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LATTICE VIBRATION AND MECHANICAL STABILITY IN AN IDEALIZED ALLOY

by

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ABSTRACT

In this paper we use a simple model of a metallic alloy to treat lattice vibrations and to probe the mechanical stability of the close-packed crystal structures. Letting ion cores interact according to the two-body Friedel potential, we compute dispersion relations for transverse phonons propagating perpendicular to the close-packed planes of the FCC and HCP lattices. Generalized dispersion curves are found as a function of the conduction electron to atom ratio Z, and elastic constants are determined as a function of Z using the method of long waves. The regions of Z over which imaginary frequencies appear are identified; these correspond to regions of mechanical instability of the lattice.

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I. INTRODUCTION

In a previous paper[1] we used a simple model of a metallic alloy to compare the relative cohesive energies of selected metallic crystal structures as a function of the conduction electron to atom ratio Z. In this paper we use the same approach to model lattice vibrations in metallic alloys and to probe the mechanical stability of the close-packed crystal structures.

The model begins from the observation in pseudopotential theory (Harrison[2]) that to second order perturbations the cohesive energy of a simple metal may be written

$$E = E_0 + E_1 + \sum_{ij} V(r_{ij}) \tag{1}$$

where the zeroth and first order terms depend on the nature of the atom and on the atomic volume. The structural contribution to the cohesive energy appears first in the second order term, which is expressible as a sum of two-body interactions in real space. The potential $V(r_{ij})$ depends on the precise pseudopotential assumed, but has the asymptotic form

$$V(r) \rightarrow V_0 \frac{\cos(2k_F r)}{(2k_F r)^3} , \tag{2}$$

valid for large values of $k_F r$, where V_0 is a function of structure-independent parameters from pseudopotential theory[2] and k_F is the Fermi wavenumber. We obtain a simple tractable model by approximating $V(r_{ij})$ by its asymptotic form. The structural contribution to the cohesive energy may then be written as the dimensionless sum

$$\varepsilon_{ST} = E_{ST}/V_0 = \sum_{ij} v(r_{ij}) \tag{3}$$

where v(r) is a dimensionless potential (previously referred to as the Friedel potential[1])

$$v(r) = \cos(2k_F r)/(2k_F r)^3 \tag{4}$$

For given crystal structure the energy ε_{ST} depends only on the electron to atom ratio, Z. The model may be generalized to treat alloys by simply using the mean value of Z in the alloy, a step which implicitly involves the assumption of a random solution and the use of the virtual crystal model.[3]

Equation (3) may be used to estimate the energy change on an arbitrary rearrangement of atoms at constant atomic volume. In Reference 1 we compared the cohesive energies of a selected set of common crystal structures as a function of Z. Similarly, by letting the displacement of atoms be infinitesimal and periodic equation (3) may be used to construct model phonon dispersion curves as a function of Z. This procedure yields shear elastic constants and illustrates the mechanical instabilities which limit the range of stability of crystal structures.

In the following we specifically compute the dispersion relations for transverse phonons propagating perpendicular to the close-packed planes of the face centered cubic and hexagonal close packed structures. These cases are particularly simple since the associated lattice deformation is a rigid shear of close-packed planes. The equations of motion may be written in a one dimensional form, with the planes taken to interact according to a slight modification of the Blandin-Friedel-Saada[4,1] interplanar interaction. As the electron to atom ratio Z is varied the resulting dispersion relations exhibit the two common types

of lattice mechanical instability: elastic instability, which appears as an imaginary frequency in the long wavelength limit (and which has been previously studied in this model by Cousins[5]), and other instabilities of the "soft-mode" type, which are manifested by an imaginary frequency of a short wavelength vibration while the long wavelength vibrations, and hence the elastic constants, remain well behaved.

