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Crystal equilibrium and phonon dispersion in some bcc transition metals

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A lattice-dynamical model has been developed for bcc metals which considers ion-ion interaction through second-neighbor central pair potential and electron-ion interaction based on the Sharma-Joshi theory. In the present model the ionic lattice is in equilibrium in a medium of electrons. The theory has been applied to calculate the dispersion curves in a number of transition metals. The results when compared to experimental neutron data show a reasonably good agreement in the [100] and [111] directions, while sufficient deviations are present in the [110] direction.

I. INTRODUCTION

Recently, a number of phenomenological models have been proposed by various authors$^{1-5}$ to study the lattice-dynamical properties of cubic metals. These models essentially use the effect of the electron gas on the lattice vibrations explicitly on the basis of the de Launay, Bhatia, Sharma-Joshi, and Krebs theories$^{6-9}$ which have been excellently reviewed in an article by Joshi and Rajagopal.[10] However, this review article has missed one important problem regarding the crystal equilibrium. In de Launay's analysis[6] the free-electron gas is assumed to be superimposed on the point-ion lattice of the crystal and the Cauchy discrepancy is shown to be equal to the bulk modulus of the electron gas. This model assumes that the lattice is in equilibrium under the central forces alone.[7] For the Sharma-Joshi[8] and Krebs[9] models the case is similar. These authors are not able to impose an equilibrium condition on the model solid and that is why their claim regarding the magnitude of the Cauchy discrepancy is not correct. In fact a consistent model needs that, in equilibrium, the pressure due to the ionic potential be exactly balanced by a pressure of opposite sign due to the electrons, i.e.,

$$P_0^i = -P_0^e \,, \tag{1}$$

where the subscript 0 represents the quantity in equilibrium configuration.

First of all, Bhatia[7] indicated that in a medium of electrons the derivative of the ionic interaction potential alone is not zero in equilibrium. The problem remained unnoticed for a long time and in 1968 Cheveau[11] again pointed out the weakness of such models, especially that of Krebs[9]: they need external forces to put the crystal in equilibrium. He proposed a simple model fulfilling this requirement but, as far as we know, his model has not been used to calculate the phonon-dispersion relations.

In the present work, we have developed a phenomenological model which uses ion-ion interaction through second-neighbor pair potential and electron-ion interaction on the basis of Sharma-Joshi theory.[8] The proposed model incorporates the idea of Cheveau[11] and describes a crystal in equilibrium under zero external stress. Further it gives the correct expression for the Cauchy discrepancy. The Sharma-Joshi theory[8] has been used in the calculation of electron-ion-electron part of the dynamical matrix because it is sufficiently rigorous in its theoretical development and is easy to handle computationally.[5] Moreover, this theory gives satisfactory numerical results[12] and therefore it is still used in recent lattice-dynamical studies.[13] Section II of this paper deals with the theoretical development and Sec. III with the application of the present work in the calculations of dispersion relations in transition metals, namely Fe, W, Mo, V, Nb, and Ta, crystallizing in the bcc structure.

II. THEORY

As usual, in a metal the total interaction potential is assumed to be the sum of ion-ion and electron-ion potentials, i.e.,

$$\phi = \phi^i + \phi^e \,, \tag{2}$$

where ϕ^e is the volume-dependent potential energy.

If the ions are interacting through the central pairwise potential $\phi^i(r_j)$ and the ion-ion coupling is effective only upto second-nearest neighbors, the potential energy per unit cell in a bcc metal can be written

$$\phi = \frac{1}{2}\sum_j \phi^i(r_j) + \phi^e \,, \tag{3}$$

where ϕ^e is the potential energy of electron-ion interaction per unit cell and j $(=1,2)$ represents the nearest neighbors.

