

Derivation of elastic constants from the embedded-atom potential in a lattice model

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(Received 26 December 1991; revised manuscript received 19 May 1992)*

Empirical N -body potentials, such as the embedded-atom potentials [M.S. Daw, and M. I. Baskes, *Phys. Rev. B* **29**, 6443 (1984)]; have recently been used to describe the atomic interactions in hexagonal close-packed (hcp) structures and are in principle suited to describe the interactions in less symmetric structures. But together with the decreasing symmetry in the lattices studied, the relations used to fit the potential parameters to elastic constant data are not valid anymore. In noncentrosymmetric lattices the elastic constants are composed of a homogeneous and an inhomogeneous contribution, but the latter contribution is usually not taken into consideration. In this paper a rigorous derivation of the expressions for elastic constants from the embedded-atom total-energy function is given. These expressions have been applied to potentials previously derived for hcp metals, showing that the inhomogeneous contribution for most of these potentials should not be neglected. Furthermore we will argue that the Raman frequencies can be used as empirical data to fit the relative magnitudes of the homogeneous and inhomogeneous contributions to the elastic constants.

I. INTRODUCTION

Semiempirical atomistic simulations have become an important tool in the study of the structure and properties of materials. The atomic interactions are described with a semiempirically fitted potential function. Pair potentials have been popular in describing metallic bonding because of their computational simplicity. But they suffer from two major shortcomings. First the vacancy formation energy for a given potential is always the same as the cohesive energy, and second the elastic constants always satisfy the Cauchy relation $C_{11} = C_{44}$.¹ These problems can be overcome by including a volume-dependent energy term,¹ introducing many-body interactions, but this term is poorly defined near extended defects and surfaces.

Daw and Baskes² developed an alternative model known as the embedded-atom method (EAM), based on density-functional and effective-medium theory.³⁻⁵ As with pair-potential models, the energetics of an arbitrary arrangement of atoms can be calculated quickly, but the ambiguity of the volume dependence is avoided, while including many-body interactions. Finnis and Sinclair⁶ developed independently a model (FS) which is mathematically equivalent to the EAM, but has been deduced using the second-moment approximation to the density of states in the tight-binding method.⁷ Ercolessi, Tosatti, and Parrinello⁸ have used the same approach and refer to their work as the "glue" model. We will refer to these potentials as N -body potentials.

Since their development, N -body potentials have been successfully applied in a number of studies in transition and noble metals, including, for example, analysis of surface relaxations and reconstructions,^{2,9-14} studies of

point defects,^{6,12,15,16} grain boundaries,^{12,14,17-19} structures of liquids,²⁰ surface self-diffusion,²¹ structural transformations,²² and bulk and surface phonons.²³⁻²⁵

The FS potentials have originally been constructed for body-centered-cubic (bcc) metals^{6,26} but they have been applied to face-centered-cubic (fcc) noble metals and Ni too.¹² Conversely, the EAM has mostly been used in studies of materials with close-packed cubic structures (fcc metals and L_1_2 ordered alloys) and recently it has been extended to bcc metals²⁷⁻²⁹ giving a fairly successful description of many physical properties. Recently, both the EAM and the FS method have been applied to hcp transition metals^{22,30-32} and attempts are being made to describe the atomic interactions in silicon in the framework of the EAM.^{33,34} So, an important feature of the N -body potentials is that they can be used, at least in principle, as an empirical scheme for the description of atomic interactions in less symmetric structures.

In the process of developing an interatomic potential for a particular material, elastic-constant data are commonly used as experimental input. But with the decreasing symmetry in the lattices studied, the relations for the elastic constants derived before^{2,6,12} do not hold. As we will show, they were derived using the method of homogeneous deformations, which has never been explicitly mentioned. In noncentrosymmetric lattices this method cannot be applied straightforwardly. Born and Huang³⁵ pointed out that in noncentrosymmetric lattices the elastic constants are composed of two terms. The first term is related to a homogeneous strain in the system, while the second term arises due to the possible relative displacements of different sublattices when a macroscopic homogeneous strain is applied. Wallace³⁶ and Martin^{37,38} analyzed the elastic constants in detail and showed that

the influence of sublattice relaxations for hcp and diamond crystals cancels out for pair potentials. For many-body potentials, however, they showed that this contribution does not cancel out and has to be included in the evaluation of the elastic constants. However, most authors developing potentials for hcp metals did not discuss the occurrence of the second term,^{22,30,32} or did not evaluate it, but stated that it was negligible.³¹ Furthermore, in Ref. 34 it was shown that for a diamond cubic material, simulated with an angular modified EAM potential, the inhomogeneous contribution to the elastic shear constant is significant, clearly indicating the need for a more rigorous analysis of the inhomogeneous contributions to elastic constants in N -body potentials.

Thus, whereas pair potentials are mainly applied to metals with cubic lattices, the field of application of the N -body potentials is recently being extended to describe structures with increasing complexity. At the same time, however, the basic equations used to calculate elastic constants have not been modified to cope with these structures. But very often the elastic constants are the main experimental data used in the process of fitting the model parameters to the properties of the metal. And they play an essential role in determining if the model can simulate the behavior of the material adequately.

The aim of this paper is to derive expressions for the elastic constants for crystals with arbitrary symmetry from the EAM potential functions. We will discuss the approximations made to arrive at these expressions and review the derivation of the elastic constants for a general many-body potential. We will follow the discussion of Wallace,³⁶ starting in Sec. II with the thermodynamic definition of the elastic constants, introducing the different strain parameters. Then we introduce the general crystal potential expansion and give a summary of the derivation of the elastic constants from this expansion.

In Sec. III we derive the potential-energy coefficients for the EAM potential, substitute them in the equations for the elastic constants, and derive simplified expressions. The EAM was chosen because it provides a framework for the application to alloy systems, and it gives a possibility of fitting the embedding function to a larger range of electron densities,³⁰ instead of one equilibrium electron density. But the extension to the FS model is straightforward.

In Sec. IV we discuss the application of these expressions to hcp metals. We will show that neglecting the inhomogeneous contribution to the elastic constants is not always justified. We conclude this paper with a discussion of the main points.

II. DEFINITION OF ELASTIC CONSTANTS

Thermodynamic definition

When we consider the crystal to be a homogeneous, anisotropic elastic medium, the homogeneous strains due to a uniform stress can be described with the nine independent displacement gradients $u_{ij} = \partial u_i / \partial X_j$. Here \mathbf{u} denotes the displacement vector of a small element of

mass, \mathbf{X} and \mathbf{x} are the initial and final positions of this element, respectively, and i, j are Cartesian coordinates. The displacement gradients give a complete description of the deformation of the crystal, including the rotational component. This rotational component, however, can be avoided by applying a symmetrical stress. Therefore, the Lagrangian strain parameters are introduced,

$$\eta_{ij} = \frac{1}{2} \left[u_{ij} + u_{ji} + \sum_k u_{ki} u_{kj} \right], \quad (1)$$

which are rotational invariant. They define the change in length of a vector, $\Delta \mathbf{X}$, due to the homogeneous deformation

$$|\Delta \mathbf{x}|^2 - |\Delta \mathbf{X}|^2 = 2 \sum_{ij} \eta_{ij} \Delta X_i \Delta X_j. \quad (2)$$

The equilibrium thermodynamic definition of the elastic constants follows now by expanding the thermodynamic state functions in powers of the Lagrangian strains. The internal energy U , for example, can be considered as a function of the configuration and entropy, S , so that

$$\begin{aligned} U(\mathbf{x}, S) &= U(\mathbf{X}, \eta_{ij}, S) \\ &= U(\mathbf{X}, S) + V \sum_{ij} C_{ij}^S \eta_{ij} \\ &\quad + \frac{1}{2} V \sum_{ijkl} C_{ijkl}^S \eta_{ij} \eta_{kl} + \dots, \end{aligned} \quad (3)$$

defining the adiabatic elastic constants C^S , where V is the volume of the system. Similarly, the expansion of the Helmholtz free energy, F , in powers of the Lagrangian strains, defines the isothermal elastic constants C^T . The first-order elastic constants are equal to the stresses applied to the system, $C_{ij} = \tau_{ij}$, and the condition that the applied stresses are zero, $\tau_{ij} = 0$, provides a logical equilibrium condition for the crystal.

