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Crystal equilibrium versus phenomenological models of cubic metals with central forces

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The phenomenological models of metals with pure central forces are bound to obey the crystal equilibrium condition (CEC). When the correct value of the pressure of the electron gas (p_e) on CEC ($p_e = 0$) is used in these models, identical expressions are obtained for the elastic constants derived from the method of long waves or the homogeneous deformation.

The earlier phenomenological models of metals are those of de Launay[1] and Bhatia.[2] The recent successful ones are those of Sharma-Joshi[3] and Krebs.[4] While the interionic interactions in metallic crystals in Bhatia's[2] model is governed by a two-body pair potential, such interactions in the models of de Launay, Sharma-Joshi,[3] and Krebs[4] are based on purely central forces. As regards the evaluation of the model parameters, all the models have used Fuchs'[5] relations among elastic constants determined by the method of long waves (MLW). It was Bhatia[2] who first pointed out that the model of de Launay lacks the crystal equilibrium condition (CEC). Without going into a critical analysis Cheveau[6] and Upadhyaya *et al.*[7] have also repeated the statement of Bhatia[2] on de Launay's model, as well as on other models (Sharma-Joshi[3] and Krebs[4]) where also the interionic interactions between metal ions are purely central. Upadhyaya *et al.*[7] went a step further by developing a model where they have used an approximate value of p_e on CEC together with Fuchs' relations on MLW to determine the parameters of their model. Their work received immediate recognition in the sense that Rai and Hemker,[8] Gupta and Hemker,[9] and Rahore and Verma[10] have also utilized their scheme to develop new models of metals. In this note we would discuss two important properties of phenomenological models, which are

(1) CEC can be satisfied by all phenomenological models containing purely central forces.

(2) The use of the correct value of p_e and the pressure of the electron gas can predict identical expressions for the elastic constants obtained on MLW and the method of homogeneous deformation (MHD).

CEC FOR PURELY CENTRAL FORCES

Let ϕ_i and ϕ_E, respectively, represent the potential energy for the ionic lattice and the electronic lattice, then the potential energy of the metals would be given by

$$\phi = \phi_i + \phi_E . \tag{1.1}$$

The CEC gives

$$\frac{d\phi}{d\Omega} = \frac{d\phi_i}{d\Omega} + \frac{d\phi_E}{d\Omega} = 0 , \tag{1.2}$$

where Ω is the volume of the crystal. Equation (1.2) gives

$$\frac{d\phi_i}{d\Omega} = -\frac{d\phi_E}{d\Omega} . \tag{1.3}$$

As a matter of fact, for free-electron gas we have

$$p_e = -\frac{d\phi_E}{d\Omega} . \tag{1.4}$$

It is not possible to know an exact relation for ϕ_E or $d\phi_E/d\Omega$. That is why the evaluation of p_e is normally done by the relation (see de Launay[1])

$$p_e = \tfrac{3}{5} Ke . \tag{1.5}$$

There is a common mistake committed by all the workers in the study of metals. They take the value of $p_e = \frac{3}{5} Ke$ irrespective of the fact whether the model considered by them contains a purely central interionic interaction or a more general one. If we look critically at Eq. (1.3) and (1.4), it would be clear that p_e has two values, i.e., $p_e = 0$, as

$$\frac{d\phi_i}{d\Omega} = 0 \tag{1.6}$$

for the models where the interionic interactions are purely central, and $p_e \neq 0$ as

$$\frac{d\phi_i}{d\Omega} \neq 0 \tag{1.7}$$

for all the models where interionic interactions are more general (two-body pair potential,[2] ax-

ially symmetric,[11] noncentral,[12] and tensor force).[13]

An important conclusion can be drawn from Eqs. (1.2), (1.6), and (1.7) in the sense that in order to satisfy CEC the value of p_e should be zero for the models having purely central forces.

ELASTIC CONSTANTS ON MLW AND MHD

Following Fuchs'[5] hypothesis on the effect of conduction electrons on the computed elastic constants, and denoting by primed indices the ionic part of the computed elastic constants and by unprimed indices the experimental elastic constants, we have on MLW:

$$C_{11} = C'_{11} + Ke\,, \tag{2.1}$$

$$C_{12} = C'_{12} + Ke\,, \tag{2.2}$$

$$C_{44} = C'_{44}\,, \tag{2.3}$$

where Ke is the bulk modulus of the electron gas. The Cauchy deviation is given by

$$(C_{12} - C_{44}) = (C'_{12} - C'_{44}) + Ke\,. \tag{2.4}$$

For the model of de Launay, Sharma-Joshi,[3] and Krebs,[4] $C'_{12} = C'_{44}$, Eq. (2.4) modifies to

$$(C_{12} - C_{44}) = Ke\,. \tag{2.5}$$

In MHD for the models having purely central interionic interactions the relation between the computed and experimental elastic constants can be deduced from the work of Martin[14]:

$$C_{11} = C^C_{11} + p_e + Ke\,, \tag{3.1}$$

$$C_{12} = C^C_{12} - p_e + Ke\,, \tag{3.2}$$

$$C_{44} = C^C_{44} + p_e\,. \tag{3.3}$$

In the above equations C^C_{ij} denotes the computed values of the elastic constants on pure central forces; p_e and Ke are the same as appeared in earlier equations.

The expression for the Cauchy deviation on the MHD is given by

$$(C_{12} - C_{44}) = (C^C_{12} - C^C_{44}) - 2p_e + Ke\,. \tag{3.4}$$

As in the general $C^C_{12} = C^C_{44}$, Eq. (3.4) reduces to

$$(C_{12} - C_{44}) = -2p_e + Ke\,. \tag{3.5}$$

A careful look at the result obtained on CEC showing that $p_e = 0$ for the models having purely central forces and substituting this value of p_e in relations (3.1), (3.2), (3.3), and (3.5) would predict identical results for C_{11}, C_{12}, C_{44}, and $(C_{12} - C_{44})$ as those obtained using Eqs. (2.1), (2.2), (2.3), and (2.5) on MLW.

In a recent work of Upadhyaya,[15] where he has chosen arbitrarily two different values of p_e, i.e., $p_e = \frac{3}{5} Ke$ and $p_e = \frac{1}{2} Ke$ for two different models of metals, some confusion has been created regarding the Cauchy discrepancy for the models of Krebs[4] and Sharma-Joshi.[3] While utilizing the value of $p_e = \frac{1}{2} Ke$ in the Eq. (3.5) he obtains the value of $Ke = 0$ for the models of Krebs[4] and Sharma-Joshi.[3] From the result presented in this paper it would be clear that the only value of p_e admissible in the model of Sharma-Joshi[3] and Krebs[4] is that of $p_e = 0$. Such a relation gives

$$Ke = (C_{12} - C_{44})\,. \tag{2.5}$$

On the other hand both approximate values of p_e are admissible in the model of Upadhyaya *et al.*[7] The use of $p_e = \frac{3}{5} Ke$ in that model gives $Ke = -5(C_{12} - C_{44})$. Substitution of $p_e = \frac{1}{2} Ke$ would give $Ke = 0$. To solve the dilemma as to which value of Ke is best in the model of Upadhyaya *et al.*[7] we must resort to the use of the correct value of $p_e = d\phi_i/d\Omega = (2\alpha_1 + 2\alpha_2)$.

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