If the solid is in equilibrium at zero external stress, the derivative of the total potential ϕ must vanish, i.e.,

$$\left.\frac{\partial\phi}{\partial\Omega}\right|_0 = 0\,, \quad \text{i.e.,} \quad P_0^i + P_0^e = 0\,, \tag{4}$$

which is the same as Eq. (1). Further, in view of Eq. (3), we obtain

$$\alpha_1 + \alpha_2 + \tfrac{1}{2} a P_0^e = 0\,, \tag{5}$$

where

$$\alpha_j = \left(\frac{1}{r_j}\frac{d\phi^i(r_j)}{dr_j}\right)_0 .$$

Taking $P_0^e = \frac{3}{5} K_e$ for the free-electron gas[6,7] the equilibrium condition (5) assumes the form

$$\alpha_1 + \alpha_2 + \tfrac{3}{10} a K_e = 0\,, \tag{6}$$

where K_e is the bulk modulus of the free-electron gas.

By considering the central pairwise interaction between the ion at the origin and the nearest neighbors up to second-nearest neighbor, we obtain the ionic contribution to the dynamical matrix $D(\vec{q})$ (Maradudin *et al.*[14]) i.e.,

$$D_{\alpha\beta}(\vec{q}) = -\sum_j \sum_{j\text{th neighbors}} \left(\alpha_j \delta_{\alpha\beta} + (\beta_j - \alpha_j)\frac{x_\alpha(j) x_\beta(j)}{r_j^2}\right) e^{i\vec{q}\cdot\vec{r}}\,, \tag{7}$$

where $\beta_j = [d^2\phi^i(r_j)/dr_j^{\,2}]_0$ and $\alpha, \beta = 1, 2, 3$.

The electron-ion part of the dynamical matrix is obtained on the basis of the Sharma-Joshi theory[8]:

$$D_{\alpha\beta}^{e-i}(\vec{q}) = K_e q_\alpha q_\beta \Omega G^2(r_0 q)\,, \tag{8}$$

where r_0 is the radius of Wigner-Seitz sphere, the function $G(r_0q) = 3(\sin r_0 q - r_0 q \cos r_0 q)/(r_0 q)^3$, and Ω is the atomic volume.

The sum of the ion-ion and electron-ion parts gives the dynamical matrix elements $D_{\alpha\beta}(\vec{q})$, and the solution of the secular equation

$$|D(\vec{q}) - m\omega^2 I| = 0 \tag{9}$$

gives the phonon frequencies ω, where m is the mass of the ion and I is the unit matrix.

When we solve Eq. (9) in the long-wavelength limit, the following expressions are obtained for the elastic constants C_{ij}:

$$aC_{11} = \tfrac{2}{3}(2\alpha_1 + \beta_1) + 2\beta_2 + aK_e\,, \tag{10}$$

$$aC_{12} = -\tfrac{8}{3}\alpha_1 + \tfrac{2}{3}\beta_1 - 2\alpha_2 + aK_e\,, \tag{11}$$

$$aC_{44} = \tfrac{2}{3}(2\alpha_1 + \beta_1) + 2\alpha_2\,. \tag{12}$$

Equations (6) and (10)–(12), together with relation (13) for the phonon frequency of the zone boundary, form a sufficient set of equations to determine the parameters of the theory, α_j, β_j, and K_e.

$$4\pi^2 m \nu_L^2(100) = \tfrac{16}{3}(2\alpha_1 + \beta_1) + K_e q_m^2 \Omega G^2(r_0 q_m)\,, \tag{13}$$

where q_m is the maximum value of q at the zone boundary in the [100] direction.

III. NUMERICAL RESULTS AND DISCUSSION

The input data for finding the parameters of the theory are given in Table I and the calculated parameters α_j, β_j and K_e are given in Table II. Substituting the values of the parameters in the secular equation (9), the dispersion curves were calculated for Fe, W, Mo, V, Nb, and Ta in the three crystallographic symmetry directions [100], [111], and [110]. The computed results have been shown in Figs. 1–6 with the experimental

TABLE I. Elastic constants in units of 10^{11} dyn/cm^2 and phonon frequencies (the references for phonon frequencies are given in the text) in 10^{12} cps.

Property	Fe	W	Mo	V	Nb	Ta
m (amu)	55.846	183.85	95.94	50.942	92.906	180.948
a (Å)	2.86	3.16	3.14	3.04	3.3008	3.30
C_{11}	24.31 [a]	53.255 [b]	45.002 [b]	22.8 [c]	24.6 [c]	26.09 [d]
C_{12}	13.81	20.495	17.292	11.88	13.40	15.74
C_{44}	12.19	16.313	12.503	4.26	2.87	8.18
ν_L (100)	8.70	5.55	5.57	7.70	6.49	5.03

[a] B. N. Brockhouse *et al.*, Solid State Commun. 5, 211 (1967).