It is useful to consider also the expansion of the thermodynamic state functions in the displacement gradients, which give a full description of the distortion of the crystal. The expansion of the internal energy

$$\begin{aligned} U(\mathbf{X}, u_{ij}, S) &= U(\mathbf{X}, S) + V \sum_{ij} A_{ij}^S u_{ij} \\ &\quad + \frac{1}{2} V \sum_{ijkl} A_{ijkl}^S u_{ij} u_{kl} + \dots \end{aligned} \quad (4)$$

defines the so-called adiabatic wave propagation coefficients A^S . By substituting the Lagrangian strains, Eq. (1), in the expansion, Eq. (3), the relation between the wave propagation and elastic constants is easily found to be

$$A_{ij} = C_{ij}, \quad (5)$$

$$A_{ijkl} = C_{ji} \delta_{ik} + C_{ijkl}, \quad (6)$$

where δ_{ik} is the Kronecker delta. The elastic constants have complete Voigt symmetry, i.e., they are invariant for interchanging the indices i and j , or the pairs ij and kl . Therefore each pair of Cartesian coordinates can be replaced by a single Voigt index α .

The crystal potential energy

We will now consider the crystal to be a finite array of interacting atoms in the presence of externally applied forces, neglecting surface effects. We will denote the equilibrium positions of the atoms by $\mathbf{R}(M\mu) = \mathbf{R}(M) + \mathbf{R}(\mu)$, where M labels the unit cell and μ the atom in the cell. The total potential energy of the crystal, Φ , is presumed to be a function of the configuration only. We can now expand the potential energy in the displacements of the atoms from the initial position, $\mathbf{U}(M\mu)$,

$$\begin{aligned} \Phi = & \Phi_0 + \sum_{M\mu} \sum_i \Phi_i(M\mu) U_i(M\mu) \\ & + \frac{1}{2} \sum_{MN\mu\nu} \sum_{ij} \Phi_{ij}(M\mu, N\nu) U_i(M\mu) U_j(N\nu) \\ & + \frac{1}{3!} \sum_{MNP\mu\nu\pi} \sum_{ijk} \Phi_{ijk}(M\mu, N\nu, P\pi) \\ & \quad \times U_i(M\mu) U_j(N\nu) U_k(P\pi) + \dots \end{aligned} \quad (7)$$

Here Φ_0 is the potential energy for the equilibrium configuration and the potential-energy coefficients $\Phi_i(M\mu)$, $\Phi_{ij}(M\mu, N\nu)$, \dots , are obviously derivatives of the potential, evaluated at the equilibrium configuration,

$$\Phi_i(M\mu) = \partial\Phi / \partial U_i(M\mu), \quad (8)$$

$$\Phi_{ij}(M\mu, N\nu) = \partial^2\Phi / \partial U_i(M\mu) \partial U_j(N\nu). \quad (9)$$

External forces enter these equations only implicitly, since they determine the equilibrium configuration $\mathbf{R}(M\mu)$, around which the potential Φ is expanded. Now explicitly consider a force $\mathbf{f}(M\mu)$ applied on atom $M\mu$. For a virtual process in which the crystal is deformed while the external forces are held constant, the work done by the external forces on atom $M\mu$ is

$$W(\mathbf{R}(M\mu)) = \sum_i f_i(M\mu) U_i(M\mu), \quad (10)$$

so that the expansion of the system potential, $\Psi(\mathbf{R}(M\mu)) = \Phi(\mathbf{R}(M\mu)) - W(\mathbf{R}(M\mu))$, in the displacements is

$$\begin{aligned} \Psi = & \Psi_0 + \sum_{M\mu} \sum_i [\Phi_i(M\mu) - f_i(M\mu)] U_i(M\mu) \\ & + \frac{1}{2} \sum_{MN\mu\nu} \sum_{ij} \Phi_{ij}(M\mu, N\nu) U_i(M\mu) U_j(N\nu) + \dots \end{aligned} \quad (11)$$

Equilibrium, invariance, and stability

For the system to be in equilibrium, the total force $\partial\Psi / \partial U_i(M\mu)$ on each atom must vanish:

$$\Phi_i(M\mu) - f_i(M\mu) = 0, \quad \forall M, \mu, i. \quad (12)$$

The macroscopic equilibrium condition requires the total applied force and the total applied torque to be zero [with the help of Eq. (12)]:

$$\sum_{M\mu} f_i(M\mu) = \sum_{M\mu} \Phi_i(M\mu) = 0, \quad \forall i; \quad (13)$$

and

$$\sum_{M\mu} f_i(M\mu) R_j(M\mu) \quad (14)$$

is symmetric in $i, j \forall i, j$ since the collection of atoms representing a crystal should not experience a net force or torque as a result of the interactions among the atoms.

The invariance conditions require the total system potential to be invariant under translation or rotation of the entire system of atoms and external forces. Wallace³⁶ showed that these conditions put the following constraints on the second-order potential coefficients: translational invariance

$$\sum_{N\nu} \Phi_{ij}(M\mu, N\nu) = 0, \quad \forall M, \mu, i, j \quad (15)$$

and rotational invariance

$$\sum_{N\nu} \Phi_{ij}(0\mu, N\nu) R_k(N\nu) + \Phi_j(0\mu) \delta_{ik}, \quad (16)$$

is symmetric in $j, k \forall \mu, i$. The equilibrium and invariance conditions place restrictions upon the potential-energy coefficients, and these conditions must be satisfied by any physically acceptable model for the interactions among the atoms in a crystal.

Stability requires that the system potential Ψ for the equilibrium configuration of atoms plus external forces is at a minimum with respect to arbitrary small displacements of the atoms from equilibrium. This condition is satisfied if the homogeneous quadratic form in the expansion, Eq. (11), is positive definite, i.e., positive for any value of the displacements $U_i(M\mu)$,

$$[\Phi_{ij}(M\mu, N\nu)] > 0. \quad (17)$$

Strain expansions of the potential

For simplicity, the external forces will be restricted to surface forces, representing arbitrary mechanical stresses applied to the crystal, so that

$$f_i(M\mu) = \Phi_i(M\mu) = 0, \quad \forall M, \mu, i \quad (18)$$

in the interior of the material.

In the following, the calculations are the mechanical analog of the thermodynamics of the preceding section. The potential energy can be considered to be an approximation of the thermodynamic state functions, namely the potential approximation. In this approximation the equivalents of the stresses and elastic constants are given by strain derivatives of Φ .

The displacement of the atoms from the initial equilibrium configuration, for a homogeneous deformation, does not have to be strictly homogeneous. The atoms in the different sublattices can undergo a displacement relative to the lattice, a sublattice displacement $\mathbf{S}(\mu)$. Therefore the displacement of the atoms under a homogeneous deformation u_{ij} can be expressed as

$$U_i(M\mu) = S_i(\mu) + \sum_j u_{ij} R_j(M\mu). \quad (19)$$

Now substitute the atomic displacements in the potential-energy expansion, Eq. (7), and eliminate the

sublattice displacements, being dependent variables, in favor of the displacement gradients

$$\Phi = \Phi_0 + V \sum_{ij} \tilde{A}_{ij} u_{ij} + \frac{1}{2} V \sum_{ijkl} \tilde{A}_{ijkl} u_{ij} u_{kl} + \dots \quad (20)$$

This equation defines formally the mechanical analog of the wave propagation coefficients \tilde{A} in terms of the potential-energy coefficients. Similarly the crystal potential can be expanded in the η_{ij} ,

$$\Phi = \Phi_0 + V \sum_{ij} \tilde{C}_{ij} \eta_{ij} + \frac{1}{2} V \sum_{ijkl} \tilde{C}_{ijkl} \eta_{ij} \eta_{kl} + \dots, \quad (21)$$

defining the mechanical equivalents of the elastic constants. However, an expression like Eq. (19) for the Lagrangian strains is not so easily established. It is more convenient to derive expressions for the \tilde{A} coefficients and calculate \tilde{C} with the aid of Eqs. (5) and (6). Henceforth in this paper, terms of higher order than quadratic in the strain parameters will not be considered.

