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GRÜNEISEN CONSTANT, THERMAL EXPANSION OF CRYSTALS AND THE LAW OF INTERATOMIC FORCES

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(*Received April* 9, 1965 ; *Resubmitted November*, 18, 1965)

In principle it should always be possible to compute the different macroscopic properties of crystals from the reliable knowledge of interatomic forces. Various attempts have been made in this direction from time to time and the purpose of this note is to present such simple and new relations for the Gruneisen constant and the coefficient of thermal expansion

The familiar Gruneisen relation is (Kittel 1956)

$$\gamma = \frac{3\alpha V}{\beta C_v}, \qquad \ldots \quad (1)$$

where γ is the Grüneisen constant, α and β the coefficients of thermal expansion and compressibility respectively, V the molar volume and C_v the molar specific heat at constant volume. On the basis of the extended Born-Mayer theory of the interatomic forces of ionic crystals we can write for the total energy per cell, $\Phi(r)$, as

$$\Phi(r) = -\frac{\alpha e^2}{r} + A\exp(-r/\rho) - \frac{C}{r^6} - \frac{D}{r^8}. \qquad (2)$$

Here α is the Madelung constant, e the electronic charge, r the interatomic separation, A and ρ the two potential parameters, and C and D are the van der Waals constants. The constants A and ρ are determined from the familiar conditions of Born and Mayer (1932) but we quote here a simplified version of their second relation which is pertinent for our discussion here viz.,

$$r^2 \frac{d^2\Phi(r)}{dr^2} = \frac{9V}{N\beta}, \qquad \ldots \quad (3)$$

N being the Avogadro number.

Further if ν is the vibrational frequency of the atoms in the crystal we have

$$\gamma = -\frac{d\ln\nu}{d\ln V}. \qquad \ldots \quad (4)$$

If we make an additional assumption that these atomic vibrations are simple harmonic in nature we have

$$\nu = 2\pi\sqrt{\frac{f}{m}}, \qquad \ldots \quad (5)$$

m is the mass of the atom and f the force constant. Relation (5) leads to

$$\frac{d\nu}{\nu} = \frac{df}{2f} \qquad \ldots \quad (6)$$

We also have $V = Ncr_0^3$, where r_0 is the equilibrium interatomic separation, and c a constant which depends upon the crystal structure This leads to the relation

$$\frac{dV}{V} = \frac{3}{r}\, dr\,. \qquad \ldots \quad (7)$$

One can also write at $r = r_0$,

$$\frac{d^2\Phi(r)}{dr^2} = -f. \qquad \ldots \quad (8)$$

Equations (6), (7) and (8) on substitution in Eq. (4) lead to the following desired relation :

$$\gamma = -\frac{r_0}{6}\left(\frac{d^3\Phi(r_0)}{dr^3}\right)\left(\frac{d^2\phi(r_0)}{dr^2}\right)^{-1}. \qquad \ldots \quad (9)$$

An interesting relation results if the values of γ and β as given by expressions (9) and (3) respectively are substituted in Eq (1). We finally get

$$\alpha = -\frac{C_v}{2Nr_0}\left[\frac{d^3\phi(r_0)}{dr^3}\right]\left[\frac{d^2\phi(r_0)}{dr^2}\right]^{-2}. \qquad \ldots \quad (10)$$

The relation (10) has also been derived by Saxena and Kachhava (1965) earlier in an entirely different approach based on the simple statistical mechanics result of expressing the average atomic displacement from the equilibrium position in terms of the interatomic potential. That these two results are identical with each other substantiates the various approximations made here in deriving the relation (9) We now check the accuracy of the derived relation (9) by performing calculations on alkali halides where fortunately experimental data are also available.

In the table we list the experimental values of γ for almost all the alkali halides. Also recorded are the calculated values according to Eq (9). In these computations we have used the r_0 values as compiled by us (1963) earlier, the two potential parameters A and ρ needed in connection with evaluation of the various derivatives of $\Phi(r)$ have also been reported by Kachhava and Saxena (1965),

while C and D are given by Mayer (1933). The agreement is satisfactory on the whole while it becomes excellent in some cases.

