is applied through a pressure medium or, more commonly, by means of a diamond or tungsten

carbide anvil. The sample may be a single crystal or in powder form. Both film-and-camera arrangements as well as diffractometer can be used replacing the common specimen holder by a pressure cell. While X-ray radiation is commonly employed, Bartholin *et al.* [87] used neutrons and Will *et al.* [88] used synchrotron radiation.

Considerable work on determination of compressional data by the X-ray diffraction method has been done by Perez-Albuern *et al.* [89], Jamieson [90], McWhan and Jayaraman [91], Barnett and Hall [92] and Takahashi and Bassette [93].

One advantage in this method is that a small sample is required. Another unique advantage is that in a single experiment, linear compression can be studied in different directions. A common problem in high pressure work is that the pressure experienced by the sample is not necessarily the same as the applied pressure. In the X-ray diffraction method, this problem is overcome by using a ‘marker’ or an internal standard. On the other hand, the application of the method is limited by the use of Mo radiation which causes fluorescence in some materials. Also, the short wavelength of the Mo radiation limits the accuracy with which the lattice parameters can be evaluated. Leger *et al.* [94] refer to the effect of uniaxial stresses on the results. Vaidya and Kennedy [12] consider the X-ray method to be of ‘‘extremely poor precision’’.

2.4. Optical interferometric method

Optical interferometry has also been employed to determine the linear compressibilities and, from them, the bulk modulus. The optical interferometer, the sample holder and the schematic diagram of the set-up used by Montalvo and Langer [48] are shown in Figs 4 and 5.

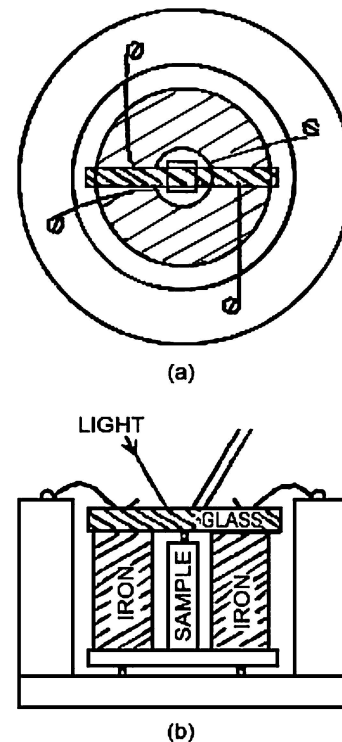


Figure 4 Optical interferometer (a) view from above, (b) view from side.

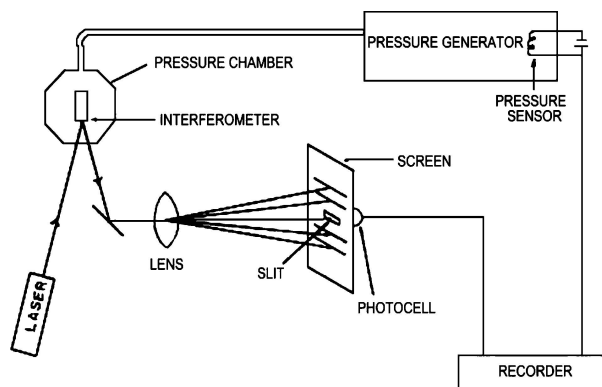


Figure 5 Schematic diagram of the optical method.

The interferometer consists of a glass plate resting over the surface of an iron cylinder. The sample with a flat face was held in the annular space of the iron cylinder. The incident light beam from a He-Ne laser was reflected from the lower surface of the glass plate and the top surface of the sample. The whole interferometer was placed in a pressure vessel containing isopentane as the pressure fluid. The interference fringes were sensed by a photocell coupled to a recorder. The experimental procedure was to count the fringes as the pressure changed from 1 to 10 kbar.

The optical interferometric measurements yield isothermal values of compressibilities and bulk modulus. Montalvo and Langer [48] used this method to determine the linear compressibilities of several II-VI compound crystals and claimed an accuracy of 1%. However several of their values differ from accurate ultrasonic values by amounts larger than this value and also the isothermal-adiabatic conversion correction. Factors like the errors in the value of the compressibility of iron used in the calculations, the change in refractive index of the pressure fluid with pressure change and relative motion between glass and sample surfaces contribute to the final uncertainty in the results.

2.5. Ultrasonic method

The measurement of velocity of ultrasonic waves is a popular method for determination of elastic constants of crystals. The sound velocity in a crystal is a function of the elastic constants. For example, for cubic crystals, we have

$$\rho v^2 = (C_{11} - C_{12})/2 \quad (3)$$

where ρ is the density, C_{11} and C_{12} are two of the three elastic constants and v is the velocity of a sound wave propagating in the [110] direction with particle displacement in the [1 $\bar{1}$ 0] direction. There are similar equations for other combinations of elastic constants and also for the elastic constants of crystals of other symmetries. Relations between velocities and elastic constants for hexagonal and tetragonal crystals are given by Cline *et al.* [79] and Farley and Saunders [95] respectively.

The composite oscillator method for determination of elastic constants was developed by Balamuth [96], Rose [97] and Bhagavantam and Bhimasenachar [98].

Huntington [99], Williams and Lamb [100] and McSkimin [101] employed different versions of the pulse method.

In the pulse comparison technique of Williams and Lamb [100] which was further modified by Raju and Reddy [102], two phase-coherent RF pulses are applied in quick succession to the transducer attached to the crystal surface. On transmitting through the sample, each pulse will generate its own train of echoes. When the separation of the second pulse is adjusted such that the echoes from the two coincide, destructive interference occurs successively at a number of frequencies. From a knowledge of these null frequencies and the thickness of the sample, the ultrasonic velocity can be estimated.

Other technical details of the method are given by Bente [49], Cline *et al.* [79], Chung *et al.* [103] and McSkimin *et al.* [15]. While the electronics is capable of measurement with high accuracy, various factors like the characteristics of the bonding material, the accuracy of measurement of thickness and the accuracy of orientation of the sample introduce errors.

The ultrasonic method yields adiabatic values of elastic constants. It is by far the only method that gives elastic constants of single crystals. From the single crystal elastic constants, the isotropic bulk and shear moduli can be computed. Alternatively, the ultrasonic method can be used to find the sound velocities in polycrystalline samples from which the elastic moduli can be determined. In this method, very often a density correction has to be applied as the polycrystalline samples may not be packed to crystal density.

The ultrasonic method is by far the most accurate. To cite an example, Bateman [47] has reported the elastic constants of ZnO with an accuracy of 0.1%.

2.6. Other methods

For the sake of completeness, we shall mention a few other methods. Though these methods have not been used very frequently, they have been employed to study some crystals for which data are in conflict.

(i) *Ultrasonic-optic method*: In this method, a transparent crystal is excited into resonant vibration by a quartz plate. The result is that the crystal acts like a 3-d diffraction grating with respect to optical light. From the diffraction pattern, orientation of the crystal, crystal density and the resonant frequency, the elastic constants are evaluated. This is known as the Schaefer-Bergmann [104] method.

(ii) *Optical scattering method*: A method based on frequency shifts of the Brillouin components appearing in the thermal scattering of light has been developed by Krishnan [105] to determine the elastic constants.

