

only of U'_{i1} , but also of ion-electron and electron-electron interactions, to be denoted by U'_{ie} and U'_{ee} , respectively. For a metal, the jellium model (a lattice of positive point ions embedded in a uniform sea of electrons) will be used here. This is the model used for the electrostatic energy in the pseudopotential theory of metals.¹² Denoting the uniform electron density by $n_0 = Z \langle \mathfrak{z} \rangle / \Omega_0$, it follows that

$$U'_{ie} + U'_{ee} = - \frac{Ze^2}{\lambda \Omega_0} \frac{1}{s N_{\text{cell}}} \times \sum_{\nu} \mathfrak{z}_{\nu} \int_{\Omega'} d^3 x' \frac{n_0' \lambda}{|\vec{x}' - \vec{R}'(\nu)|} + \frac{e^2}{2\lambda \Omega_0} \frac{1}{s N_{\text{cell}}} \int_{\Omega'} d^3 y' \int_{\Omega'} d^3 x' \frac{(n_0')^2 \lambda}{|\vec{y}' - \vec{x}'|}, \quad (9)$$

where N_{cell} is the number of unit cells. Changing variables of integration leads to $U'_{ie} = -2U'_{ee}$, and then using the Γ -function definition, it follows that¹³

$$U'_{ie} + U'_{ee} = -U'_{ee} = - \frac{Z^2 e^2}{2\lambda \Omega_0} \sigma^{-1} \left(\frac{\lambda^3}{\Omega_0'} \right) \langle \mathfrak{z} \rangle^2 (1+D). \quad (10)$$

Thus, the electrostatic energy density U'_{es} for both metallic and ionic structures may be written

$$U'_{\text{es}} = \frac{Z^2 e^2}{2\Omega_0 \lambda} \left[\sigma^{1/2} \frac{1}{s} \sum'_{\nu\mu} \mathfrak{z}_{\nu} \mathfrak{z}_{\mu} \Phi_{-1/2} \left(\frac{\sigma \pi |\vec{R}'(\nu\mu)|^2}{\lambda^2} \right) + \sigma^{-1} \frac{\lambda^3}{\Omega_0'} \sum'_{\mu} |S'(\vec{G}'(\mu))|^2 \Phi_0 \left(\frac{\lambda^2 |\vec{G}'(\mu)|^2}{4\pi\sigma} \right) - 2\sigma^{1/2} \langle \mathfrak{z}^2 \rangle - \sigma^{-1} \frac{\lambda^3}{\Omega_0'} \langle \mathfrak{z} \rangle^2 \right], \quad (11)$$

remembering that $\langle \mathfrak{z} \rangle = 0$ for ionic structures. The parameter σ is a convergence parameter and is usually chosen so that the real-lattice and reciprocal-lattice sums converge at about the same rate. However, results are independent of the choice for σ .

There are two choices for the parameter λ which are of particular interest here. For $\lambda = (\Omega_0')^{1/3}$, all the strained-volume dependence of U'_{es} is contained in the $(1/\Omega_0')^{1/3}$ factor outside of the square bracket in Eq. (11), and the square bracket contains only volume-conserving shear dependence. This choice is convenient for taking Fuchs-type strain derivatives of U'_{es} . The second choice, and the one to be used throughout this paper, is $\lambda = (\Omega_0)^{1/3}$. This choice is convenient for differentiating U'_{es} with respect to the Lagrangian strain parameters,

$$\eta_{ij} = \frac{1}{2} (J_{ki} J_{kj} - \delta_{ij}), \quad (12)$$

where repeated indices are to be summed and δ_{ij} is the Kronecker δ . The transformation coefficients are given by

$$J_{ij} = \frac{\partial x'_i}{\partial x_j}, \quad (13)$$

where \vec{x} and \vec{x}' are the position vectors of a material particle in the initial and deformed states, respectively. Derivatives of U'_{es} with respect to η_{ij} give directly the electrostatic contributions to the Brugger-type elastic constants, which will be discussed in Sec. III.