In order to get an idea of the success of the present theory and consequently of Eq. (9) we also tabulate the values as calculated from the two other approaches. One calculation uses Debye's theory and the knowledge of equation of state (method I), while in the second method we further employ the knowledge of interatomic forces The values recorded in the table are based on the simpler Born type potential (method II). It is important to note that due to the requirement of the experimental data of a rather complicated and uncertain nature it is not possible to compute γ for all the alkali halides Wherever the values are reported we find that the second method is definitely not reliable while the present method yields results better than even the first method in most of the cases

It is also interesting to point out here that calculations of Saxena and Kachhava (1965) based on Eq (10) for α of the alkali halide crystals are also satisfactory thereby substantiating the assumptions made in developing the present theory to a large extent However, the theory developed here is based on the simple Einstein's single frequency model, which is valid only at high temperatures Although the recent lattice theories are capable of giving relatively more rigorous and accurate results, yet the treatment presented here is useful because it is capable of yielding fairly reliable results in a very straightforward and simple fashion.

Experimental data as well as calculated values of γ for a few alkali halides are available other than shown in the Table. White (1961) found a value of 1 47 for KCl on the basis of the experimental data on α and other quantities White (1962), and Rubin *et al* (1961) report a value of 1 55 for NaCl. Collins (1963) on the other hand has calculated γ theoretically from the observed values of the pressure dependence of the elastic constants He finds at high temperatures for NaCl and KCl γ values as 1.61 and 1.25 respectively Barron, Leadbetter and Morrison (1964) have recently reported the values of γ calculated from the experimental values of adiabatic compressibility, specific heat at constant pressure and thermal expansion coefficient Their values extrapolated to high temperatures for NaCl and KCl are 1.585 and 1.44 respectively It will be seen that even here the agreement between theory and experiment is roughly of the same order as found in the Table on the basis of equation (9) In view of the simplicity of our approach for calculating γ we refrain comparing further with the values obtained on the basis of more complicated models.

We do not plead on the pretext of the reasonably good agreement obtained on the basis of equations (9) and (10) with the experimental values a great justification for the single frequency model The underlying idea of the present investigation has been to derive a simple expression and balance out the consequences of the various assumptions in such a way that a good working accuracy may be

achieved. We feel the present investigation achieves this goal in a better way than has been possible so far. This point is specifically made clear by comparing the results also with the two other methods.

TABLE I

Comparison of calculated and experimental values of Gruneisen constant, γ

Substance	Experimental values (a)	Calculated γ values		
		Eq (9)	Method I (b)	Method II (b)
LiF	1 99	1.80	3 02	1 97
LiCl	1 54	1 70	2 11	2.12
LiBr	—	1 66	2 06	2 16
LiI		1 69	—	—
NaF	1 57	1.63	—	—
NaCl	1 43	1 76	1.85	2.27
NaBr	1 55	1.80	1 75	2 33
NaI	1 59	1.87	—	—
KF	1 48	1.73	2 26	2.32
KCl	1 34	1.88	1 59	2.46
KBr	1.43	1 91	1 62	2.47
KI	1.58	1.97	1.54	2 52
RbF	1.28	1 81	—	—
RbCl	1.25	1 93	—	—
RbBr	1.27	1 95	1.46	2.47
RbI	1.50	2 01	1 50	2.56
CsF	1.49	1.82	—	—
CsCl	1.97	2 13	—	—
CsBr	1.93	2.30	—	—
CsI	2.00	2.21	—	—

(a) BORN, M, and HUANG, K., 1956, Dynamical Theory of Crystal Lattices (Oxford: Clarendon Press), p 52.
(b) SLATER, J. C., 1939, Introduction to Chemical Physics (London: McGraw-Hill Book Co., Inc.), p. 393.

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