PHYSICAL REVIEW B VOLUME 18, NUMBER 6 15 SEPTEMBER 1978

Crystal equilibrium and Cauchy deficiency in metals

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(Received 10 February 1977)

In cubic and hcp metals, the problem of crystal equilibrium and Cauchy discrepancy has been analyzed. It is shown that when the crystal equilibrium condition is correctly applied in de Launay, Sharma-Joshi, and Krebs models, the Cauchy deficiency turns out to be zero. Hence the use of these models in the lattice-dynamical calculations is not justified.

Most of the metals crystallize into cubic and hcp structures. If the lattice is considered to be in equilibrium under central pairwise forces and volume forces due to conduction electrons, expressions for the Cauchy deficiency in cubic and hcp metals are obtained as follows[1,2]:

$$C_{12} - C_{44} = K_e - 2P_e \quad \text{for cubic system}, \tag{1}$$

and

$$C_{13} - C_{44} = K_e - 2P_e \quad \text{for hcp system}, \tag{2}$$

where K_e is the bulk modulus and P_e is the pressure of the electron gas. Following de Launay,[3] Upadhyaya and co-workers[1,2] assume the value of $P_e = \frac{3}{5}K_e$ for the free-electron gas and hence the value of the Cauchy deficiency in their schemes turns out to be

$$C_{12} - C_{44} \ (\text{or}, \ C_{13} - C_{44}) = -0.2K_e \ . \tag{3}$$

In the actual calculations,[1,2] we have used the value $2.2K_e$ for the Cauchy deficiency because of a sign error in the electronic pressure. (The correct equation has been given earlier as an erratum.[1(b)]) Therefore the value of K_e when calculated from the elastic constants[1,2] will be off by a factor of -11. If the calculations of dispersion curves for cubic and hcp systems are done by taking the new sets of parameters, we get in general absurd results. Probably, the earlier workers (de Launay,[3] Sharma and Joshi,[4] Krebs,[5] etc) were aware of the shortcomings of their models and that is why (a) they assume arbitrarily the first derivatives of the central potential to be zero and (b) they did not impose the crystal equilibrium condition on the elastic relations. Therefore, they get $C_{12} - C_{44} = K_e$, which is one-fifth the value obtained from the relation (3) and further treat K_e as an adjustable positive or negative parameter in order to fit the measured dispersion curves. It is to be noted that the relation (3) is consistent to the recent work of Martin.[6]

If we look into the work of Brovman and Kagan[7,8] using fundamental theory, we find that there is an exact relation between compressibility and susceptibility of the electron gas, namely [Eq. (2.16) of Ref. 8]

$$K_e = n^2/\Pi(0), \tag{4}$$

where n is the charge density and $\Pi(0)$ is the value of susceptibility function in the long-wavelength limit ($\vec{q} \to 0$).

However K_e is defined to be

$$K_e = -\Omega \frac{\partial P_e}{\partial \Omega} = n \frac{\partial P_e}{\partial n} \tag{5}$$

because the total amount of charge remains constant.

Now, from Eqs. (4) and (5), we obtain

$$\frac{\partial P_e}{\partial n} = \frac{n}{\Pi(0)} \ . \tag{6}$$

Integrating it, we get [assuming $\Pi(0)$ independent of electron density]:

$$P_e = n^2/2\Pi(0) \ . \tag{7}$$

The comparison of Eqs. (4) and (7) gives us

$$P_e = \tfrac{1}{2}K_e \ . \tag{8}$$

Putting the value of P_e from the relation (8) in Eqs. (1) and (2), we obtain

$$C_{12} - C_{44} \ (\text{or}, \ C_{13} - C_{44}) = 0 \ . \tag{9}$$

Thus we see that if the de Launay, Sharma-Joshi, and Krebs models[3-5] are made consistent with crystal equilibrium, the Cauchy deficiency turns out to be zero. Therefore, these phenomenological models[3-5] and even their improved versions[1,2,9] cannot be justified in the calculation of force parameters from elastic-constant data; nor should force constants so obtained be used in the dynamical matrix to calculate phonon frequencies.

Not only these parametrization schemes, but also the simple pseudopotential theory in second order suffers from the shortcoming of zero Cauchy deficiency[7,8] (at fixed electron density) because in this approach one uses essentially a central paired interaction which also takes care of the compressibility term. The latter point, related to the free-

electron-gas compressibility, has been more clearly investigated by Finnis.[10] He shows that the conventional dynamical-matrix theory, using second-order perturbation theory, is not suitable for the calculation of the elastic moduli and phonon spectrum of metals. If we consider third- and higher-order terms in the pseudopotential for the total electron energy, we get an expression for the Cauchy deficiency even by imposing the equilibrium condition.[7,8] In fact, third- and higher-order terms are responsible for the unpaired forces in the interaction system and hence a multi-ion potential is necessary in the calculation of elastic constants and phonon frequencies of metals from the dynamical matrix. The force-constant analysis of Upadhyaya and Sharma[11] and the first-principles calculation of Brovman *et al.*[12] are satisfactory from this point of view.

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