[b] F. H. Featherson and J. R. Neighbours, Phys. Rev. 130, 1324 (1963).

[c] D. I. Bolef, J. Appl. Phys. 32, 100 (1961).

[d] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1967), p. 111.

TABLE II. Force constants in units of 10^3 dyn/cm and bulk modulus (K_e) in 10^{11} dyn/cm^2.

Parameter	Fe	W	Mo	V	Nb	Ta
α_1	−1.0074	5.1232	−10.3373	1.4277	4.5864	0.4442
β_1	53.183	77.6064	54.7034	30.3298	33.0153	51.1412
α_2	0.3756	3.3212	8.2868	−4.5865	−9.3261	−3.8462
β_2	16.6542	58.6861	55.8926	18.3295	18.6377	20.0353
K_e	0.7364	1.9009	2.1768	3.4636	4.7864	3.4364

points of Minkiewicz *et al.*,[15] Chen and Brockhouse,[16] Woods and Chen,[17] Collela and Battermann,[18] Nakagawa and Woods,[19] and Woods,[20] respectively. The calculated curves are in reasonably good agreement with experiment, with effectively a four-parameter theory. The discrepancies are more pronounced near the zone boundary especially in [110] direction for V, Nb, and Ta. However, they compare well with the results of Bose *et al.*,[3] using a five-parameter theory and fitting the parameters to one more zone-boundary frequency.

The advantages of the present model over similar other models need to be mentioned: (i) The model is in equilibrium without the application of external forces; (ii) the model predicts the discrepancy in the Cauchy relation to be

$$C_{12} - C_{44} = K_e - (4/a)(\alpha_1 + \alpha_2)\,. \tag{14}$$

In view of the equilibrium condition (6), we have

$$C_{12} - C_{44} = 2.2\,K_e\,, \tag{15}$$

which for $K_e = 0$ (in absence of free electrons) gives the famous Cauchy relation for cubic metals. This result must be obtained for central pairwise potentials.[21] However, the models of Lehman *et al.*[22] and Shukla *et al.*[23] do not lead to the desired result, while the axially symmetric model used by them is derivable from central pair potentials. Further, in de Launay, Sharma-Joshi, and Krebs models[6,8,9] the second term of Eq. (14) is zero but in the present analysis it is essentially nonzero and the obtained correct magnitude of the Cauchy discrepancy is equal to $2.2\,K_e$ for central pairwise potentials. (iii) In equilibrium this model considers the derivative of the total potential energy equal to zero. The models of de Launay,[6] Sharma-Joshi,[8] and Krebs[9] assume that in equilib-

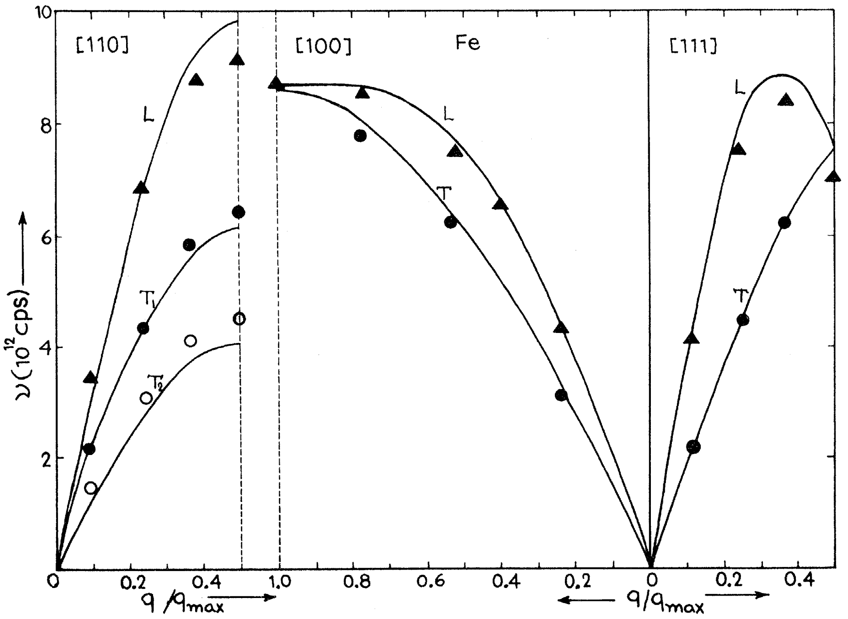

FIG. 1. Phonon dispersion in Fe: ▲ ● ○ experimental points of Minkiewicz (Ref. 15).