Wallace³⁶ performed the expansion of the crystal potential in the displacement gradients and we will shortly discuss his derivation. After substituting the atomic displacements for a homogeneous deformation, Eq. (19), in the displacement expansion of the potential, Eq. (7), we find

$$\begin{aligned} \Phi = & \Phi_0 + \sum_{M\mu} \sum_i \Phi_i(M\mu) [S_i(\mu) + \sum_j u_{ij} R_j(M\mu)] \\ & + \frac{1}{2} \sum_{MN\mu\nu} \sum_{ij} \Phi_{ij}(M\mu, N\nu) \\ & \times \left\{ S_i(\mu) S_j(\nu) + 2S_i(\mu) \sum_k u_{jk} R_k(N\nu) \right. \\ & \left. + \sum_{kl} u_{ik} u_{jl} R_k(M\mu) R_l(N\nu) \right\}. \quad (22) \end{aligned}$$

The \sum_M in the first term involving $S_i(\mu)$ in Eq. (22) is the same for all atoms in the interior, so it may be evaluated at $\mathbf{R}(0\mu)=0$ and multiplied by N_0 to account for the \sum_M ,

$$\sum_{M\mu} \sum_i \Phi_i(M\mu) S_i(M\mu) = N_0 \sum_{\mu} \sum_i \Phi_i(0\mu) S_i(0\mu) = 0, \quad (23)$$

since $\Phi_i(0\mu)=0$. Since this term vanishes, the sublattice displacements do not influence the stresses and the $S_i(\mu)$ need to be determined only to first order in the u_{ij} .

Solving the sublattice displacements to first order in u_{ij} by requiring that the net force on each atom is zero results in a set of inhomogeneous equations for the $S_j(\nu)$;

$$\begin{aligned} \sum_{N\nu} \sum_j \Phi_{ij}(0\mu, N\nu) S_j(\nu) \\ = - \sum_{N\nu} \sum_{jk} \Phi_{ij}(0\mu, N\nu) R_k(N\nu) u_{jk}. \quad (24) \end{aligned}$$

Translational invariance, Eq. (15), leads to solutions $\mathbf{S}(\nu)=\mathbf{T}$, with $u_{jk}=0$. These correspond to a general displacement \mathbf{T} of the lattice. This ambiguity can be removed by setting the sublattice displacement at zero for

any desired sublattice σ , $\mathbf{S}(\sigma)=0$. Then the homogeneous equations are considered only for $\mu, \nu \neq \sigma$ and the $(3n-3)(3n-3)$ matrix of coefficients $\sum_N \Phi_{ij}(0\mu, N\nu)$ is no longer singular and may be inverted by a real symmetric matrix Γ ,

$$\sum_{\mu i} \Gamma_{ki}(\pi, \mu) \sum_N \Phi_{ij}(0\mu, N\nu) = \delta_{kj} \delta_{\pi\nu}, \quad \pi, \mu, \nu \neq \sigma. \quad (25)$$

For convenience, set $\Gamma_{ij}(\mu, \nu)=0$ for $\mu, \nu=\sigma$. With these equations the inhomogeneous equations are solved for $S_i(\mu)$, $\mu \neq \sigma$, to give

$$S_i(\mu) = - \sum_{N\nu\pi} \sum_{jkl} \Gamma_{ij}(\mu, \nu) \Phi_{jk}(0\nu, N\pi) R_l(N\pi) u_{kl}, \quad (26)$$

and $S_i(\sigma)=0$. The solution for the sublattice displacements can be abbreviated by introducing the coefficient

$$X_{i,jk}(\mu) = - \sum_{N\nu\pi} \sum_l \Gamma_{il}(\mu, \nu) \Phi_{lj}(0\nu, N\pi) R_k(N\pi). \quad (27)$$

Then the $S_i(\mu)$ are related to the strains u_{ij} by

$$S_i(\mu) = \sum_{jk} X_{i,jk}(\mu) u_{jk}. \quad (28)$$

Elimination of the sublattice displacements from the expansion, Eq. (22), and comparison with the expansion of Φ in powers of u_{ij} , Eq. (20), gives the \tilde{A} coefficients,

$$\begin{aligned} \tilde{A}_{ij} = & V^{-1} \sum_{M\mu} \Phi_i(M\mu) R_j(M\mu), \quad (29) \\ \tilde{A}_{ijkl} = & V^{-1} \left\{ \sum_{MN\mu\nu} \Phi_{ik}(M\mu, N\nu) R_j(M\mu) R_l(N\nu) \right. \\ & + N_0 \sum_{N\mu\nu} \sum_m \Phi_{mk}(0\mu, N\nu) \\ & \left. \times R_l(N\nu) X_{m,ij}(\mu) \right\}, \quad (30) \end{aligned}$$

where V is the volume of the system and N_0 the number of unit cells in the system. The \tilde{A}_{ijkl} coefficients are composed of two terms. The first term is related to the homogeneous strain in the system, while the second term arises from the possible sublattice displacements when a homogeneous strain is applied. The sublattice displacements, and with it the second contribution, will disappear for lattices with inversion symmetry, this can be seen by writing the right-hand side of Eq. (24) for the $S_j(\nu)$ as

$$- \sum_{N\nu} \sum_{jk} \Phi_{ij}(0\mu, N\nu) [R_k(N\nu) - R_k(\mu)] u_{jk}, \quad (31)$$

where the added term in $R_k(\mu)$ vanishes by translational invariance. The $\sum_{N\nu}$ counts atoms at $\pm[R_k(N\nu) - R_k(\mu)]$, for which $\Phi_{ij}(0\mu, N\nu)$ is the same by inversion symmetry, and hence the sum vanishes for any j, k, l . Therefore all $S_i(\mu)$ vanish.

Now with Eqs. (5) and (6) expressions for the elastic constants can be derived. After evaluating Eq. (29) in the interior of the crystal, the first-order elastic constants follow,

$$\tilde{C}_{ij} = V_C^{-1} \sum_{\mu} \Phi_i(0\mu) R_j(0\mu), \quad (32)$$

where $V_C = V/N_0$ is the volume per unit cell. To eliminate surface effects from the first term in Eq. (30), take a combination symmetric in j, l , and define this combination as

$$\tilde{A}_{ikjl} = \frac{1}{2}(\tilde{A}_{ijkl} + \tilde{A}_{ilkj}) . \quad (33)$$

With this definition

$$\hat{A}_{ikjl} = \frac{1}{2}V_C^{-1} \left\{ - \sum_{N\mu\nu} \Phi_{ik}(0\mu, N\nu)[R_j(N\nu) - R_j(\mu)][R_l(N\nu) - R_l(\mu)] \right. \\ \left. + \sum_{N\mu\nu} \sum_m \Phi_{mk}(0\mu, N\nu)[R_l(N\nu)X_{m,ij}(\mu) + R_j(N\nu)X_{m,il}(\mu)] \right\} . \quad (34)$$

And with this definition, expressions for the \tilde{A} and \tilde{C} coefficients can be derived,

$$\tilde{A}_{ijkl} = \hat{A}_{ikjl} + \hat{A}_{jkil} - \hat{A}_{ijkl} - \tilde{C}_{il}\delta_{jk} + \tilde{C}_{kl}\delta_{ij} , \quad (35)$$

$$\tilde{C}_{ijkl} = \hat{A}_{ikjl} + \hat{A}_{jkil} - \hat{A}_{ijkl} - \tilde{C}_{jl}\delta_{ik} - \tilde{C}_{il}\delta_{jk} + \tilde{C}_{kl}\delta_{ij} . \quad (36)$$

III. THE EAM INTERATOMIC POTENTIAL

EAM potential-energy coefficients

In the preceding section expressions were derived for the (mechanical approximation of the) elastic constants, starting with the assumption that the potential energy can be described with a function of the atomic coordinates. We will now apply this formulation to the EAM.² In the literature, expressions for the elastic constants, derived from the EAM potentials, have been given.^{2,6,12} However, these expressions were always restricted to crystals with lattices which satisfy inversion symmetry. The formulation given in Sec. II is valid for all Bravais lattices with an arbitrary number of atoms per unit cell.