(iii) *X-ray diffuse scattering method*: Ramachandran and Wooster [106, 107] developed a method for determining the elastic constants of crystals from observations on the thermal diffuse scattering of X-rays. They used the method to determine the elastic constants of diamond, sodium chlorate and iron pyrites among other crystals.

2.7. Relative merits and limitations

The piston-displacement method, the shock wave method and the X-ray diffraction methods are commonly employed for determination of bulk moduli whereas the ultrasonic method is used mostly to determine the single crystal elastic constants.

Bridgman was the pioneer in the development of the piston displacement method. He was continuously refining his equipment and procedure from the nineteen twenties through forties. At a certain stage, Bridgman himself revised his earlier data by 10–20% (Grover *et al.* [108]). Vaidya and Kennedy [12] call Bridgman's results 'remarkably discordant'. As mentioned in Section 2.1, several factors related to the high pressure assembly need care and correction. Vaidya and Kennedy [12] claim that their own set-up and method are 3–10 times more precise than other methods.

Rice *et al.* [83] estimate an error of 0.7–3% in compression data obtained from shock-wave method. The shock-wave data has been found to be consistent with piston-displacement data (Vaidya and Kennedy [12]) as well as X-ray diffraction data (Drickamer *et al.* [86]). However, Drickamer *et al.* [86] refer to the requirement of a large number of corrections to the shock-wave results. Actually, several entries in Table I from shock-wave data were found to be not the best.

The ultrasonic techniques are highly accurate but they have in some cases led to dubious results. There are also intrinsic analytical difficulties in retrieving elastic constant data from velocity data, particularly with regard to lower symmetry crystals.

3. Consistency checks for bulk moduli

Some consistency checks for bulk moduli are discussed in this section. These are categorized as (1) phenomenological relations (2) theoretical consistency checks and (3) empirical relations as consistency checks.

3.1. Phenomenological relations as consistency checks

(a) Relations between elastic moduli

The bulk modulus (B), Young's modulus (Y), shear modulus (G) and the Poisson's ratio (σ_P) are interrelated as follows:

$$Y = 2G(1 + \sigma_P) \quad (4)$$

$$B = Y/[3(1 - 2\sigma_P)] \quad (5)$$

$$\sigma_P = \frac{1}{2} - (Y/6B) \quad (6)$$

The following features may be noted.

- (i) If any two parameters are known, the other two can be calculated and checked with experimental values.
- (ii) The elastic moduli are all positive.
- (iii) The Poisson's ratio is positive. Further, from Equation 6, it follows that $0 < \sigma_P < 0.5$. Empirically, σ_P is found to be close to 0.3 for most solids.

As an example of the use of phenomenological relations as consistency checks, we shall consider the bulk modulus of selenium. Gschneidner [23] quoted literature values of 591 kbar and 92.7 kbar for the Young's modulus and the bulk modulus; the bulk modulus was from Bridgman's work. Substituting these values in Equation 6, one gets a value of -0.562 for σ_P which is physically unacceptable in view of (iii) above and indicates an error in the value of Y/B . Since the value of Y is reasonable from various considerations, Gschneidner concluded that there is an error in Bridgman's value for B for Se, which should have been much larger. Subsequently, Mort [25] reported single crystal elastic constants of Se from which Sirdeshmukh and Subhadra [24] calculated the isotropic elastic moduli and obtained the following values:

$$B = 174 \text{ kbar}$$

$$Y = 234 \text{ kbar}$$

$$\sigma_P = 0.27$$

This value of B is much larger than the Bridgman value. Further, σ_P is +ve and close to 0.3. Thus these values are phenomenologically consistent. The much lower value of 92.7 kbar quoted from Bridgman's work for the bulk modulus of Se (hex.) has to be ignored and the ultrasonic value of 174 kbar is recommended.

It may be mentioned that values for B of Se larger than that reported by Bridgman were predicted by Gschneidner [23] from an empirical relation between B and the cohesive energy and by Sirdeshmukh [109] by using a theoretical method; these will be discussed later in this section. It may be also mentioned that a value of 79 kbar reported later by Vaidya and Kennedy [19] is much lower than Bridgman's value and open to the same criticism as Bridgman's value.

It is to be noted that the condition that σ_P cannot be negative is useful only in finding whether the B value is physically valid or not. At best, it helps in estimating a lower bound for B but it cannot estimate, by itself, the correct value of B .

We may have occasion to refer to the Poisson's ratio again in Section 4.

(b) Relations between elastic constants

The quadratic stress (or strain) energy is positive definite. This condition results in interrelationships between the single crystal elastic constants. These have been discussed by Sundara Rao [110], Born and Huang [111], Nye [112], Alers and Neighbours [113] and Alton and Barlow [114] for various crystal classes. We shall refer to these relationships in analyzing data on some crystals in Section 3.2(d)(iii) and in Section 4.

3.2. Theoretical consistency checks

The bulk modulus may be calculated by theoretical methods and the calculated value may be compared with the experimental values. Alternatively, the experimental bulk modulus may be used to calculate other

physical properties theoretically and these calculated properties may then be compared with their respective experimental values. Some approaches of this type are discussed below.

(a) Knopoff's universal relation

By an interpolation of the equations of state obtained from the finite strain theory and the Thomas-Fermi model, Knopoff [115] derived an expression for the bulk modulus B of a solid in terms of the atomic volume (V_a), atomic number (Z) and some universal constants. The relation is:

$$[BZ^{-10/3}][ZV_a]^{7/3} = [\pi^{10/3}6^{2/3}/15]a_0^3 e^2 = 34.17 \text{ Mbar } \text{\AA}^7 \quad (7)$$

For compounds, V_a is the mean atomic volume and Z is given by

$$Z^{2/3} = \frac{\sum_i n_i Z_i^{5/3}}{\sum_i n_i Z_i} \quad (8)$$

where n_i is the number of times an atom i with atomic number Z_i occurs in the chemical formula.

The various reported values of B for selenium are given in Table I. Since Gschneidner [23] had expressed doubts regarding the soundness of the Bridgman value on the basis of the “+ve σ_P criterion”, Sirdeshmukh [116] applied Knopoff's method to estimate the bulk moduli of some elemental solids including selenium. These calculated values are given in Table V along with experimental values quoted by Gschneidner [23]. It is seen that agreement between experimental and calculated values is good in the case of Zr and W but otherwise there are differences of as much as 30–50% in other cases. The largest difference occurs in the case of selenium. The calculated value of 526 kbar is much larger than Bridgman's value of 92 kbar. Further, the calculated value combined with the Young's modulus value quoted by Gschneidner yields a value of 0.3 for the Poisson's ratio.

However, as mentioned in Section 3.1, later determination of elastic constants of Se has led to a consistent set of elastic moduli which yield a value of 174 kbar for the bulk modulus and a Poisson's ratio value of 0.27. In view of the high accuracy of ultrasonic results, we have to infer that the value obtained from Knopoff's relation is an overestimate.