By performing the appropriate lattice and reciprocal-lattice sums in Eq. (11), the electrostatic energy for any given metallic or ionic structure can be obtained. For metallic structures, the electrostatic energy per ion is usually written in the form

$$E_{\text{es}} (\text{per ion}) = \Omega_0 U_{\text{es}} = \alpha_a \left(\frac{Z^2 e^2}{a} \right) = \alpha_0 \left(\frac{Z^2 e^2}{2r_0} \right), \quad (14)$$

where a is the lattice constant and r_0 is the radius of the ionic sphere, given by $\frac{4}{3} \pi r_0^3 = \Omega_0$. Similarly for ionic structures, the electrostatic energy per molecule is written

$$E_{\text{es}} (\text{per molecule}) = 2\Omega_0 U_{\text{es}} = \alpha_a \left(\frac{Z^2 e^2}{a} \right) = \alpha_R \left(\frac{Z^2 e^2}{R} \right), \quad (15)$$

where R is the nearest-neighbor distance. The α coefficients entering in Eqs. (14) and (15) are known as geometric coefficients when referring to metals, and as Madelung constants when referring to ionic structures. We have evaluated these coefficients for six metallic and five ionic structures and have listed the results in Table I. For those structures involving a c/a ratio, the evaluations were performed for the case of ideal close packing of spheres, i. e., $c/a = 1$ for the simple hexagonal structure, and $c/a = \sqrt{3/2}$ for the hcp and WC-type structures. For the wurtzite structure, $c/a = \sqrt{8/3}$ and $u = \frac{3}{8}$, which gives equal bond lengths and bond angles.

III. GENERAL EXPRESSIONS FOR BRUGGER ELASTIC CONSTANTS

Having determined the electrostatic energy density of a deformed lattice, one can now calculate the electrostatic contributions to the elastic constants by the method of homogeneous deformation. Since internal-strain effects may be treated separately (see Appendix A), here we will only consider the case of zero internal strain, i. e., $\vec{w} = 0$. Internal-strain contributions to the elastic constants will be treated in Sec. IV. The Lagrangian strain derivatives of U'_{es} can be easily performed

(see Appendix B), thus yielding the electrostatic Brugger elastic constants

$$C_{ijkl\dots}^{es} \equiv \left(\frac{\partial^n U_{es}(\vec{\eta}, \vec{w}=0)}{\partial \eta_{ij} \partial \eta_{kl} \dots} \right)_{\vec{\eta}=0} \quad (16)$$

Introducing the dimensionless parameters $\vec{r} = \vec{R}(r_0/\Omega_0)^{1/3}$ and $\vec{g} = \Omega_0^{1/3} \vec{G}(h)/2\pi$, the expressions for the first-, second-, and third-order elastic constants are

$$C_{ij}^{es} = -\frac{Z^2 e^2}{2\Omega_0^{4/3}} \left\{ \sigma^{1/2} (1/s) \sum'_{\nu\mu} \partial_\nu \partial_\mu (2\pi\sigma) r_i r_j \Phi_{+1/2}(\sigma\pi|\vec{r}|^2) + \sigma^{-1} \sum'_h |S(\vec{g})|^2 [X_{ij} \Phi_0(\sigma^{-1}\pi|\vec{g}|^2) - (2\pi\sigma^{-1}) g_i g_j \Phi_{+1}(\sigma^{-1}\pi|\vec{g}|^2)] - \sigma^{-1} \langle \partial \rangle^2 X_{ij} \right\}, \quad (17)$$

$$C_{ijkl}^{es} = \frac{Z^2 e^2}{2\Omega_0^{4/3}} \left\{ \sigma^{1/2} (1/s) \sum'_{\nu\mu} \partial_\nu \partial_\mu (2\pi\sigma)^2 r_i r_j r_k r_l \Phi_{+3/2}(\sigma\pi|\vec{r}|^2) + \sigma^{-1} \sum'_h |S(\vec{g})|^2 [X_{ijkl} \Phi_0(\sigma^{-1}\pi|\vec{g}|^2) - (2\pi\sigma^{-1}) Y_{ijkl} \Phi_{+1}(\sigma^{-1}\pi|\vec{g}|^2) + (2\pi\sigma^{-1})^2 g_i g_j g_k g_l \Phi_{+2}(\sigma^{-1}\pi|\vec{g}|^2)] - \sigma^{-1} \langle \partial \rangle^2 X_{ijkl} \right\}, \quad (18)$$

and

$$C_{ijklmn}^{es} = \frac{Z^2 e^2}{2\Omega_0^{4/3}} \left\{ \sigma^{1/2} (1/s) \sum'_{\nu\mu} \partial_\nu \partial_\mu (2\pi\sigma)^3 r_i r_j r_k r_l r_m r_n \Phi_{+5/2}(\sigma\pi|\vec{r}|^2) + \sigma^{-1} \sum'_h |S(\vec{g})|^2 [X_{ijklmn} \Phi_0(\sigma^{-1}\pi|\vec{g}|^2) - (2\pi\sigma^{-1}) Y_{ijklmn} \Phi_{+1}(\sigma^{-1}\pi|\vec{g}|^2) + (2\pi\sigma^{-1})^2 Z_{ijklmn} \Phi_{+2}(\sigma^{-1}\pi|\vec{g}|^2) - (2\pi\sigma^{-1})^3 g_i g_j g_k g_l g_m g_n \Phi_{+3}(\sigma^{-1}\pi|\vec{g}|^2)] - \sigma^{-1} \langle \partial \rangle^2 X_{ijklmn} \right\}, \quad (19)$$