In the EAM the energy of each atom is computed from the energy needed to embed the atom in the local electron density as provided by the other atoms of the metal, supplied with an energy contribution due to the core-core overlap. The electron density is approximated by the superposition of atomic electron densities, while the core-core overlap is assumed to be a pair potential with a Coulombic origin.

Computationally, the EAM can be evaluated with

about the same amount of work as for simple pair potentials. Therefore, it is feasible to perform large-scale computer simulations for a wide variety of phenomena and the EAM provides a powerful technique for atomistic calculations of metallic systems. Finnis and Sinclair⁶ developed independently a model (FS) which is mathematically equivalent to the EAM but which has a different physical interpretation.

The basic equations, defining the potential energy, of the embedded-atom method are

$$\Phi = \sum_{M\mu} f_{\mu}(\rho^a(M\mu)) + \frac{1}{2} \sum_{M\mu} \sum_{N\nu \neq M\mu} \varphi_{\mu\nu}(R(M\mu, N\nu)) , \quad (37)$$

$$\rho^a(M\mu) = \sum_{N\nu \neq M\mu} \rho_{\nu}(R(M\mu, N\nu)) , \quad (38)$$

where $\rho_{\nu}(R(M\mu, N\nu))$ is the electron density at location $M\mu$ due to atom $N\nu$, $\rho^a(M\mu)$ is the total electron density at location $M\mu$, due to all surrounding atoms, $f_{\mu}(\rho^a(M\mu))$ is the embedding function defining the energy to embed the atom $M\mu$ in the electron density ρ^a , and $\varphi_{\mu\nu}(R(M\mu, N\nu))$ is the pair interaction between atom $M\mu$ and $N\nu$. The functions $\rho_{\nu}(R(M\mu, N\nu))$ and $\varphi_{\mu\nu}(R(M\mu, N\nu))$, which are functions of the interatomic distance

$$R(M\mu, N\nu) = |\mathbf{R}(N\nu) - \mathbf{R}(M\mu)| \quad (39)$$

only, will be abbreviated as $\rho_{\nu}(M\mu, N\nu)$ and $\varphi_{\mu\nu}(M\mu, N\nu)$. Furthermore, we abbreviate $f_{\mu}(\rho^a(M\mu))$ as $f_{\mu}(M\mu)$.

The first-order potential-energy coefficients $\Phi_i(M\mu)$ are

$$\Phi_i(M\mu) = - \sum_{N\nu \neq M\mu} \{ f'_{\mu}(M\mu)\rho'_{\nu}(M\mu, N\nu) + f'_{\nu}(N\nu)\rho'_{\mu}(N\nu, M\mu) + \frac{1}{2}[\varphi'_{\mu\nu}(M\mu, N\nu) + \varphi'_{\nu\mu}(N\nu, M\mu)] \} \frac{R_i(M\mu, N\nu)}{R(M\mu, N\nu)} \\ = - \sum_{N\nu \neq M\mu} [H'(M\mu, N\nu) + H'(N\nu, M\mu)] R_i(M\mu, N\nu) , \quad (40)$$

where

$$H'(M\mu, N\nu) = [f'_{\mu}(M\mu)\rho'_{\nu}(M\mu, N\nu) + \frac{1}{2}\varphi'_{\mu\nu}(M\mu, N\nu)] \frac{1}{R(M\mu, N\nu)} . \quad (41)$$

The second-order potential coefficients $\Phi'_{ij}(M\mu, N\nu)$ with $(M\mu \neq N\nu)$

$$\Phi'_{ij}(M\mu, N\nu) = \frac{\partial^2 \Phi}{\partial R_i(M\mu) \partial R_j(N\nu)}$$

$$= -f''_{\mu}(M\mu) \rho'_{\nu}(M\mu, N\nu) \frac{R_j(M\mu, N\nu)}{R(M\mu, N\nu)} \sum_{P\pi \neq M\mu} \rho'_{\pi}(M\mu, P\pi) \frac{R_i(M\mu, P\pi)}{R(M\mu, P\pi)}, \quad (42a)$$

$$-f''_{\nu}(N\nu) \rho'_{\mu}(N\nu, M\mu) \frac{R_i(N\nu, M\mu)}{R(N\nu, M\mu)} \sum_{P\pi \neq N\nu} \rho'_{\pi}(N\nu, P\pi) \frac{R_j(N\nu, P\pi)}{R(N\nu, P\pi)}, \quad (42b)$$

$$+ \sum_{P\pi \neq N\nu, M\mu} f''_{\pi}(P\pi) \rho'_{\mu}(P\pi, M\mu) \frac{R_i(P\pi, M\mu)}{R(P\pi, M\mu)} \rho'_{\nu}(P\pi, N\nu) \frac{R_j(P\pi, N\nu)}{R(P\pi, N\nu)}, \quad (42c)$$

$$- [H''(M\mu, N\nu) + H''(N\nu, M\mu)] \frac{R_i(M\mu, N\nu) R_j(M\mu, N\nu)}{R(M\mu, N\nu)^2}, \quad (42d)$$

$$- [H'(M\mu, N\nu) + H'(N\nu, M\mu)] \left[\delta_{ij} - \frac{R_i(M\mu, N\nu) R_j(M\mu, N\nu)}{R(M\mu, N\nu)^2} \right], \quad (42e)$$

where

$$H''(M\mu, N\nu) = f'_{\mu}(M\mu) \rho''_{\nu}(M\mu, N\nu) + \frac{1}{2} \phi''_{\mu\nu}(M\mu, N\nu), \quad (43)$$

and the self-coupling coefficients $\Phi^s_{ij}(M\mu, M\mu)$, which have to be calculated separately,

$$\Phi^s_{ij}(M\mu, M\mu) = \frac{\partial^2 \Phi}{\partial R_i(M\mu) \partial R_j(M\mu)}$$

$$= f''_{\mu}(M\mu) \sum_{N\nu \neq M\mu} \rho'_{\nu}(M\mu, N\nu) \frac{R_i(M\mu, N\nu)}{R(M\mu, N\nu)} \sum_{P\pi \neq M\mu} \rho'_{\pi}(M\mu, P\pi) \frac{R_j(M\mu, P\pi)}{R(M\mu, P\pi)}$$

$$+ \sum_{N\nu \neq M\mu} f''_{\nu}(N\nu) \rho'_{\mu}(N\nu, M\mu) \frac{R_i(N\nu, M\mu)}{R(N\nu, M\mu)} \rho'_{\nu}(N\nu, M\mu) \frac{R_j(N\nu, M\mu)}{R(N\nu, M\mu)}$$

$$+ \sum_{N\nu \neq M\mu} [H''(M\mu, N\nu) + H''(N\nu, M\mu)] \frac{R_i(M\mu, N\nu) R_j(M\mu, N\nu)}{R(M\mu, N\nu)^2}$$

$$+ \sum_{N\nu \neq M\mu} [H'(M\mu, N\nu) + H'(N\nu, M\mu)] \left[\delta_{ij} - \frac{R_i(M\mu, N\nu) R_j(M\mu, N\nu)}{R(M\mu, N\nu)^2} \right]. \quad (44)$$

The expression for the elastic constants can be found by substituting the potential-energy coefficients in the equations derived above. By using the symmetry properties of the crystal, however, the equations can be substantially simplified.

Evaluation of the elastic constants for homogeneous deformation

From Eqs. (30) and (36) it is clear that the second-order elastic constants are a superposition of two contributions, due to the homogeneous and inhomogeneous parts of the deformation.

$$\tilde{C}_{ijkl} = \tilde{C}^{(1)}_{ijkl} + \tilde{C}^{(2)}_{ijkl}, \quad (45)$$

where

$$\tilde{C}^{(1)}_{ijkl} = \hat{A}^{(1)}_{ikjl} + \hat{A}^{(1)}_{jkil} - \hat{A}^{(1)}_{ijkl} - \tilde{C}_{jl} \delta_{ik} - \tilde{C}_{il} \delta_{jk} + \tilde{C}_{kl} \delta_{ij}, \quad (46)$$

with

$$\hat{A}^{(1)}_{ijkl} = -\frac{1}{2} V_C^{-1} \sum_{N\mu\nu} \Phi_{ik}(0\mu, N\nu) R_j(0\mu, N\nu) R_l(0\mu, N\nu), \quad (47)$$

due to the homogeneous deformation of the lattice and

$$\tilde{C}^{(2)}_{ijkl} = \tilde{A}^{(2)}_{ijkl}$$

$$= V_C^{-1} \sum_{N\mu\nu} \sum_m \Phi_{mk}(0\mu, N\nu) R_l(N\nu) X_{m,ij}(\mu), \quad (48)$$

expressing the contribution of the sublattice displacements to the elastic constants.