TABLE V Values of B for some elemental solids

Element	B (kbar)	
	Calc. from Equation 7	Expt.
Al	645	735
Ti	709	1075
Mg	270	361
Zr	901	850
W	4000	3333
Li	80	118
Se	526	92.7

Knopoff's method is used to analyse the data on MnF_2 and Fe_3O_4 . Values of 90 kbars and 2800 kbars respectively are obtained for the bulk modulus of these two compound crystals. It is found that the value for MnF_2 is lower than both the values given in Table I but between the two values, it is closer to the piston displacement value. In the case of magnetite, the Knopoff value is much higher than all the values quoted in Table I but is closer to the piston displacement and X-ray values.

Knopoff's method is simple and universal; it is independent of bonding and structure. Yet, in view of the cases discussed above, we may conclude that Knopoff's method may be used to provide corroborative rather than conclusive evidence.

(b) Bulk modulus from molecular data

From simple considerations, it can be shown that there is a direct relation between the bulk modulus (B) and the interatomic force constant (k). Waser and Pauling [117] showed that that

$$B = (Nr^2/9V_c)k \quad (9)$$

where N is the number of equivalent bonds. Yean and Riter [118] proposed an equivalent relation:

$$B = (2\rho N_0 r^2/9A)k \quad (10)$$

While Waser and Pauling [117] used Equation 9 to estimate the force constant of several elemental and compound crystals from known values of their bulk modulus, Yean and Riter [118] proceeded in the reverse direction; they estimated the bulk modulus from Equation 10 using known values of the force constant. In doing so, Yean and Riter made the important assumption that the interatomic force constant between two atoms in the solid state is the same as the stretching force constant for the same two atoms in the molecular state. The stretching force constant for molecules can be evaluated from i.r. and Raman spectroscopic data. The force constants and bulk moduli estimated by Yean and Riter [118] for some systems are given in Table VI.

The value of 960 kbar estimated for the bulk modulus of Ge compares well with Bridgman's value of 787 kbar quoted by Gschneidner [23] and the value of 778 kbar quoted by Simmons and Wang [7] from ultrasonic data. Further, Yean and Riter predicted the value of 2240 kbar for the bulk modulus of SiC without the knowledge of any experimental value. However,

TABLE VI Stretching force constants (k) and estimated bulk moduli (B) for some crystals

Molecule	k (millidyne/cm)	Crystal	B from Equation 10 (kbar)
C_2H_6	4.36	C (diamond)	4070
Si_2H_6	1.73	Si	1060
Ge_2H_6	1.62	Ge	960
Sn_2H_6	1.40	Sn (α)	720
CH_3SiH_3	2.19	SiC (β , cubic)	2240

the bulk modulus of SiC was earlier determined by Einspruch and Clairborne [119] who obtained a value of 2140 kbar from ultrasonic measurements on a polycrystalline sample. Thus, the method seems to work well. Comparing the value of the bulk modulus of Si calculated from the spectroscopic data with the values given in Table I, Yean and Riter recommended rejection of the abnormally large literature value of 3120 kbar.

It is clear that this method is suitable only for molecular and crystalline systems having a common bond and which are amenable to spectroscopic measurements.

(c) Bulk modulus from Szigeti's theory of dielectrics

Considering the dielectric polarization in ionic crystals, Szigeti [120] derived the following equation:

$$B = (1/\psi) = [r^2 \mu \omega_0^2 (\epsilon_0 + 2)] / [3u(n^2 + 2)] \quad (11)$$

Using appropriate values for the various quantities in Equation 11, Szigeti calculated the bulk modulus. The calculated and experimental values of the bulk modulus ($B_{\text{calc.}}$ and $B_{\text{exp.}}$ respectively) and the ratio $B_{\text{exp.}}/B_{\text{calc.}}$ for some crystals are given in Table VII.

The values of $B_{\text{exp.}}/B_{\text{calc.}}$ for the alkali halides are all close to unity showing that Equation 11 works well, particularly for perfectly ionic crystals like alkali halides. For MgO, Szigeti got a low value for $B_{\text{exp.}}/B_{\text{calc.}}$. Anderson and Glynn [121] felt that the value of ω_0 used by Szigeti was inaccurate. They redetermined ω_0 from the reflectivity curve for MgO and recalculated B . The revised value for $B_{\text{exp.}}/B_{\text{calc.}}$ is, again, close to unity.

This method is now applied to analyse the bulk modulus data for CaO and SrO given in Table I. For CaO, the value of $B_{\text{exp.}}/B_{\text{calc.}}$ obtained by Szigeti using Bridgman's value for B is low. The alkaline earth oxides are not as ionic as the alkali halides and some deviations $B_{\text{exp.}}/B_{\text{calc.}}$ from unity can be expected. But the value 0.13 obtained by Szigeti is too low. The values for this ratio have been recalculated using the other experimental values of the bulk modulus for CaO given in Table I. It is seen that with the new values of B , the ratio $B_{\text{exp.}}/B_{\text{calc.}}$ has a value ~ 0.66 which is much better than the Szigeti value of 0.13. Clearly, Equation 11

TABLE VII Calculated and experimental values of bulk moduli for some crystals

Crystal	B_{calc} (Kbars)	B_{exp} (kbars)	$B_{\text{exp}}/B_{\text{calc}}$ (kbars)
LiF	670	670	1.00
NaCl	242	239	0.99
KBr	160	152	0.95
MgO	3570	1690	0.47
	1640*		1.04*
CaO	1660	218	0.13
		1120*	0.67*
		1090*	0.65*
SrO	680	880*	1.29*
		1183*	1.73*

*For starred data, see discussion in text; rest of the data are from Szigeti [120], reproduced by Anderson and Glynn [121].

is able to show that Bridgman's value of bulk modulus of CaO is in error and the more recent values are reasonable.

For SrO, again, Szigeti [120] calculated the value of B from Equation 11; data on $B_{\text{exp.}}$ was not available to him to make a comparison. Now that the bulk modulus of SrO has been determined, the values of $B_{\text{exp.}}/B_{\text{calc.}}$ have been calculated using data in Table I leading to values of 1.29 and 1.73; the lower value of 880 kbar (Son and Bartels [39]), appears more reasonable than the larger value of 1183 kbar (Weir, [10]) for the bulk modulus of SrO.

(d) Theoretical calculation of physical properties using the bulk modulus as an input

(i) Cohesive energy. For an ionic crystal, the interaction energy u_{ij} between two ions i and j may be represented by

$$u_{ij} = -z_i z_j e^2 r_{ij}^{-1} - c_{ij}(6)r_{ij}^{-6} - d_{ij}(8)r_{ij}^{-8} + b_i b_j f_{ij} \exp(-r_{ij}/\rho) \quad (12)$$

where the terms represent the Coulomb, dipole-dipole, dipole-quadrupole and repulsion interactions respectively (for the meaning of each term, see Tosi, [122]). For a crystal as a whole, the cohesive energy is obtained by summation over all ions. The cohesive energy may be represented by:

$$U = U_e + U_d(6) + U_d(8) + U_r \quad (13)$$

where U is the cohesive energy and the four terms, again, represent the contributions of the four interactions. The parameters in the expression, particularly those in the repulsion term, are calculated from the conditions:

$$dU/dr = 0 \quad (14)$$

$$r^2(d^2U/dr^2) = 9VB \quad (15)$$

where r is the interatomic distance, V the molar volume and B the zero pressure bulk modulus. Once these parameters are known, one may go back to Equation 13 to get the cohesive energy. In this way, the bulk modulus comes into the calculation of the cohesive energy. Comparison of the calculated value and the 'experimental' value of cohesive energy helps to judge the reliability of the value of the bulk modulus used as input.