II. COMPUTATION OF DISPERSION RELATIONS

For lattice vibrations oriented along certain symmetry directions in a crystal, the normal modes are polarized into one purely longitudinal and two purely transverse components.[6] The transverse component of such a mode impels a rigid, parallel displacement of planes of atoms perpendicular to the propagation direction. With the introduction of interplanar stiffness constants[6,7] the problem of determining dispersion relations reduces to a vibration problem in one dimension. The appropriate dispersion relation is

$$\omega^2 = \frac{1}{M} \sum_{p \neq 0} C_p [1 - \cos(qpd)]$$

where ω is the angular frequency associated with the phonon of wave number q, M is the mass of the ion, and C_p is the stiffness constant between a plane serving as origin and a parallel plane a distance pd from the origin. For a transverse phonon propagating along the stacking direction of close-packed planes the values of C_p can be easily approximated through use of the interplanar form[4,8] of the Friedel potential, an observation first made by Koenig.[9]

To formulate generalized dispersion relations it is useful to consider the dimensionless frequency

$$(\omega')^2 = ma^2\omega^2/V_0 \qquad (5)$$

The dispersion relation is then

$$(\omega')^2 = \sum_{p\neq 0} C_p'[1 - \cos(qpd)] \tag{6}$$

where C_p' is the dimensionless stiffness constant

$$C_p' = ma^2 C_p/V_0 \tag{7}$$

It can be shown (Blandin, Friedel, and Saada[4]) that if ion cores interact by the Friedel potential then parallel close-packed planes of ions seperated by a normal distance x will have a total (dimensionless) interaction energy

$$\phi(x) = \sum_{\underset{\sim}{g}_\perp} \psi(\underset{\sim}{g}_\perp, x) \cos(\underset{\sim}{g}_\perp \cdot \underset{\sim}{b}) \tag{8}$$

where the sum is over the set of reciprocal lattice vectors perpendicular to the stacking direction, $\underset{\sim}{b}$ is a translation vector, parallel to the planes, which would carry one plane into the other if the two were superimposed, and $\psi(\underset{\sim}{g}_\perp, x)$ is a functional coefficient. The stiffness coefficients C_p' follow directly from equation (8). Let a plane a distance (pd) from a plane which serves as origin undergo an infinitesimal translation $\underset{\sim}{\delta}$, of magnitude δ, perpendicular to the stacking direction. The change in energy per ion is

$$\Delta\phi(pd) = \sum_{\underset{\sim}{g}_\perp} \psi(\underset{\sim}{g}_\perp, pd)\{\cos(\underset{\sim}{g}_\perp \cdot (\underset{\sim}{b}+\underset{\sim}{\delta})) - \cos(\underset{\sim}{g}_\perp \cdot \underset{\sim}{b})\} \tag{9}$$

Assuming the lattice is initially in equilibrium (though this equilibrium may be unstable) a Taylor expansion in the small quantity δ gives the stiffness constant

$$C_p' = \frac{\partial^2}{\partial\delta^2}[\Delta\phi(pd)] = -\sum_{\underset{\sim}{g}_\perp} g_{\perp\delta}^2 \psi(\underset{\sim}{g}_\perp, pd)\cos(\underset{\sim}{g}_\perp \cdot \underset{\sim}{b}) \tag{10}$$

where $g_{\perp\delta}$ is the projection of $\underset{\sim}{g}_\perp$ in the direction of $\underset{\sim}{\delta}$.

Equation (8) may be simplified considerably. First, since the stacking direction of close-packed planes is a symmetry direction, the value of the summation is independent of the direction of $\underset{\sim}{\delta}$. Second, the summation is dominated by those terms for which $|\underset{\sim}{g}_\perp| < 2k_F$.[4,8] When there are such terms the larger values of $\underset{\sim}{g}_\perp$ may be neglected. Let

$$\gamma = (d/a)/(d/a)_{IDEAL}, \tag{11}$$

the non-ideality ratio, where d is the interplanar spacing, a is the interatomic spacing in a close-packing, and $(d/a)_{IDEAL}$ is $\sqrt{2/3}$. Then in an FCC or HCP crystal the first set of non-zero reciprocal lattice vectors, $\underset{\sim}{g}_\perp$, falls below $2k_F$ at an electron-atom ratio $Z = Z_c = 1.14\gamma$.[8] The next smallest set remains greater than $2k_F$ until $Z = \sqrt{27}\, Z_c = 5.92\gamma$. Hence over the range of Z which includes most of the close-packed metals the summation in equation (8) is well approximated by a single term.