For primitive lattices or lattices which exhibit inversion symmetry the sublattice displacements are zero and we can bypass the formal theory. The elastic constants can be calculated directly by deriving the Lagrangian strain expansion of the potential with zero sublattice displacement. The homogeneous deformation is

$$U_i(M\mu) = \sum_j u_{ij} R_j(M\mu) \text{ for } S_i(\mu) = 0, \quad (49)$$

and according to Eq. (2) the squared distance between the ions

$$\bar{\rho} = \rho(R^2), \quad \bar{\rho}' = \partial\rho(R^2)/\partial R^2, \quad \bar{\rho}'' = \partial^2\rho(R^2)/\partial(R^2)^2, \quad (51)$$

$$\begin{aligned} & |\mathbf{R}(M\mu) + \mathbf{U}(M\mu) - \mathbf{R}(N\nu) - \mathbf{U}(N\nu)|^2 \\ &= |\mathbf{R}(M\mu) - \mathbf{R}(N\nu)|^2 \\ &+ 2 \sum_{ij} \eta_{ij} R_i(M\mu, N\nu) R_j(M\mu, N\nu). \end{aligned} \quad (50)$$

It is convenient to consider ρ and φ as a function of the distance squared, and use the notation

$$\bar{\varphi} = \varphi(R^2), \quad \bar{\varphi}' = \partial\varphi(R^2)/\partial R^2, \quad \bar{\varphi}'' = \partial^2\varphi(R^2)/\partial(R^2)^2. \quad (52)$$

With Eq. (50), which defines the relation between the atomic displacements and the Lagrangian strains, we can now expand the function $\bar{\varphi}_{\mu\nu}(M\mu, N\nu)$ defined above, in powers of the strains η_{ij} as

$$\begin{aligned} \bar{\varphi}_{\mu\nu}(M\mu, N\nu) &= \bar{\varphi}_{\mu\nu}(M\mu, N\nu) + 2\bar{\varphi}'_{\mu\nu}(M\mu, N\nu) \sum_{ij} \eta_{ij} R_i(M\mu, N\nu) R_j(M\mu, N\nu) \\ &+ 2\bar{\varphi}''_{\mu\nu}(M\mu, N\nu) \sum_{ijkl} \eta_{ij} \eta_{kl} R_i(M\mu, N\nu) R_j(M\mu, N\nu) R_k(M\mu, N\nu) R_l(M\mu, N\nu) + \dots \end{aligned} \quad (53)$$

and similarly for $\bar{\rho}_\nu(M\mu, N\nu)$. Furthermore, the embedding function can be expanded in powers of the deviation of the equilibrium electron density,

$$f_\mu(\rho + \Delta\rho) = f_\mu(\rho) + \Delta\rho f'_\mu(\rho) + \frac{\Delta\rho^2}{2} f''_\mu(\rho) + \dots \quad (54)$$

Substituting these expressions in the EAM functions Eqs. (37) and (38), and comparing this expression with the Lagrangian strain expansion of the crystal potential, Eq. (21), immediately gives expressions for the elastic constants,

$$\tilde{C}_{ij}^{(1)} = V_C^{-1} \sum_{N\nu\nu} [2\bar{\rho}'_\nu(0\mu, N\nu) f'_\mu(0\mu) + \bar{\varphi}'_{\mu\nu}(0\mu, N\nu)] R_i(0\mu, N\nu) R_j(0\mu, N\nu), \quad (55)$$

$$\begin{aligned} \tilde{C}_{ijkl}^{(1)} &= 2V_C^{-1} \left\{ \sum_{\mu} 2f''_\mu(0\mu) \sum_{N\nu} \bar{\rho}'_\nu(0\mu, N\nu) R_i(0\mu, N\nu) R_j(0\mu, N\nu) \sum_{P\pi} \bar{\rho}'_\pi(0\mu, P\pi) R_i(0\mu, P\pi) R_j(0\mu, P\pi) \right. \\ &\left. + \sum_{N\mu\nu} [2\bar{\rho}''_\nu(0\mu, N\nu) f'_\mu(0\mu) + \bar{\varphi}''_{\mu\nu}(0\mu, N\nu)] R_i(0\mu, N\nu) R_j(0\mu, N\nu) R_k(0\mu, N\nu) R_l(0\mu, N\nu) \right\}. \end{aligned} \quad (56)$$

The functions in these definitions are a function of R^2 ; rewriting these functions as a function of R results in the elastic constants for homogeneous deformation,

$$\tilde{C}_{ij}^{(1)} = V_C^{-1} \sum_{N\mu\nu} [\rho'_\nu(0\mu, N\nu) f'_\mu(0\mu) + \frac{1}{2} \varphi'_{\mu\nu}(0\mu, N\nu)] \frac{R_i(0\mu, N\nu) R_j(0\mu, N\nu)}{R(0\mu, N\nu)}, \quad (57)$$

$$\begin{aligned} \tilde{C}_{ijkl}^{(1)} &= V_C^{-1} \sum_{\mu} f''_\mu(0\mu) \sum_{N\nu} \rho'_\nu(0\mu, N\nu) \frac{R_i(0\mu, N\nu) R_j(0\mu, N\nu)}{R(0\mu, N\nu)} \sum_{P\pi} \rho'_\pi(0\mu, P\pi) \frac{R_k(0\mu, P\pi) R_l(0\mu, P\pi)}{R(0\mu, P\pi)} \\ &+ V_C^{-1} \sum_{N\mu\nu} \left\{ \left[\rho''_\nu(0\mu, N\nu) - \frac{\rho'_\nu(0\mu, N\nu)}{R(0\mu, N\nu)} \right] f'_\mu(0\mu) + \frac{1}{2} \left[\varphi''_{\mu\nu}(0\mu, N\nu) - \frac{\varphi'_{\mu\nu}(0\mu, N\nu)}{R(0\mu, N\nu)} \right] \right\} \\ &\times \frac{R_i(0\mu, N\nu) R_j(0\mu, N\nu) R_k(0\mu, N\nu) R_l(0\mu, N\nu)}{R(0\mu, N\nu)^2}. \end{aligned} \quad (58)$$

These expressions are the ones given before^{2,6,12} and are generally used for EAM potentials. Their use, however, is restricted to homogeneously deformed crystals, i.e., those that do not exhibit sublattice displacements.

The inhomogeneous contribution to the elastic constants

When the sublattice displacements are not zero, a second contribution is superimposed on the homogeneous elastic constants. This second contribution has to be calculated by evaluating Eq. (48). To do this, introduce the

coefficients $\theta_{ij}(\mu, \nu)$ and $\Omega_{i,jk}(\mu)$,

$$\theta_{ij}(\mu, \nu) = \sum_N \Phi_{ij}(0\mu, N\nu) \quad (59)$$

and

$$\Omega_{i,jk}(\mu) = \sum_{N\nu} \Phi_{ij}(0\mu, N\nu) R_k(N\nu), \quad (60)$$

known as the second- and first-order inner elastic constant matrices, respectively,³⁸ so that we can write

$$X_{i,jk}(\mu) = - \sum_{\nu} \sum_l \Gamma_{il}(\mu, \nu) \Omega_{l,jk}(\nu), \quad (61)$$

where

$$\sum_{\mu i} \Gamma_{ki}(\pi\mu) \theta_{ij}(\mu, \nu) = \delta_{kj} \delta_{\pi\nu}, \quad \pi, \mu, \nu \neq \sigma \quad (62)$$

and

$$\begin{aligned} \tilde{C}_{ijkl}^{(2)} &= V_C^{-1} \sum_{\mu} \sum_m \Omega_{m,kl}(\mu) X_{m,ij}(\mu) \\ &= -V_C^{-1} \sum_{\mu\nu} \sum_{mn} \Omega_{m,kl}(\mu) \Gamma_{mn}(\mu, \nu) \Omega_{n,ij}(\nu). \end{aligned} \quad (63)$$

Also the invariance conditions can be expressed as functions of $\theta_{ij}(\mu, \nu)$ and $\Omega_{i,jk}(\mu)$. The translational invariance condition, Eq. (15), can be written as a function of $\theta_{ij}(\mu, \nu)$,

$$\sum_{\nu} \theta_{ij}(\mu, \nu) = 0, \quad \forall \mu, i, j \quad (64)$$

and the rotational invariance condition, Eq. (16), as a function of $\Omega_{i,jk}(\mu)$,

$$\Omega_{i,jk}(\mu) + \Phi_j(0\mu) \delta_{ik}, \quad (65)$$

is symmetric in $j, k \forall \mu, i$.