Benson *et al.* [123] employed this approach in the case of ThO₂ and UO₂. They assumed various values of B to calculate U from Equation 13 and constructed a $B - U$ plot (Fig. 6) from which they read off the values of B corresponding to the experimental values of U (-2413 and -2461 kcal mole⁻¹ for ThO₂ and UO₂ respectively, quoted by Benson *et al.* [123]). These values are given in Table VIII along with experimental values which were available from ultrasonic measurements on sintered samples. There is a

TABLE VIII Bulk moduli of ThO₂ and UO₂

Method	B (kbar)	
	ThO ₂	UO ₂
Expt. (polycrystalline samples)	2403	2127
Predicted from B – U plot	2770	2958
Expt. (single crystal)	1930	2127
Minimum value predicted from B-σ plot	1500	2000

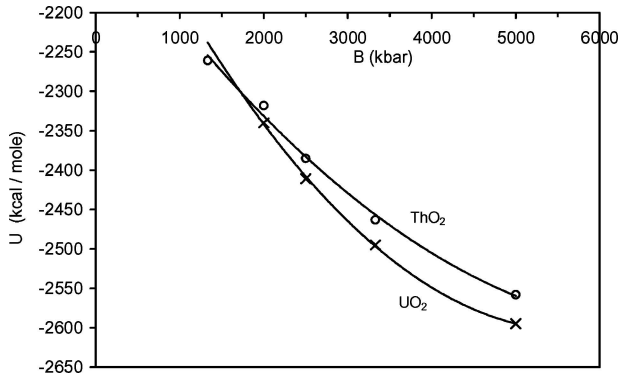


Figure 6 Bulk modulus (B) versus cohesive energy (U) plot for ThO₂ and UO₂.

difference of 10–30% between these two sets of values. Benson *et al.* [123] suggested that this difference could be because the experimental B values were based on experiments on sintered samples. However, later accurate ultrasonic measurements on single crystals yielded values which show the same (or even larger) difference from the B – U plot values. Thus, the difference between experimental values and those from the B – U plot persists.

We may cautiously conclude that the procedure of calculating the bulk modulus by comparing the calculated value of the cohesive energy with the ‘experimental’ value leads only to an ‘order-of-magnitude’ check on the B-values.

(ii) *Surface energy.* Starting with Equation 12, one can proceed to obtain an expression for the surface energy. The expression depends on the structure of the crystal and also the plane for which the surface energy is to be calculated. As in the case of the cohesive energy, the surface energy will also have four terms:

$$\sigma = \sigma_e + \sigma_d(6) + \sigma_d(8) + \sigma_r \quad (16)$$

Benson *et al.* [123] calculated σ for the (111) plane of ThO₂ and UO₂ assuming different values of the bulk modulus to evaluate the repulsion parameters. The exact expressions for Equation 16 for the (111) plane of the fluorite structure are worked out by Benson and Dempsey [124].

The variation of σ with the assumed value of B is shown in the B- σ plot (Fig. 7). If the surface energy is known from experiment, one may read off the value of B from the plot corresponding to the experimental value of σ . Experimental values of σ are, however, not known for ThO₂ and UO₂. Some information can still

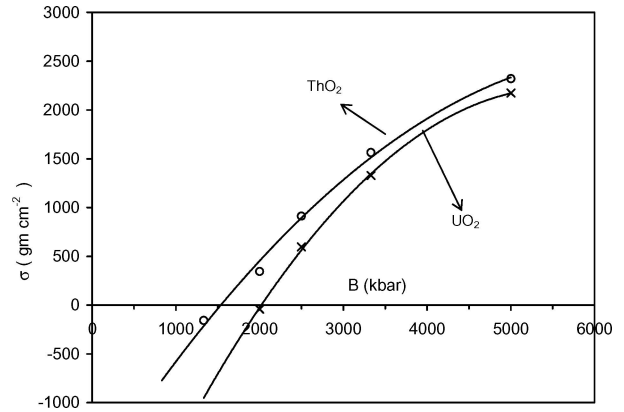


Figure 7 Bulk modulus (B) versus surface energy (σ) plot for ThO₂ and UO₂.

be extracted from the B- σ plot. It can be seen from Fig. 7 that σ depends on B in a sensitive manner. In fact, σ assumes +ve and –ve values for different ranges of B. Physically, σ cannot assume –ve values. Thus, we can read off the B value for which σ changes from +ve to –ve values. This is the minimum value for B. The correct value for B will be larger than this value. These minimum values estimated from Fig. 7 are given in Table VIII. The two sets of experimental values of B as well as those estimated from the B – U plot are all larger than the minimum value from Fig. 7. Thus, surface energy calculations can only predict the lower bound for the bulk modulus and serve only as an order-of-magnitude check on bulk modulus values.

(iii) *Calculation of single crystal elastic constants with bulk modulus as input.* The Krishnan-Roy theory [125] provides a method for evaluation of elastic constants of ionic crystals. Krishnan and Roy assume the following simple expression for the cohesive energy of ionic crystals like the alkali halides:

$$U = N_0 [-\alpha_M z^2 e^2 / r] + b \exp(-r/\rho) \quad (17)$$

where α_M is the Madelung constant, and b and ρ are constants in the repulsion term. The parameter r/ρ may be denoted by δ . Application of Equations 14 and 15 to Equation 17 leads to

$$B = \left[\frac{z^2 \alpha_M e^2}{9Vr} \right] [\delta - 2] \quad (18)$$

δ can be determined from the bulk modulus by the use of Equation 18. Krishnan and Roy obtained the following relations for the elastic constants:

$$C_{11} = [2\alpha_M(1 + \delta) - 6X](z^2 e^2 / r^4), \quad (19)$$

$$C_{12} = C_{44} = 3(X - \alpha_M)(z^2 e^2 / r^4), \quad (20)$$

X is a lattice sum which depends on the crystal structure. For the NaCl structure, $X = 3.14$. Thus, with B, as input, δ can be evaluated and with δ as input, the elastic constants C_{11} and C_{12} can be evaluated. The equality of C_{12} and C_{44} is a consequence of the assumption of

TABLE IX Values of elastic constants of LiH from Equations 19 and 20

B (kbar)	C_{11} (kbar)	$C_{12} = C_{44}$ (kbar)	C_{11}/C_{12}
500	580	460	1.25
357	140	460	0.29
270	-110	460	-0.24
228	-240	460	-0.52

central forces. Krishnan and Roy calculated the elastic constants of several alkali halides and found good agreement with experimental values. Mathur *et al.* [38] calculated the elastic constants of alkaline earth chalcogenides from the Krishnan and Roy equations. Sirdeshmukh and Subhadra [126] applied the Krishnan-Roy theory to some transition metal oxides with NaCl structure.

