

The coulomb contribution to the elastic constants arises from the change of the classical electrostatic energy of a structure by strain, assuming that no re-distribution of charge is brought about by the strain. Analytically, the coulomb contribution to the elastic constants has the form e^2/r^4 . For example, in the case of the sodium chloride structure, the coulomb contributions to C and C' are $C_{\text{coul}} = \frac{1.28}{2} \cdot \frac{e^2}{R^4}$ and $C'_{\text{coul}} = -\frac{1.33}{2} \cdot \frac{e^2}{R^4}$ where R is the cation-anion separation in the

crystal. For this important contribution to the elastic constants, $\frac{d \ln C}{d \ln r} = -4$. Experimentally, it is observed that the values range from -2.8 to -21 , indicating that important contributions to the C 's are non-coulombic. It is in these differences that the effects of strain on the various contributions to the crystal cohesive energy are sorted out.

Formally, one can write an elastic stiffness at 0°K as the second derivative of the crystal binding energy with respect to the appropriate strain, i.e. $\Omega C = \frac{\partial^2 U_o}{\partial \epsilon^2}$ where Ω is the crystal volume, U_o the total cohesive energy, ϵ the strain associated with the constant C . The differentiating with respect to $\ln r$, r being a distance in the crystal,

$$\frac{\Omega}{d \ln r} \frac{dC}{d \ln r} + 3\Omega C = \frac{\partial^2 U_o}{\partial \epsilon^2 \partial \ln r}$$

For the sake of definiteness, consider the series: U_o , the crystal energy at 0°K , the equilibrium condition, the bulk modulus, and the strain derivative of the bulk modulus, all taken at 0°K , for a simple model of the binding energy of NaCl, following the treatment in Kittel,²⁹ with modifications and addition of $d B_T/d \ln r$. Numbers above the terms in the equations give their relative contributions.

$U_o = N\phi$ where N = number of molecules, ϕ = energy per molecule, U_o = crystal energy.

$$U_o = N \left(\frac{\lambda A_n}{R^n} - \frac{\alpha e^2}{R} \right) \text{ a model in which the second term is the electrostatic energy of the}$$

assembly of positive and negative ions, the Madelung energy, the first term a repulsive interaction between ion cores, varying as a higher power of R , the cation-anion separation in the crystal. λ , A_n , n and α are constants.

$$\text{Now } p = -\frac{dU_o}{dV} = -\frac{dU_o}{dR} \cdot \frac{dR}{dV}, \quad V = 2NR^3$$

$$\text{so that } p = -1/3 \frac{N}{2NR^3} \left[-\frac{n\lambda A_n}{R^n} + \frac{\alpha e^2}{R} \right]$$

$$\text{at the equilibrium spacing, } p = 0, \text{ i.e. } -\frac{n\lambda A_n}{R^n} + \frac{\alpha e^2}{R} = 0.$$

$$\text{The bulk modulus } B_T = -V \left(\frac{\partial P}{\partial V} \right)_T$$

$$B_T = \frac{N}{9V} \left[(n+3) \cdot \frac{n\lambda A_n}{R^n} - \frac{4\alpha e^2}{R} \right]$$

$$\text{using } n \text{ evaluated, } 9.4, \text{ and equilibrium condition } \frac{n\lambda A_n}{R^n} = \frac{\alpha e^2}{R}.$$

The strain derivative of B_T is given by:

$$\frac{dB_T}{d \ln R} = \frac{N}{9V} \left[-(n^2 + 6n + 9) \cdot \frac{n\lambda A_n}{R^n} + \frac{16\alpha e^2}{R} \right], \quad \left(= -3 B_T \frac{dB_T}{dP} \right)$$

Table I

Values of the hydrostatic strain derivatives of elastic constants of materials, $\frac{d \ln C}{d \ln r}$.