The elastic constants and the invariance conditions can be calculated by evaluating the equations above, and the only task left is to obtain expressions for $\theta_{ij}(\mu, \nu)$ and $\Omega_{i,jk}(\mu)$ by substituting the second-order EAM potential

derivatives,

$$\theta_{ij}(\mu, \nu) = \sum_{\substack{N \\ N\nu \neq M\mu}} \Phi'_{ij}(0\mu, N\nu) + \delta_{\mu\nu} \Phi_{ij}^s(0\mu, 0\mu), \quad (66)$$

$$\begin{aligned} \Omega_{i,jk}(\mu) &= \sum_{\substack{N \\ N\nu \neq M\mu}} \Phi'_{ij}(0\mu, N\nu) R_k(N\nu) \\ &\quad + \Phi_{ij}^s(0\mu, 0\mu) R_k(0\mu). \end{aligned} \quad (67)$$

First consider the three f'' contributions in Eq. (42) to $\theta_{ij}(\mu, \nu)$. The first f'' contribution, Eq. (42a), reduces to

$$-f''_{\mu}(0\mu) g_j(\mu, \nu) \sum_{\pi} g_i(\mu, \pi)$$

after substitution in Eq. (66), where

$$g_i(\mu, \nu) = \sum_{\substack{N \\ N\nu \neq 0\mu}} \rho'_v(0\mu, N\nu) \frac{R_i(0\mu, N\nu)}{R(0\mu, N\nu)}. \quad (68)$$

The second f'' contribution, Eq. (42b), can be simplified by using the inversion symmetry of Bravais lattices, i.e., for every N there must be a $-N$ with $\mathbf{R}(-N) = -\mathbf{R}(N)$, resulting in

$$-f''_{\nu}(0\nu) g_i(\nu, \mu) \sum_{\pi} g_j(\nu, \pi). \quad (69)$$

The interactions in the third contribution, Eq. (42c), expand further than the atoms in the cutoff range of the function $\rho(\mathbf{R})$. This contribution can be simplified by splitting it in two parts,

$$\begin{aligned} \sum_{\pi} f''_{\pi}(0\pi) &\left[\sum_{\substack{P \\ P\pi \neq 0\mu}} \rho'_\mu(P\pi, 0\mu) \frac{R_i(P\pi, 0\mu)}{R(P\pi, 0\mu)} \sum_{\substack{N \\ N\nu \neq P\pi}} \rho'_\nu(P\pi, N\nu) \frac{R_j(P\pi, N\nu)}{R(P\pi, N\nu)} \right. \\ &\quad \left. - \delta_{\mu\nu} \sum_{\substack{P \\ P\pi \neq 0\mu}} \rho'_\mu(P\pi, 0\mu) \frac{R_i(P\pi, 0\mu)}{R(P\pi, 0\mu)} \rho'_\mu(P\pi, 0\mu) \frac{R_j(P\pi, 0\mu)}{R(P\pi, 0\mu)} \right], \end{aligned} \quad (70)$$

which can be written as

$$\sum_{\pi} f''_{\pi}(0\pi) [g_i(\pi, \mu) g_j(\pi, \nu) - \delta_{\mu\nu} g_{2ij}(\mu, \pi)], \quad (71)$$

where

$$g_{2ij}(\mu, \pi) = \sum_{\substack{P \\ 0\pi \neq P\mu}} \rho'_\mu(0\pi, P\mu)^2 \frac{R_i(0\pi, P\mu) R_j(0\pi, P\mu)}{R(0\pi, P\mu)^2}, \quad (72)$$

so that the $\theta_{ij}(\mu, \nu)$ coefficients, for the EAM potentials, can be expressed as

$$\begin{aligned} \theta_{ij}(\mu, \nu) &= -f''_{\mu}(0\mu) g_j(\mu, \nu) \sum_{\pi} g_i(\mu, \pi) - f''_{\nu}(0\nu) g_i(\nu, \mu) \sum_{\pi} g_j(\nu, \pi) \\ &\quad + \sum_{\pi} f''_{\pi}(0\pi) [g_i(\pi, \mu) g_j(\pi, \nu) - \delta_{\mu\nu} g_{2ij}(\mu, \pi)] \\ &\quad - \sum_{\substack{N \\ N\nu \neq 0\mu}} [H''(0\mu, N\nu) + H''(N\nu, 0\mu)] \frac{R_i(0\mu, N\nu) R_j(0\mu, N\nu)}{R(0\mu, N\nu)^2} \\ &\quad - \sum_{\substack{N \\ N\nu \neq 0\mu}} [H'(0\mu, N\nu) + H'(N\nu, 0\mu)] \left[\delta_{ij} - \frac{R_i(0\mu, N\nu) R_j(0\mu, N\nu)}{R(0\mu, N\nu)^2} \right] + \delta_{\mu\nu} \Phi_{ij}^s(0\mu, 0\mu). \end{aligned} \quad (73)$$

In a similar way, an expression for $\Omega_{i,jk}(\mu)$ can be derived,

$$\begin{aligned} \Omega_{i,jk}(\mu) = & -f''_{\mu}(0\mu) \sum_{\nu} h_{jk}(\mu, \nu) \sum_{\pi} g_i(\mu, \pi) \\ & - \sum_{\pi} f''_{\pi}(0\pi) \left\{ g_{2ij}(\mu, \pi) R_k(\mu) - g_i(\pi, \mu) \left[\sum_{\nu} h_{jk}(\pi, \nu) - R_k(\pi) \sum_{\nu} g_j(\pi, \nu) \right] \right\} \\ & - \sum_{N\nu \neq 0\mu} [H''(0\mu, N\nu) + H''(N\nu, 0\mu)] \frac{R_i(0\mu, N\nu) R_j(0\mu, N\nu)}{R(0\mu, N\nu)^2} R_k(N\nu) \\ & - \sum_{N\nu \neq 0\mu} [H'(0\mu, N\nu) + H'(N\nu, 0\mu)] \left[\delta_{ij} - \frac{R_i(0\mu, N\nu) R_j(0\mu, N\nu)}{R(0\mu, N\nu)^2} \right] R_k(N\nu) + \Phi_{ij}^s(0\mu, 0\mu) R_k(0\mu), \end{aligned} \quad (74)$$

where

$$h_{ij}(\mu, \nu) = \sum_{N\nu \neq 0\mu} \rho'_v(0\mu, N\nu) \frac{R_i(0\mu, N\nu)}{R(0\mu, N\nu)} R_j(N\nu), \quad (75)$$

and the self-coupling coefficients can also be expressed in the variables $g_i(\mu, \nu)$ and $g_{2ij}(\mu, \nu)$,

$$\begin{aligned} \Phi_{ij}^s(0\mu, 0\mu) = & f''_{\mu}(M\mu) \sum_{\nu} g_i(\mu, \nu) \sum_{\pi} g_j(\mu, \pi) + \sum_{\nu} f''_{\nu}(0\nu) g_{2ij}(\mu, \nu) \\ & + \sum_{N\nu \neq 0\mu} [H''(0\mu, N\nu) + H''(N\nu, 0\mu)] \frac{R_i(0\mu, N\nu) R_j(0\mu, N\nu)}{R(0\mu, N\nu)^2} \\ & + \sum_{N\nu \neq 0\mu} [H'(0\mu, N\nu) + H'(N\nu, 0\mu)] \left[\delta_{ij} - \frac{R_i(0\mu, N\nu) R_j(0\mu, N\nu)}{R(0\mu, N\nu)^2} \right]. \end{aligned} \quad (76)$$

IV. DISCUSSION

In the preceding sections, expressions for the mechanical approximation of the elastic constants were derived. These expressions have been applied to the EAM potential, resulting in equations for the elastic constants which are valid for all possible equilibrium crystal structures.