Subhadra and Sirdeshmukh [127] used the method of Krishnan and Roy [125] to analyse the several differing values of the bulk modulus of lithium hydride which has the NaCl structure and is considered highly ionic. Apart from the values 270, 228 and 357 (kbar) quoted in Table I, Pretzel *et al.* [128] quoted values of 400, 312 and 208 (kbar) for the bulk modulus of LiH by other methods. Subhadra and Sirdeshmukh [127] calculated the values of the elastic constants of LiH from Equations 19 and 20 using values of bulk moduli in the range 200–500 kbar as input. Some of their results are given in Table IX. They plotted the values of C_{11} and C_{11}/C_{12} against the values of B used as input. The plots (Figs 8 and 9) are smooth curves. Subhadra and

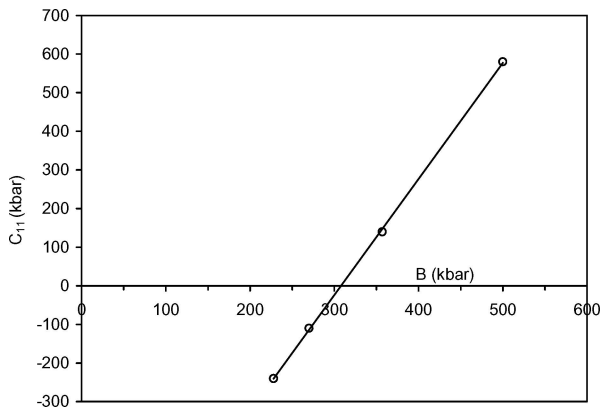


Figure 8 B versus C_{11} plot for LiH.

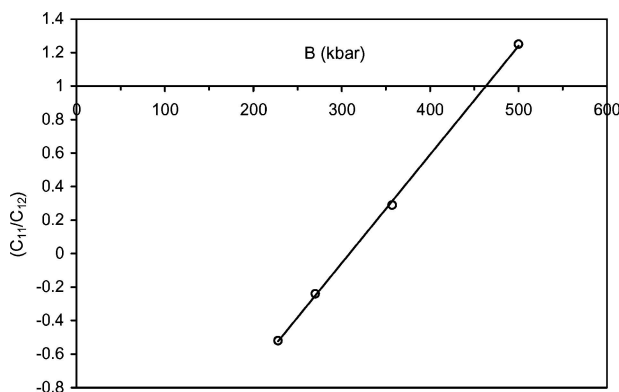


Figure 9 B versus C_{11}/C_{12} plot for LiH.

Sirdeshmukh [127] would have used experimental values of C_{11} and C_{12} to read off the correct value of B . However, such data was not available to them.

An interesting feature of the C_{11} vs. B and (C_{11}/C_{12}) vs. B plots is that both C_{11} and C_{11}/C_{12} are very sensitive to the value of B assumed for the calculations. In fact C_{11} and C_{11}/C_{12} assume -ve values for a range of B values. Subhadra and Sirdeshmukh [127] invoked the stability conditions proposed by Born and Huang [111] and Alers and Neighbours [113] according to which, in cubic crystals

$$C_{11} > 0 \quad (21)$$

and

$$(C_{11}/C_{12}) > 1 \quad (22)$$

From Figs 8 and 9, it is seen that for both the stability conditions to be satisfied B should be greater than 465 kbar. Thus, 465 kbar is the lower bound for the bulk modulus of LiH. It may be noted that the Krishnan-Roy theory assumes central forces, neglects the Van der Waal interactions and treats the crystal as completely ionic. Subsequent to the analysis by Subhadra and Sirdeshmukh [127], Haussuhl and Skorezyk [129] measured the single crystal elastic constants of LiH. They observed a large difference in the values of C_{12} and C_{44} indicating considerable departure from ionicity. In view of these limitations, it may not be proper to fix a sharp limit for the lower bound of B . Thus, the value of 357 kbar reported by Stephen and Lilley [31] may be treated as the best among the several B values.

3.3. Empirical relations as consistency checks

There are several empirical relations between the bulk modulus and other physical properties. Although these correlations do not have a rigorous theoretical support, they are otherwise well-established and can be used to check data on bulk moduli. Some of these empirical relations are discussed below.

(a) Relation between bulk modulus (B) and volume (V)

Keyes [130] showed from dimensional analysis that the bulk modulus varies inversely as a^4 where a is the lattice constant. He verified this relationship for crystals with zinc blende structure. Mitra and Marshall [131] found that for alkali halides the bulk modulus is inversely proportional to a^3 . Anderson and Nafe [132] drew $\log B$ vs. $\log V$ plots for several systems and proposed a relation:

$$BV = \text{constant} \quad (23)$$

Subsequently linear $\log B$ vs. $\log V$ plots have been reported for several systems (Table X).

Anderson and Nafe [132], Anderson and Anderson [135] and Jayaraman *et al.* [133] showed that a

TABLE X Systems for which linear log B vs. log V plots have been reported

System(s)	Reference
Oxides, alkaline earth fluorides	Anderson and Nafe [132]
Wurtzite type crystals	Cline <i>et al.</i> [79]
Alkali halides, divalent chalcogenides and trivalent rare earth chalcogenides	Jayaraman <i>et al.</i> [133]
Divalent oxides and lead chalcogenides	Sirdeshmukh and Subhadra [134]
Uranium pnictides	Leger <i>et al.</i> [94]
Rare earth chalcogenides	Vedal <i>et al.</i> [41]

relationship close to Equation 23 can be derived on the basis of interatomic forces. Neumann [136] suggested that a better fit with experimental data is obtained by using a modified equation:

$$B = ba^{-m} (1 - g f_i) \quad (24)$$

where ' a ' is the lattice constant, f_i the Phillips ionicity and b , m and g are constants for a family of crystals.

However, the simple log B vs. log V plots have proved quite useful. Jayaraman *et al.* pointed out that these plots are useful in scaling bulk modulus data, in estimating ionic charge and in predicting bulk moduli where they are not available. Sirdeshmukh and Subhadra [134] pointed out another application of the log $B - \log V$ plots viz. in sifting the correct value of bulk modulus when several differing values are reported. Thus, they were able to show that among the three values for PbSe given in Table II, the value 3470 kbar deviates severely from the log B vs. log V plot (or the B vs. V^{-1} plot) and is to be disregarded. Similarly, Vedel *et al.* [41] showed that between the two values for CeS given in Table I, the value 820 kbar is close to the log B vs. log V plot for the rare earth chalcogenides in contrast to the other value of 1300 kbar which shows a strong deviation.

The log B vs. log V plots have now been redrawn for the alkali halides with NaCl structure (Fig. 10), alkali halides with cesium chloride structure (Fig. 11), NaCl-type oxides (Fig. 12), chalcogenides with NaCl structure (Fig. 13) and wurtzite type chalcogenides (Fig. 14) including several new B -values. It is seen

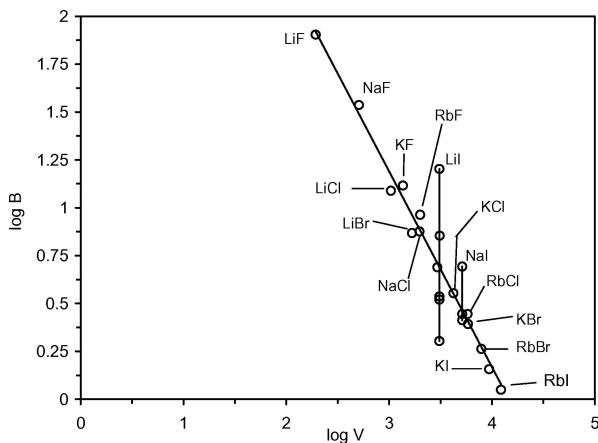


Figure 10 Plot of log B versus log V for NaCl type alkali halides.