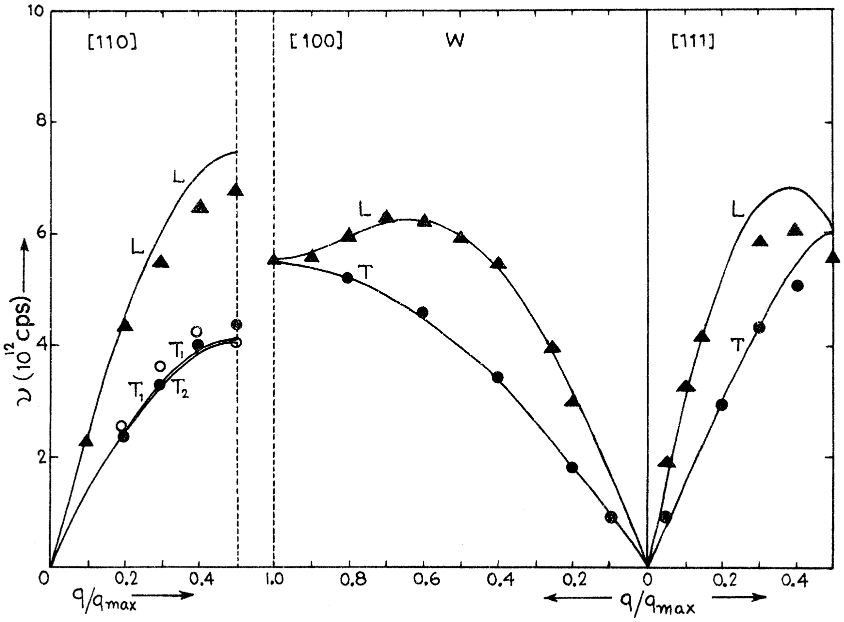

FIG. 2. Phonon dispersion in W: ▲ ● ○ experimental points of Chen and Brockhouse (Ref. 16).

rium the derivatives of the potential energy for each set of neighboring ions (i.e., α_j) are individually zero, in addition to the fact that they neglect electronic pressure. In this context the work of Thomas[24] needs to be mentioned. He has also stressed that energy terms and hence their first derivatives cannot be set separately equal to zero in an equilibrium configuration. Further, he has emphasized that elastic-constant theory only applies to a solid in equilibrium and that, in utilizing empirical models of lattice cohesion, an equilibrium condition must be imposed explicitly.

Recently, Animalu[25] has proposed a new transition-metal model potential (TMMP) of Heine-