We discussed that the elastic constants for homogeneous deformation, Eqs. (57) and (58), are equal to those given before.^{2,6,12} Their application is confined to crystals which exhibit a purely homogeneous deformation, which is generally only the case for centrosymmetric lattices. The homogeneous second-order elastic equations, however, possess a very comfortable numerical property. They are sums of contributions from each interaction term $\Phi_{ij}(0\mu, N\nu)$, in contrast to the inhomogeneous contribution to the elastic constants, which involves the inversion of the inner elastic constant matrix.

Since the elastic constants are routinely used in the process of fitting the potential parameters, this linearity of the homogeneous equations has obvious numerical advantages. When the potential functions are linear in their parameters, the fitting routine can be linear. It is possible to derive fairly simple analytical expressions to calculate parameter gradients. Or when the interaction is limited to nearest neighbors the equations defining the elastic constants can be inverted, resulting in analytical expressions for the embedding function or even potential pa-

rameters.^{39,40} This gives an explanation for the reluctance to use the full equations for the elastic constants. But since the elastic constants are very often used as the main experimental input defining the interatomic forces in the material, we find that the use of these simple equations is not justified and the inhomogeneous contribution has at least to be evaluated to see if it is neglectable. But one can question if it is justifiable to search for a neglectable inhomogeneous contribution. The sublattice displacements, and the inhomogeneous elastic constants, are related to the interatomic forces and may therefore play an essential role in determining if the model can simulate the behavior of the material adequately. To show the influence of the inhomogeneous contribution, we will calculate the magnitude of this contribution for some hcp potentials previously published in the literature.

The inhomogeneous elastic constants in hcp

To calculate the magnitude of the inhomogeneous contribution we will derive simplified expressions for this contribution. The x , y , and z directions are along $[\bar{1}2\bar{1}0]$, $[\bar{1}010]$, and $[0001]$, respectively (see Fig. 1). Due to the symmetry of hcp crystals, the contribution of the atoms in each neighbor shell to $g_i(\mu, \nu)$ [see (68)] cancels out, so that $g_i(\mu, \nu) = 0$ (see Fig. 1).

Since $g_i(\mu, \nu) = 0$, the equations for $\theta_{ij}(\mu, \nu)$ and $\Omega_{i,jk}(\mu)$ substantially simplify:

$$\theta_{ij}(\mu, \nu) = \sum_{\pi} [\delta_{\mu\nu} - \delta_{\pi\nu}] \sum_{\substack{P \\ P\pi \neq 0\mu}} [H''(0\mu, P\pi) + H''(P\pi, 0\mu)] \frac{R_i(0\mu, P\pi)R_j(0\mu, P\pi)}{R(0\mu, P\pi)^2} \\ + \sum_{\pi} [\delta_{\mu\nu} - \delta_{\pi\nu}] \sum_{\substack{P \\ P\pi \neq 0\mu}} [H'(0\mu, P\pi) + H'(P\pi, 0\mu)] \left[\delta_{ij} - \frac{R_i(0\mu, P\pi)R_j(0\mu, P\pi)}{R(0\mu, P\pi)^2} \right] \quad (77)$$

and

$$\Omega_{i,jk}(\mu) = - \sum_{N\nu \neq 0\mu} [H''(0\mu, N\nu) + H''(N\nu, 0\mu)] \frac{R_i(0\mu, N\nu)R_j(0\mu, N\nu)}{R(0\mu, N\nu)^2} R_k(0\mu, N\nu) \\ - \sum_{N\nu \neq 0\mu} [H'(0\mu, N\nu) + H'(N\nu, 0\mu)] \left[\delta_{ij} - \frac{R_i(0\mu, N\nu)R_j(0\mu, N\nu)}{R(0\mu, N\nu)^2} \right] R_k(0\mu, N\nu). \quad (78)$$

Due to the symmetry it can be shown that $\theta_{ij}(\mu, \nu) = 0$ for $i \neq j$, and $\theta_{xx}(\mu, \nu) = \theta_{yy}(\mu, \nu)$, $\forall \mu, \nu$. Also $\theta_{ij}(\mu, \mu) = \theta_{ij}(\nu, \nu) = -\theta_{ij}(\mu, \nu)$ for $\mu \neq \nu$, $\forall i, j$. And all elements of $\Omega_{i,jk}(\mu)$ are zero except for

$$\Omega_{x,xy}(\mu) = \Omega_{x,yx}(\mu) = \Omega_{y,xx}(\mu) = -\Omega_{y,yy}(\mu), \quad (79)$$

so that the only nonzero elements of the inhomogeneous contribution to the elastic constants, Eq. (63), are in Voigt notation,

$$-\tilde{C}_{11}^{(2)} = -\tilde{C}_{22}^{(2)} = \tilde{C}_{12}^{(2)} = -\tilde{C}_{66}^{(2)} \\ = \tilde{C}^{(2)} = V_C^{-1} \frac{\Omega_{x,xy}(\mu)^2}{\theta_{xx}(\mu, \mu)}, \quad (80)$$

where $\mu \neq \sigma$ [see Eq. (25)], resulting in a simple expression for the inhomogeneous contribution to the elastic constants of EAM hcp crystals.

In Table I the results of the calculation of the elastic constants for the potentials given by Oh and Johnson,³⁰ Willaime and Massobrio,²² Igarashi, Khanta, and Vitek,³¹ and Johnson³² are given. We were not able to reproduce their results for Ru(2).³¹

Considering that a fit to the elastic constants within

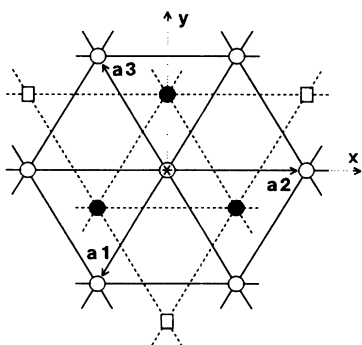


FIG. 1. View along the c axis of a hexagonal-close-packed lattice. a_1 , a_2 , and a_3 are the other hexagonal lattice vectors. The solid and dashed lines indicate the two sublattice planes, displaced a distance $\pm c/2$ along the c axis, in the hcp lattice. The atoms in the first three neighbor shells of the center atom \otimes are indicated as follows: nearest neighbors (NN), \bullet ; second-NN, \circ ; and third-NN shells, \square and \otimes at $\pm c$.

10% is generally accepted, the values in Table I show clearly that neglecting the inhomogeneous contribution to the elastic constants was not justified for most of the potentials studied here. Only for the potentials for Mg, Ti, Co, and Ru(1), defined by Igarashi, Khanta, and Vitek³¹ and the Ti potentials of Johnson,³² can neglecting this contribution, according to this criterion, be accepted. And simply adding the inhomogeneous contribution as done in the present paper generally makes the fit even worse. Only the potentials J :Ti (Ref. 32) have improved

TABLE I. The total second-order elastic constants \tilde{C}_{11} , \tilde{C}_{12} , \tilde{C}_{66} , and the inhomogeneous contribution \tilde{C} calculated from the potentials defined by Oh and Johnson (Ref. 30) (OJ), Willaime and Massobrio (Ref. 22) (WM), Igarashi, Khanta, and Vitek (Ref. 31) (IKV), and Johnson (Ref. 32) (J). Expt. denotes experimental values (Ref. 31). (%) and (−%) indicate the percentage of the inhomogeneous contribution added to and subtracted from the homogeneous component, respectively. The elastic constants are given in Mbar.