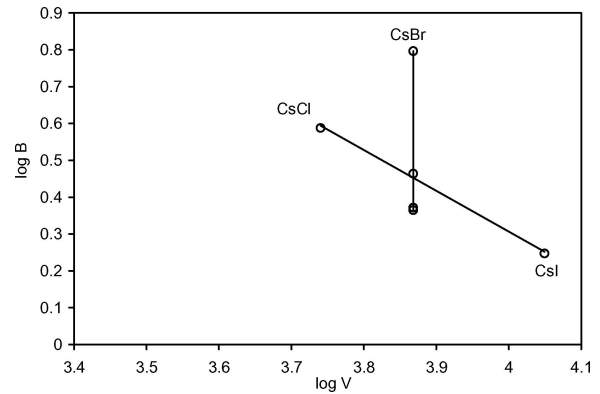


Figure 11 Plot of log B versus log V for CsCl type alkali halides.

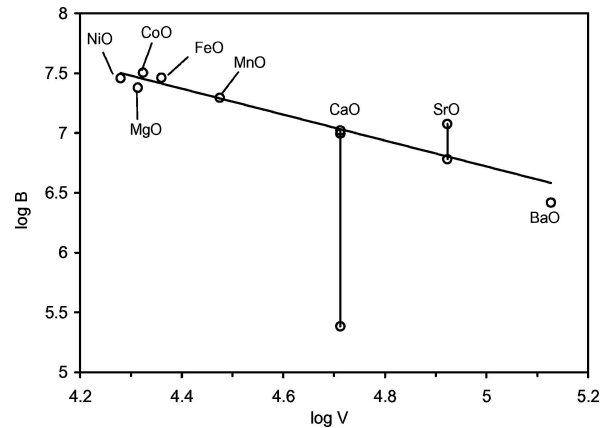


Figure 12 Plot of log B versus log V for oxides with NaCl structure.

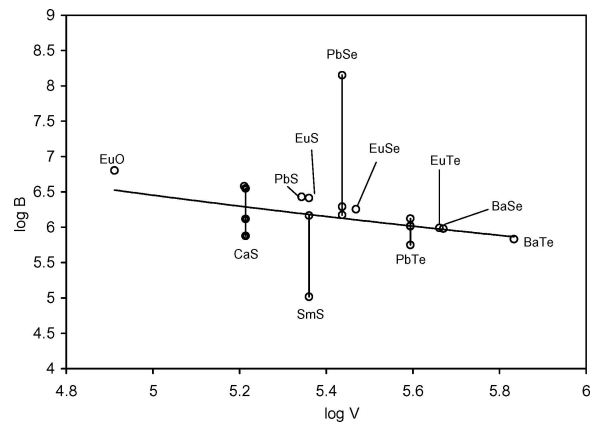


Figure 13 Plot of log B versus log V for divalent chalcogenides.

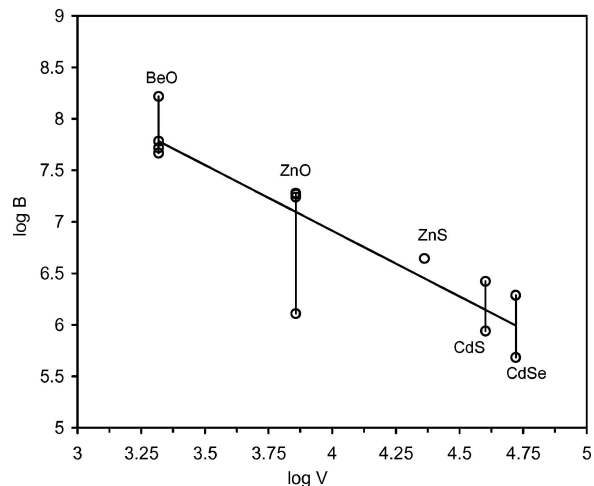


Figure 14 Plot of log B versus log V for wurtzite type chalcogenides.

that in Fig. 10, the plot is able to differentiate between the several largely differing values of B for LiI and also in the case of NaI where the difference is about 25%. Again in Fig. 11, the plot is able to show that in the case of CsBr, between the three values differing by about 60%, the largest value deviates very much from the plot and the two lower values are preferable. Fig. 12 clearly indicates that the Bridgman value of 218 kbar for CaO is to be discarded in comparison with the other values which are larger by a factor of 5. However, in the case of SrO, the deviation of the data point for the larger value of the bulk modulus is only marginal. In Fig. 13, the plot clearly shows that the largest among the B values for PbSe and the lowest among the B values for SmS deviate too much from the plot and deserve to be ignored. However the plot does not differentiate between the different data for CaS and PbTe with the same clarity. Lastly, in Fig. 14, the lesser value for ZnO is clearly off the plot but the same cannot be said about the different data points for BeO, CdS and CdSe.

Thus, the $\log B$ vs. $\log V$ plots can be effectively used to distinguish different B values particularly if the differences are large.

(b) Relation between bulk modulus and cohesive energy of elements

Gschneidner [23] pointed out that an empirical linear relation exists between the cohesive energy U and the bulk modulus of elements. The relationship is of the type

$$U = mB + b \quad (24)$$

where m and b are constants for a family of related crystals.

Gschneidner [23] plotted the values of U against B for the elements S, Se, Te and Po. He found that the data point for Se (based on Bridgman's results) deviates severely from the straight line joining the data points for the other three elements. The value of B read off from the straight line suggested a much larger value for B of Se than the Bridgman value. It is shown in other sections that other consistency checks also supported this suggestion and a later ultrasonic measurement indeed resulted in a much larger value.

The linear relation between U and B is all too empirical. In fact, Gschneidner [23] pointed out that the slope m of the straight line plot has +ve as well as -ve values for different systems. Thus the plot for any family must be clearly established before it can be put to use to analyze B values for a given solid.

(c) Empirical relation between bulk modulus and thermal expansion

Sirdeshmukh [109] proposed a linear relation between the compressibility ($1/B$) and the product of the linear coefficient of expansion (α) and volume (V). He showed linear plots of αV vs. ($1/B$) for several families of metals and the alkali halides.

(d) Relation between bulk modulus and Debye temperature

The Debye temperature is empirically given by:

$$\theta = cB^{1/2}\rho^{-1/6}m^{-1/3} \quad (25)$$

where c is a constant. This relation is known in literature as the Madelung formula. Deus and Schneider [137] modified this relation as follows

$$\theta = a_1x + a_2 \quad (26)$$

where x is ($B^{1/2}\rho^{-1/6}m^{-1/3}$) and a_1 and a_2 are constants for a family of crystals.

(e) Relation between bulk modulus and hardness

Reddy *et al.* [138] proposed an empirical relation between the bulk modulus, the hardness, the refractive index and Phillips ionicity as follows:

$$B = cHn^{0.13}f_i \quad (27)$$

where c is a constant. The relation was found to work well in ternary chalcopyrites of the $A^I B^{III} C^{VI}$ and $A^{II} B^{IV} C^V$ types with appropriate values for the constant c .