where

$$X_{ij} = \delta_{ij}, \quad (20)$$

$$X_{ijkl} = \delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}, \quad (21)$$

$$Y_{ijkl} = g_i g_j \delta_{kl} + g_k g_l \delta_{ij} + g_i g_k \delta_{jl} + g_i g_l \delta_{jk} + g_j g_k \delta_{il} + g_j g_l \delta_{ik}, \quad (22)$$

$$X_{ijklmn} = \delta_{ij} X_{klmn} + \delta_{ik} X_{jlmn} + \delta_{il} X_{jkmn} + \delta_{im} X_{kljn} + \delta_{in} X_{kljm}, \quad (23)$$

$$Y_{ijklmn} = g_i g_j X_{klmn} + g_i g_k X_{jlmn} + g_i g_l X_{jkmn} + g_i g_m X_{kljn} + g_i g_n X_{kljm} + g_j g_k X_{ilmn} + g_j g_l X_{ikmn} + g_j g_m X_{klin} + g_j g_n X_{klim} + g_k g_l X_{ijmn} + g_k g_m X_{ijln} + g_k g_n X_{ijlm} + g_l g_m X_{ijkn} + g_l g_n X_{ijkm} + g_m g_n X_{ijkl}, \quad (24)$$

and

$$Z_{ijklmn} = g_i g_j (Y_{klmn} - g_k g_l \delta_{mn}) + g_k g_l (Y_{mnij} - g_m g_n \delta_{ij}) + g_m g_n (Y_{ijkl} - g_i g_j \delta_{kl}). \quad (25)$$

It is easily seen that the coefficients $X_{ij\dots}$, $Y_{ijkl\dots}$, and Z_{ijklmn} , and thus the elastic constants $C_{ij\dots}^{es}$, satisfy Cauchy relations, i. e., the ordering of the subscripts is immaterial. Therefore, in general, all the elastic constants (through third order) can be obtained from only two types of first-order constants C_{II}^{es} and C_{JK}^{es} ; four types of second-order constants C_{IIII}^{es} , C_{IIJJ}^{es} , C_{JJJK}^{es} , and C_{IIJK}^{es} ; and seven types of third-order constants C_{IIIII}^{es} ,

C_{IIIIJJ}^{es} , C_{IIJJKK}^{es} , C_{JJJJJK}^{es} , C_{JJJKKK}^{es} , C_{IIIIJK}^{es} , and C_{IIJJJK}^{es} , where the subscripts run from 1 to 3 with $I \neq J \neq K$. For these types, the elastic constants with Cauchy relations have been listed in Table II. In that table, as well as the remainder of this paper, Voigt (reduced) notation is used for the subscripts whenever referring to specific

TABLE I. Geometric coefficients for six metallic structures and Madelung constants for five ionic structures. For metals, the electrostatic energy per ion is $\alpha_a(Z^2e^2/a) = \alpha_0(Z^2e^2/2r_0)$, where a is the lattice constant and r_0 is the radius of the ionic sphere. For the ionic structures, the electrostatic energy per molecule is $\alpha_a(Z^2e^2/a) = \alpha_R(Z^2e^2/R)$, where R is the nearest-neighbor distance.

| Metallic | α_a | α_0 |
|------------------|-----------------|-----------------|
| simple cubic | -1.418 648 7397 | -1.760 118 8842 |
| fcc | -2.292 431 0371 | -1.791 747 2304 |
| bcc | -1.819 616 7248 | -1.791 858 5114 |
| diamond | -2.693 399 0221 | -1.670 851 4055 |
| simple hexagonal | -1.497 855 9763 | -1.771 389 4740 |
| hcp | -1.620 929 3075 | -1.791 676 2409 |
| Ionic | α_a | α_R |
| NaCl type | -3.495 129 1893 | -1.747 564 5946 |
| CsCl type | -2.035 361 5095 | -1.762 674 7731 |
| zinc blende | -3.782 926 1041 | -1.638 055 0534 |
| WC type | -1.235 585 6381 | -1.235 585 6381 |
| wurtzite | -2.680 266 9939 | -1.641 321 6274 |