Potential	\tilde{C}_{11} (−%)	\tilde{C}_{12} (%)	\tilde{C}_{66} (−%)	$\tilde{C}^{(2)}$
OJ: Mg	0.607(6.9)	0.295(18.0)	0.156(22.4)	0.045
IKV: Mg	0.627(1.2)	0.265(2.8)	0.181(3.9)	0.007
Expt: Mg	0.635	0.259	0.188	
OJ: Ti	1.660(7.8)	0.906(18.2)	0.377(27.0)	0.140
IKV: Ti	1.742(1.3)	0.887(2.7)	0.427(5.2)	0.023
J : Ti(1)	1.801(2.9)	0.831(6.9)	0.485(10.0)	0.054
J : Ti(2)	1.894(3.1)	0.796(8.2)	0.549(10.0)	0.061
Expt: Ti	1.761	0.869	0.446	
OJ: Zr	1.496(6.1)	0.803(13.9)	0.347(22.0)	0.098
WM: Zr	1.507(7.0)	0.880(14.8)	0.314(26.4)	0.113
IKV: Zr	1.376(11.5)	0.851(26.5)	0.263(40.4)	0.178
Expt: Zr	1.554	0.672	0.441	
IKV: Zn	1.674(6.4)	0.491(31.8)	0.592(16.4)	0.116
Expt: Zn	1.791	0.375	0.708	
IKV: Co	3.110(2.0)	1.709(3.9)	0.700(8.4)	0.064
Expt: Co	3.195	1.661	0.767	
IKV: Ru(1)	5.419(2.7)	2.021(8.0)	1.699(8.1)	0.149
Expt: Ru(1)	5.763	1.872	1.946	
IKV: Hf	1.712(9.9)	0.931(25.1)	0.391(32.4)	0.187
Expt: Hf	1.901	0.745	0.578	
IKV: Be	2.881(6.1)	0.494(61.6)	1.193(13.6)	0.188
Expt: Be	2.994	0.276	1.359	

after adding $\tilde{C}_{\alpha\beta}^{(2)}$.

But as stated before, instead of trying to find a neglectable inhomogeneous contribution, it might be worthwhile to fit the total elastic constants. In their paper Igarashi, Khanta, and Vitek³¹ found that their potentials were partly successful in reproducing the Raman frequencies, which are the phonon frequencies evaluated at $\mathbf{q}=\mathbf{0}$. But Martin³⁸ already showed that these frequencies can be directly related to the inner elastic constant matrix, which has not been included in their model of the elastic constants. It may be expected that a better representation of the optical phonons can be obtained when the inhomogeneous contribution to the elastic constants is included in the fit, and even better when the inner elastic constant matrix is fitted to the Raman frequencies. In this case the Raman frequencies provide information about the relative magnitudes of the homogeneous and inhomogeneous elastic constants, resulting in a better representation of the interatomic forces.

V. CONCLUSION

In this paper we discussed the potential approximation of the (thermodynamic) elastic constants and derived expressions for the elastic constants for the EAM potential in an arbitrary crystal system in a rigorous way. We compared these equations with those given before^{2,6,12}

and showed that the latter are in fact the equations for the elastic constants for a purely homogeneous deformation, which restricts their use to primitive or centrosymmetric lattices.

Among other data, elastic constants are routinely used to fit potential parameters in order to obtain a good representation of the interatomic forces in the model. Despite their limitations several authors have applied the homogeneous equations to fit the potential parameters for hcp metals. Calculation of the total elastic constants for these potentials shows that neglecting the inhomogeneous contribution was not justified for all of these potentials. These contributions should be included in the fitting process to obtain a representation of the interatomic forces in the metal. Moreover, fitting of the inner elastic constant matrix to the Raman frequencies gives the possibility of including explicit information about the inhomogeneous contribution to the elastic constants in the process of developing metals.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Rico Keim for carefully reading the manuscript and Professor B. H. Kolster for supporting their work. Furthermore the foundation for Advanced Metals Science (SGM) is gratefully acknowledged for financial support.

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¹R. A. Johnson, *Phys. Rev. B* **6**, 2094 (1972).

²M. S. Daw and M. I. Baskes, *Phys. Rev. B* **29**, 6443 (1984).

³J. K. Nørskov and N. D. Lang, *Phys. Rev. B* **22**, 2131 (1980).

⁴K. W. Jacobsen, J. K. Nørskov, and M. J. Puska, *Phys. Rev. B* **35**, 7423 (1987).

⁵M. S. Daw, in *Atomistic Simulation of Materials: Beyond Pair Potentials*, edited by V. Vitek, and D. J. Srolovitz (Plenum, New York, 1989), p. 181.

⁶M. W. Finnis and J. E. Sinclair, *Philos. Mag. A* **50**, 45 (1984).

⁷G. J. Ackland, M. W. Finnis, and V. Vitek, *J. Phys. F* **18**, L153 (1988).

⁸F. Ercolessi, E. Tosatti, and M. Parrinello, *Phys. Rev. Lett.* **57**, 719 (1986).

⁹S. M. Foiles, M. I. Baskes, and M. S. Daw, *Phys. Rev. B* **33**, 7983 (1986).

¹⁰G. J. Ackland and M. W. Finnis, *Philos. Mag. A* **54**, 301 (1986).

¹¹S. P. Chen, A. F. Voter, and D. J. Srolovitz, *Phys. Rev. Lett.* **57**, 1308 (1986).

¹²G. J. Ackland, G. Tichy, V. Vitek, and M. W. Finnis, *Philos. Mag. A* **56**, 735 (1987).

¹³M. W. Foiles, *Surf. Sci.* **191**, L779 (1987).

¹⁴S. P. Chen, D. J. Srolovitz, and A. F. Voter, *J. Mater. Res.* **4**, 62 (1989).

¹⁵C. C. Matthai and D. J. Bacon, *Philos. Mag. A* **52**, 1 (1985).

¹⁶J. M. Harder, and D. J. Bacon, *Philos. Mag. A* **54**, 651 (1986).

¹⁷V. Vitek, *Philos. Mag. A* **58**, 193 (1988).

¹⁸M. W. Foiles, *Acta. Metall.* **37**, 2815 (1989).

¹⁹B. J. Pestman, J.Th.M. de Hosson, V. Vitek, and F. W.

Schapink, *Philos. Mag. A* **64**, 951 (1991).

²⁰M. W. Foiles, *Phys. Rev. B* **32**, 3409 (1985).

²¹C. L. Liu, J. M. Cohen, J. B. Adams, and A. F. Voter, *Surf. Sci.* **253**, 334 (1991).

²²F. Willaime and C. Massobrio, *Phys. Rev. Lett.* **63**, 2244 (1989).

²³M. S. Daw and R. L. Hatcher, *Solid State Commun.* **56**, 697 (1985).

²⁴R. Rebonato and J. Q. Broughton, *Philos. Mag. Lett.* **55**, 225 (1987).

²⁵J. S. Nelson, E. C. Sowa, and M. S. Daw, *Phys. Rev. Lett.* **61**, 1977 (1988).

²⁶G. J. Ackland and R. Thetford, *Philos. Mag. A* **56**, 15 (1987).

²⁷J. Eridon and S. Rao, *Philos. Mag.* **59**, 31 (1989).

²⁸R. A. Johnson and D. J. Oh, *J. Mater. Res.* **4**, 1195 (1989).

²⁹J. B. Adams and S. M. Foiles, *Phys. Rev. B* **41**, 3316 (1990).

³⁰D. J. Oh and R. A. Johnson, *J. Mater. Res.* **3**, 471 (1988).

³¹M. Igarashi, M. Khanta, and V. Vitek, *Philos. Mag. B* **63**, 603 (1991).

³²R. A. Johnson, *Philos. Mag. A* **63**, 865 (1991).

³³M. I. Baskes *Phys. Rev. Lett.* **59**, 2666 (1987).

³⁴M. I. Baskes, J. S. Nelson, and A. F. Wright, *Phys. Rev. B* **40**, 6085 (1989).

³⁵M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, 1954).

³⁶D. C. Wallace, *Thermodynamics of Crystals* (Wiley, New York, 1972).

³⁷J. W. Martin, *J. Phys. C* **8**, 2837 (1975).

³⁸J. W. Martin, *J. Phys. C* **8**, 2858 (1975).

³⁹R. A. Johnson, *Phys. Rev. B* **37**, 3924 (1988).

⁴⁰J. O. A. Idiodi, E. J. D. Garba, and O. Akinlade, *Surf. Sci.* **256**, 195 (1991).