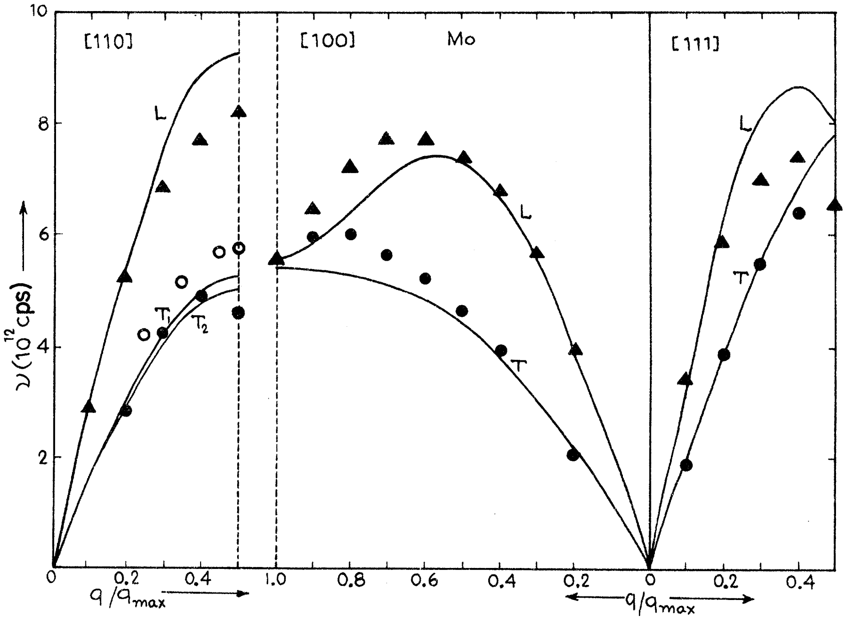

FIG. 3. Phonon dispersion in Mo: ▲ ● ○ experimental points of Woods and Chen (Ref. 17).

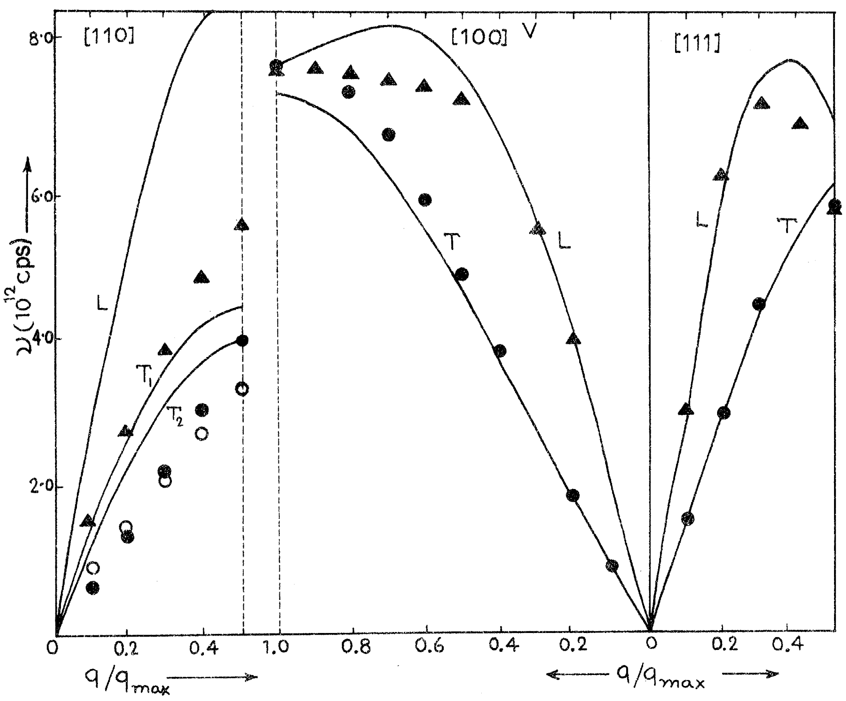

FIG. 4. Phonon dispersion in V: ▲ ● ○ experimental points of Collela and Battermann (Ref. 18).

Abarenkov–type to study the lattice dynamics of transition metals. The agreement between theoretical and experimental dispersion curves is poor for bcc metals. The most likely source of discrepancy in Animalu's analysis may be traced to some form of close-range forces as pointed out by Pindore and Pynn.[26] This theory uses second-order terms in the total electron energy, so that