With these simplifications the interplanar stiffness constant is

$$C_p' = \begin{cases} -16\pi^2\psi(p,Z) & \underset{\sim}{b} = 0 \\ 8\pi^2\psi(p,Z) & \underset{\sim}{b} \neq 0 \end{cases} \tag{12}$$

where the first form gives the stiffness constant for equivalent planes (e.g., A-A in the ABC... stacking notation) and the second applies to inequivalent planes (e.g., A-B or A-C). The coefficient $\psi(p,Z)$ is[8]

$$\psi(p,Z) = -0.205\theta \sin p\theta/(2\pi)^3 Z^{5/3}\gamma^{4/3}p^2 \tag{13}$$

where

$$\theta = 5.67(Z^{2/3} - Z_c^{2/3})^{1/2}\gamma^{2/3} \tag{14}$$

Equation (13) differs from a similar relation given by Blandin, Friedel, and Saada[4] only through the inclusion of the non-ideality factor γ.

Inserting equations (12) and (13) into equation (6) and performing the summation for the stacking sequence ABCABC... we obtain a dispersion relation for a transverse mode propagating in a <111> direction in an FCC crystal:

$$\begin{aligned}\omega'^2(q) = F(Z)\{&\alpha_2(\theta) - \tfrac{1}{2}\alpha_2(\theta+qd) - \tfrac{1}{2}\alpha_2(\theta-qd) \\ &- \tfrac{1}{3}\alpha_2(3\theta) + \tfrac{1}{6}\alpha_2(3\theta+3qd) + \tfrac{1}{6}\alpha_2(3\theta-3qd)\}\end{aligned} \tag{15}$$

where

$$F(Z) = 0.41\theta/\pi Z^{5/3}\gamma^{4/3} \tag{16}$$

and

$$\alpha_2(\theta) = \sum_{m=1}^{\infty} \sin(n\theta)/n^2 = -\theta \ln 2|\sin\theta/2| + 2\int_0^{\theta/2} \phi d\phi/\tan\phi. \tag{17}$$

A similar summation for the stacking sequence ABAB... yields the dispersion relation for a transverse mode propagating parallel to an <001> direction in an HCP crystal:

$$\begin{aligned}\omega'^2(q) = F(Z)\{&\alpha_2(\theta) - \tfrac{1}{2}\alpha_2(\theta+qd) - \tfrac{1}{2}\alpha_2(\theta-qd) \\ &- \tfrac{3}{4}\alpha_2(2\theta) + \tfrac{3}{8}\alpha_2(2\theta+2qd) + \tfrac{3}{8}\alpha_2(2\theta-2qd)\}\end{aligned} \tag{18}$$

Elastic constants for these model crystals may be found through the method of long waves. If the dispersion relation is expanded about q=o,

the lead term will be of the form

$$\omega'^2 = C'(qd)^2 \tag{19}$$

where C' is the dimensionless form of the elastic constant appropriate to the vibrational mode to which the dispersion relation applies: C_{66} for the $\langle 001\rangle_T$ mode in HCP and $[C_{11}-C_{12}+C_{44}]/3$ for the $\langle 111\rangle_T$ mode in FCC. Performing the expansion, we obtain:

$$C'_{66} = \frac{1}{2}F(Z)\{3\frac{d^2}{d\theta^2}\alpha_2(2\theta) - \frac{d^2}{d\theta^2}\alpha_2(\theta)\} \quad \text{(HCP)} \tag{20}$$

and

$$(C'_{11}-C'_{12}+C'_{44})/3 = \frac{1}{2}F(Z)\{3\frac{d^2}{d\theta^2}\alpha_2(3\theta) - \frac{d^2}{d\theta^2}\alpha_2(\theta)\} \quad \text{(FCC)} \tag{21}$$

Equations (15), (18), (20) and (21) give generalized model dispersion relations and elastic constants, which depend on the crystal structure and the electron-to-atom ratio (Z) only. Given the simple form of the bonding function used, we do not expect these relations to be precise. We might, however, expect them to give generally reasonable answers. To test this we computed dispersion curves for aluminum (FCC, Z=3) and magnesium (HCP, Z=2), using values of V_0 calculated from Harrison's[2] formula using the pseudopotentials of Appapillai and Williams.[10] In Figure 1 we compare the results to the experimental dispersion curves for the $\langle 111\rangle_T$ mode in Al and the $\langle 001\rangle_T$ mode in Mg.[11,12] The results show anticipated trends. At small q in the acoustic branch the agreement between the model and experiment seem excellent, given the simplicity of the model. As q increases toward the edge of the Brillouin zone, discrepancies become evident, and the optical mode of Mg is poorly modelled. These discrepancies would appear to arise from the importance of short

range forces in the short wavelength vibrations at larger q; short-range interactions are not well modelled by the Friedel potential, which approximates the asymptotic interaction at long range.