4. Consistency checks for single crystal elastic constants

As mentioned in Section 2, single crystal elastic constants C_{ij} are almost invariably determined by ultrasonic methods which are highly accurate. While the velocity determination, per se, is accurate, inaccuracies enter by way of factors like (i) sample history, wall reflections and bonding problems and (ii) analytical difficulty in converting velocities into C_{ij} 's. Several examples of strong differences in reported values of C_{ij} 's are cited in Tables II-IV.

In this section, some consistency checks are considered which facilitate sifting of correct data from several reported values of elastic constants. Again, the checks are based on (i) phenomenological constraints and (ii) use of C_{ij} 's to calculate other physical properties.

In analyzing data on single crystal elastic constants use is also made of inter-relations between elastic constants resulting from stability conditions. Some of these relations and constraints are as follows:

(a) Cubic (Born and Huang [111]; Alers and Neighbours [113]):

$$C_{11}, C_{12}, C_{44} > 0; \quad C_{11} - C_{12} > 0$$

(b) Hexagonal (Nye [112]):

$$C_{44} > 0; \quad C_{11} > |C_{12}|; \quad (C_{11} + C_{12})C_{33} > 2C_{13}^2$$

(c) Tetragonal (Alton and Barlow [114])

$$C_{11}, C_{33}, C_{44}, C_{66} > 0; \quad C_{11} > |C_{12}|;$$

$$C_{11}C_{66} > C_{16}^2; \quad C_{11}C_{33} > C_{13}^2$$

Alers and Neighbours [113] pointed out that for all crystal classes the diagonal elements of the elastic constant matrix are positive. They also discussed the stability conditions for the trigonal class. Sundara Rao [110] discussed the inter-relationships between the elastic constants for orthorhombic crystals.

Some of these constraints are invoked while analyzing data on some cubic, tetragonal and hexagonal crystals.

4.1. Cubic crystals

In the first three crystals for which data are quoted in Table II, the value of C_{12} differs in sign. Since the Poisson's ratio equals $C_{12}/(C_{11} + C_{12})$ a negative value for C_{12} results in a $-ve$ value for the Poisson's ratio. As discussed in Section 3.1, phenomenologically, σ_P cannot be $-ve$. Poisson's ratio values for different sets of elastic constants are given in Table II. The sets of elastic constants for FeS_2 , $NaClO_3$ and $PbTe$ with $-ve$ values of C_{12} can be straight away disregarded.

In the last case viz., $PbSe$, the elastic constants reported by Chudinov [67] are larger than the values from the other two sources by a factor of 3 in the case of C_{11} and a factor of 20 in the case C_{12} . This results in the bulk moduli differing by a factor of about 7. As mentioned in Section 3.3(a), the $\log B$ vs. $\log V$ plot (Fig. 12) clearly shows that the larger value of B does not fit into the correlation and hence the corresponding set of elastic constants (Chudinov [67]) has to be ignored.

4.2. Tetragonal crystals

(i) Zircon

In Table III, three sets of C_{ij} 's are quoted for zircon. Sets (ii) and (iii) broadly agree with each other, although there are differences between the values in the two sets for C_{11} , C_{12} and C_{44} . However, both sets differ from set (i) by factors ranging from 1.5 (C_{66}) to 30 (C_{13}).

Sirdeshmukh and Subhadra [139] analysed these differing results using several approaches. Their results are given in Table XI. Sirdeshmukh and Subhadra [139] calculated the Voigt-Reuss-Hill bulk modulus from the

three sets of C_{ij} 's and compared the values with those obtained from other independent methods. It is seen that the value of the bulk modulus from set (i) is very low. It is lower than the values from sets (ii) and (iii) by a factor of 8–9. It is also lower than typical values for several mineral crystals quoted by Anderson *et al.* [140]. The bulk modulus of zircon has been estimated by other independent methods. These are given in Table XI. It may be noted that the value from set (i) is in disagreement with all these values whereas the values from sets (ii) and (iii) show at least an order-of-magnitude agreement with these independently estimated values. This comparison of bulk moduli clearly indicates that the elastic constants in set (i) are unacceptable.

Sirdeshmukh and Subhadra [139] further used the bulk moduli to calculate the thermal Gruneisen constant γ given by

$$\gamma = 3\alpha VB/C_V \quad (28)$$

Using the values of the bulk moduli from the three sets together with values for the other quantities taken from literature, Sirdeshmukh and Subhadra [139] obtained the values given in Table XI for γ . In analyzing the results on γ , Sirdeshmukh and Subhadra [139] used the empirical fact that for most of solids, the value of γ lies in the range 1–3. On this basis again, the value of $\gamma = 0.11$ originating from set (i) is far too low. On the other hand the other two values of γ originating from sets (ii) and (iii) are close to ~ 1 and indicate the superiority of C_{ij} 's in sets (ii) and (iii).

Finally, Sirdeshmukh and Subhadra [139] calculated the Debye temperature of zircon from the elastic constants using Anderson's [143] method. These values are included in Table XI along with values from specific heats. The value of Debye temperature from set (i) is about half the values from sets (ii) and (iii). Also, the values from sets (ii) and (iii) are within the range of values quoted from specific heat data unlike the value from set (i). This again indicates the superiority of sets (ii) and (iii) vis-a-vis set (i).

This analysis of the elastic constants of zircon has clearly established that the elastic constants in set (i) are physically unacceptable. This analysis is an example of a comprehensive check on conflicting elastic constant data.

(ii) KDP type crystals

Two sets of elastic constants each for potassium dihydrogen phosphate (KDP) and ammonium dihydrogen phosphate (ADP) are given in Table III. In both cases there are strong differences in the values of C_{13} . More seriously, there is a difference in the sign for C_{12} . As mentioned earlier, for tetragonal crystals, one stability condition is $C_{11} > |C_{12}|$. Thus there is no constraint on the sign of C_{12} . Both sets satisfy the requirement $C_{11} > |C_{12}|$.

The bulk moduli calculated from the elastic constants also show a difference of 40% in the case of ADP and a difference of 80% in the case of KDP. However, the bulk moduli are not known from any other independent

TABLE XI Bulk modulus (B), Debye temperature (θ) and Gruneisen constant (γ) of zircon

Set	B (kbar)		θ (K)		γ
	From C_{ij}	From other methods	From C_{ij}	From sp. heats	
i	190		300		0.11
ii	2040		601		0.89
iii	2030		725	600–900 ^c	0.99
		3731 ^a (X-ray)			
		3875 ^a (Neutron)			
		2702 ^b			

^aWorlton *et al.* [141]; ^bKnopoff [115]; ^cOzkan and Cartz [142].

method. Being an important family of crystals, the elastic constant data of these crystals deserves further analysis.

(ii) Strontium molybdate

Strontium molybdate (SrMoO_4), along with CaWO_4 and CaMoO_4 , belongs to T II Laue symmetry. There are several intrinsic difficulties in the determination of elastic constants of these crystals. Firstly, there are seven (instead of the usual 6) independent elastic constants; the existence of the seventh elastic constant C_{16} complicates measurements. Secondly, the axes of acoustic symmetry in the (001) plane do not coincide with the $\langle 100 \rangle$ and $\langle 110 \rangle$ directions which makes the determination of C_{16} ambiguous. Thirdly, the equations for the elastic constants C_{11} , C_{66} , C_{12} and C_{16} have four different solutions.