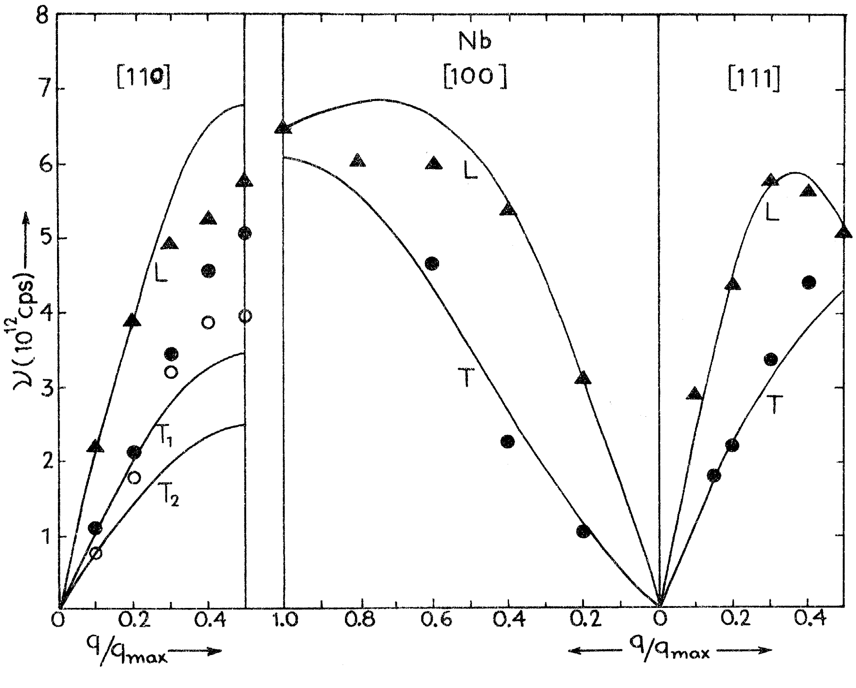

FIG. 5. Phonon dispersion in Nb: ▲ ● ○ experimental points of Nakagawa and Woods (Ref. 19).

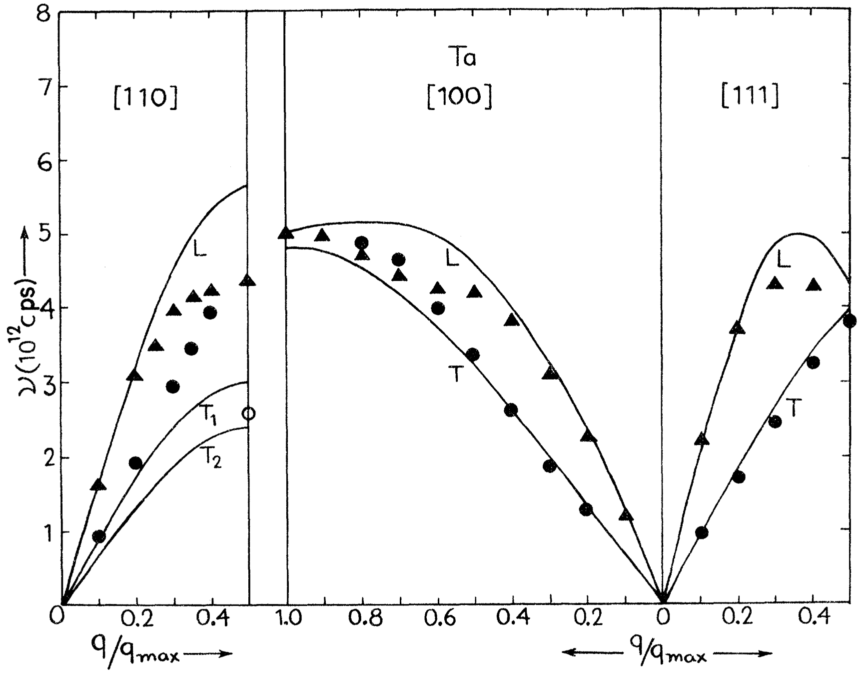

FIG. 6. Phonon dispersion in Ta: ▲ ● ○ experimental points of Woods (Ref. 20).

it takes account of only central pairwise forces. Unpaired forces between ions are accounted through third-order terms and the recent works of Bertoni *et al.*[27] based on this approach show the dispersion curves in simple metals sufficiently modified in the right direction and give the correct sequence of branches in the hcp metal Be. It is expected that in case of transition metals the third-order corrections may be important. Our model uses pairwise interactions up to second neighbors and a small noncentral contribution due to electrons. We also feel that the inclusion of three-body forces in our analysis may improve the results. Moreover, the present model and other similar models assume the ionic size to be negligible. This assumption of point ions in the actual crystal seems to be incorrect, specially in case of transition metals. Further, the Sharma-Joshi theory[8] for electron-ion interaction and hence the present work do not take account of long-range screened Coulomb forces. The problem of developing a model which considers finite core size, long-range forces, and three-body interactions in a phenomenological way is under consideration.

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