For reference, values of the elastic constants in units 10^{12} dyne cm.⁻² are placed in parenthesis behind the corresponding strain derivative. The notation $C \equiv C_{44}$, $C' \equiv 1/2(C_{11} - C_{12})$ and $B_s \equiv 1/2(C_{11} + 2C_{12})$ has been used.

| | $\frac{d \ln C}{d \ln r}$ | $\frac{d \ln C'}{d \ln r}$ | $\frac{d \ln B_s}{d \ln r}$ |
|------|---------------------------|----------------------------|-----------------------------|
| Na | -7.2 (0.042) | -7.2 (0.0058) | -10.1 (0.066) |
| Li | -4.1 (0.088) | -2.8 (0.010) | — (0.012) |
| Al | -17.8 (0.283) | -15.2 (0.232) | -14.9 (0.764) |
| Cu | -12.5 (0.751) | -9.93 (0.233) | -16.3 (1.37) |
| Ag | -15.2 (0.461) | -12.73 (0.153) | -18.2 (1.04) |
| Au | -21.2 (0.420) | -14.80 (0.147) | -18.6 (1.73) |
| Ge | -3.6 (0.673) | -0.58 (0.403) | -13.6 (0.751) |
| Si | -3.0 (0.796) | -0.30 (0.511) | -15.3 (0.993) |
| RbI | +5.8 (0.0287) | — (0.112) | — (0.106) |
| NaCl | -1.84 (0.128) | -16.7 (0.184) | -16.4 (0.245) |
| KCl | +3.35 (0.630) | -15.9 (0.170) | -12.2 (0.184) |

The relative contributions of the short-range repulsion to coulombic terms for each are: short range/long range U_0 , 1:9; R_0 , 1:1; B_T , 3:1; dB_T , 10:1.

This sequence illustrates the relative increase in the importance of rapidly varying short-range contributions to the binding energy, as successive derivative quantities are considered. This is relevant even in those materials such as the alkali metals where the ion core contribution to the elastic constants is considered unimportant, since the apparent absence of a short-range contribution to the pressure derivatives provides very convincing evidence of its absence as a contributor to the cohesive energy, the equilibrium condition or the elastic constants. The equations for the contribution of the short-range terms (nearest neighbours only) and the coulomb term to the pure shear stiffnesses in the NaCl structure are:

$$C = \frac{N}{V} \left[2R \cdot \frac{dW}{dR} + 1.28 \frac{e^2}{R} \right]_{R=R_0} \quad C' = \frac{N}{V} \left[R^2 \cdot \frac{d^2W}{dR^2} + R \cdot \frac{dW}{dR} - 1.33 \frac{e^2}{R} \right]_{R=R_0}$$

$$\frac{dC}{d \ln R} = \frac{N}{V} \left[2R^2 \cdot \frac{d^2W}{dR^2} + 4R \cdot \frac{dW}{dR} - 4 \times 1.28 \cdot \frac{e^2}{R} \right]_{R=R_0}$$

$$\frac{dC'}{d \ln R} = \frac{N}{V} \left[R^3 \cdot \frac{d^3W}{dR^3} - 2R \cdot \frac{d^2W}{dR^2} + 4 \times 1.33 \cdot \frac{e^2}{R} \right]_{R=R_0}$$

In these equations $W(R)$ is the repulsive interaction energy of the anion-cation pair. The terms containing e^2/R are the electrostatic contributions to the elastic constants and their derivatives and are due to the change of the Madelung energy by shear strain. Note that because of the geometry of the lattice, the term containing d^2W/dR^2 is absent in the equation for C , and the term containing d^3W/dR^3 is missing from the equation for $dC/d \ln r$. For the power-law potential used above, the equations become:

$$C = \frac{N}{V} \left[-2n \cdot \frac{\lambda A_n}{R_0^n} + 1.28 \cdot \frac{e^2}{R_0} \right], \quad \frac{dC}{d \ln r} = \frac{N}{V} \left[(2n^2 + 6n) \cdot \frac{\lambda A_n}{R_0^n} - 4 \times 1.28 \cdot \frac{e^2}{R_0} \right]$$

$$C' = \frac{N}{V} \left[n^2 \cdot \frac{\lambda A_n}{R_0^n} - 1.33 \cdot \frac{e^2}{R_0} \right], \quad \frac{dC'}{d \ln r} = \frac{N}{V} \left[(n^3 + 3n^2 + 4n) \cdot \frac{\lambda A_n}{R_0^n} + 4 \times 1.33 \cdot \frac{e^2}{R_0} \right]$$

Physically and macroscopically the elastic constant C can be thought of as the stress-strain ratio for a simple infinitesimal strain changing only the angles between [100] type directions of the crystal and C' as the same ratio for an infinitesimal volume conserving strain generated by compressing one cubic direction of the crystal to $1 - \delta$, expanding another to $1/(1 - \delta)$. These are shown in Fig. 5. The contributions arise from the second derivative of the crystal energy by