In Table III, three sets of elastic constants are quoted for SrMoO_4 . The first set is reported by Chung and Li [74]. Chung and Li [74] gave in their paper the four solutions for C_{11} , C_{66} , C_{12} and C_{16} referred earlier. These are reproduced in Table III. It can be seen that the values of C_{ij} 's in these solutions not only differ by several factors but also in sign. Chung and Li [74] chose the first of these solutions as the most reasonable, on the basis of the stability conditions discussed by Alton and Barlow [114].

Comparing the values of C_{ij} 's reported by Chung and Li [74] with C_{ij} 's of the related crystals CaWO_4 and CaMoO_4 , James [75] noticed a similarity in the values of all C_{ij} 's except C_{16} and C_{66} . For crystals with this symmetry, the following relation must hold

$$\sum_{i=1}^3 v_i^2 = S_1/\rho = (C_{11} + C_{44} + C_{66})/\rho \quad (29)$$

where ρ is the density, S_1 a constant and v_i are velocities of propagation of sound waves in the x , y plane. James [75] found that this condition is satisfied in CaWO_4 and CaMoO_4 but not by the C_{ij} 's of SrMoO_4 reported by Chung and Li [74]. James [75] carried out a reanalysis of the velocity data of Chung and Li [74] by calculating the parameter |SUMSQ| defined by

$$|\text{SUMSQ}| = \sum_{n=1}^n \left[\frac{v_i^2(\text{calc})}{v_i^2(\text{meas})} - 1 \right]^2 \quad (30)$$

The input C_{ij} 's for calculating v_i were varied till |SUMSQ| was minimum. The values thus obtained by James [75] are given in Table III as set (ii); the new C_{16} and C_{66} values are different from those given by Chung and Li [74] but are comparable with those for CaWO_4 and CaMoO_4 .

The C_{ij} 's of SrMoO_4 were subsequently redetermined by Farley *et al.* [76] taking care regarding the choice of axes which resulted in set (iii). Farley *et al.* [144] showed that the sign of C_{16} is negative for all crystals with scheelite structure.

4.3. Trigonal and hexagonal crystals

(i) Calcite

Calcite is trigonal with six independent elastic constants. There are two reports on the low temperature elastic constants of calcite. The values from these two reports are given in Table IV. These values were read off from a diagram given by Dandekar and Ruoff [78] and pertain to a temperature of 160 K. This is the only crystal for which the elastic constants have been given in the S_{ij} notation in this paper. This has been done as the data are given in this form in the original papers and conversion into C_{ij} 's may introduce errors. There are differences of 30, 60 and 10% in the values of S_{14} , S_{13} and S_{44} . Dandekar and Ruoff [78] calculated the bulk modulus for the two sets and found values of -6300 and 700 kbar. The negative value of bulk modulus is phenomenologically unacceptable and hence the set of elastic constants reported by Ramamurthy and Reddy [77] is to be rejected.

(ii) BeO (Hex.)

For hexagonal crystals, there are only five independent elastic constants. The sixth constant C_{66} is sometimes given as it is generally measured independently; it is equal to $(C_{11} - C_{12})/2$.

The two sets of C_{ij} 's for BeO given in Table IV yield B values which agree with each other and are close to the $\log B$ vs. $\log V$ line (Fig. 14). The Debye temperatures calculated from these two sets also are close to each other and with the specific heat value. However, there is a difference of 32 and 35% in the values of C_{12} and C_{13} which is much larger than the estimated errors of 5–10% mentioned by Bente [49] and Cline *et al.* [79]. Bente obtained the values 1520 and 1630 kbar for C_{66} but retained the lower value. As mentioned, C_{12} is obtained from the difference between C_{11} and $2 C_{66}$. If the value 1630 kbar is used for C_{66} , the difference between the values of C_{12} in the two reports will reduce to 12% which is reasonable. The difference in C_{13} however remains. The solution of the velocity equation gives positive and negative values for C_{13} . But only the positive value is retained, though there is no physical reason for doing so (Cline *et al.* [79]).

(iii) LaCl₃ (Hex.)

In Table IV, values of C_{ij} 's for LaCl_3 are given. Sets (i)–(iii) are theoretical values calculated by Stedman and Newman [80] from three models. There are differences in the C_{ij} values for the three models ranging from 10% (C_{13}) to 100% (C_{66}). These differences may be of significance in relation to the models. The bulk moduli calculated from these three sets are not very different. So, it is not possible to differentiate between these sets on the basis of bulk modulus calculations.

Carlson *et al.* [81] calculated the Debye temperatures from these three sets of elastic constants and obtained values 600, 500 and 507 K respectively. The marginal difference in these values is consistent with marginal differences in the C_{ij} 's from which they originate.

However, all these Debye temperature values are larger by a factor of 3–4 than the value of 145 K obtained from specific heat data. Carlson *et al.* [81] pointed out that the θ from elastic constants can be reconciled with the θ from specific heats if all the elastic constants are reduced uniformly by a factor of 16. These reduced C_{ij} 's are shown as set (iv). They do yield a Debye temperature of ~ 150 K which is close to the specific heat value. The bulk moduli pertaining to sets (i)–(iii) have values in the range 1980–2100 kbar. On the other hand, set (iv) yields a bulk modulus value of 128 kbar.

Experimental determination of the bulk modulus and the elastic constants will help to sort out the differences in various sets of elastic constants of LaCl_3 .

5. Summary and conclusions

Several methods are now available for the determination of elastic moduli and elastic constants with a high degree of accuracy. In spite of the accuracy of the methods, there are numerous cases where the values of bulk moduli and single crystal elastic constants reported by different workers differ by amounts far exceeding the limits of errors. Several such examples are cited. When such differences exist, it is necessary to subject the reported data to consistency checks.

Several consistency checks are reviewed to analyse data on bulk modulus. These may be broadly classified as (i) phenomenological constraints (ii) theoretical estimates of bulk moduli (iii) theoretical estimates of other physical properties using the bulk modulus as input and (iv) empirical checks.

Differing results on the single crystal elastic constants are, again, analysed by using phenomenological constraints and by comparison of properties calculated from the elastic constants with independently determined values.

A common feature of most of the consistency checks discussed here is that they are able to distinguish between values (or data sets) which differ severely and cannot be forcefully applied when the differences are small. In the analysis of single crystal elastic constants, the consistency check of calculating other physical properties like the bulk modulus and Debye temperature has the limitation that these calculations involve several or all elastic constants. Thus, it is possible to comment on an entire set of elastic constants and not on each elastic constant. Another feature is that some of the checks may help to single out an unacceptable value but may not enable us to decide which among the acceptable values is best. Finally, a single check may not be enough to analyse data; application of several criteria may yield better information; the case of zircon is an example.

It is noticed that in most cases where faulty data have been reported, consistency checks have been applied by other than those who generated the data. Since several consistency checks are now available, it is desirable that whenever data on elastic properties are generated, they are subjected to one or more consistency checks before the data pass into literature.

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*Received 24 April
and accepted 22 September 2004*