The elastic constants computed from the long wavelength limit of Figure 1 are:

$$C_{66} = 1.3 \cdot 10^{11} \text{ dyne/cm}^2$$

for magnesium and

$$(C_{11}-C_{12}+C_{44})/3 = 1.4 \cdot 10^{11} \text{ dyne/cm}^2$$

for aluminum. These values show reasonable agreement with the experimental values of 1.64×10^{11} dyne/cm and 2.34×10^{11} dyne/cm, respectively.

III. LATTICE STABILITY

Any infinitesimal deformation of a crystal lattice can be regarded as a linear combination of the extended normal mode vibrations. If all the normal mode or phonon frequencies of vibration are found to be real, then the lattice is stable against any infinitesimal deformation. However, a normal mode with an imaginary frequency will grow in amplitude with time and the lattice will eventually relax to another configuration. The condition that phonon frequencies be real hence provides a criterion for the structural stability of a lattice. The stability criterion expressed by Born[13] in terms of the elastic constants of a metallic crystal are just a special case of this condition.

To test the lattice stability of the HCP and FCC structures for atoms interacting according to the Friedel potential we employed equations (15) and (18) to compute dispersion curves as a function of

electron to atom ratio (Z). The results are shown in Figure 2. To extend the curves over ranges of imaginary frequency we have plotted $-\sqrt{|\omega'^2|}$ where ω' is imaginary.

Dispersion curves for the FCC structure at various values of Z are given in Figure 2(a). The two characteristic types of vibrational instability are evident in these curves. At Z = 2.0 the lattice is elastically unstable; the elastic constant $(C_{11}-C_{12}+C_{44})$ is negative as shown by the imaginary value of ω' in the long wavelength limit. At Z = 1.5 the lattice exhibits a short-wavelength vibrational instability of the "soft mode" type; while the elastic constant is well-behaved, ω' becomes imaginary for q/q_m greater than about 0.5. At Z = 2.5, 3.0, and 3.5 the lattice vibration in the $\langle 111 \rangle_T$ mode is stable.

Figure 2(b) shows example dispersion curves for the HCP lattice (acoustic mode only). At Z=2.0 and 2.5 vibration in the $\langle 001 \rangle_T$ mode is stable. The lattice is elastically unstable at Z = 1.5, and again at Z = 3.0 and 3.5; the elastic constant C_{66} is negative at these values of the electron-atom ratio. A short-wavelength instability intrudes for Z>3.53 (not shown) though the elastic constant is positive for 3.53<Z<4.0.

The results are summarized and compared to those obtained in earlier work[1,4] in Figure 3. Plot 3(A) shows the regions of relative preference of the FCC and HCP structures as determined through direct computation of structural energies (Reference 1). These computations do not consider the possibility that the lattice is unstable. Plot 3(B) is taken from Blandin, Friedel, and Saada[4] and shows the regions over which the energy of a stacking fault in the HCP or FCC structure is

positive, hence the region of Z over which these structures are stable against the formation of a fault.

Plot 3(C) is taken from the present work, and shows the values of Z over which the FCC and HCP structures are stable to transverse vibration of the close-packed planes. Two interesting features appear from a comparison of this plot to the earlier two. First, the region of FCC preference near Z = 1.5 disappears along with the region of HCP preference near Z = 3.6. In both cases the structures show a short-wavelength instability and hence have higher energy than undetermined structures which differ through short period transverse distortions. These are not simply faulted structures since the ideal lattices are stable against faulting over these ranges of Z. Second, the region of HCP vibrational stability centered about Z = 2.0 extends into the region where the stacking fault energy of the HCP structure is negative. Since a stacking fault in a close-packed structure is a finite transverse displacement of close-packed planes, Figure 3(C) shows the region over which the HCP structure is stable in the sense that a fault will not spontaneously form through growth of an infinitesimal transverse displacement.

Finally, recognizing the result, discussed in the previous section, that the Friedel model is less reliable for short wavelength displacements where short-range interactions are important, we have included plot 3(D) which shows the regions of elastic stability for the HCP and FCC structures. The only significant distinction between this plot and that in 3(C) is the reappearance of the FCC field near Z = 1.5 and the HCP field near Z = 3.6.

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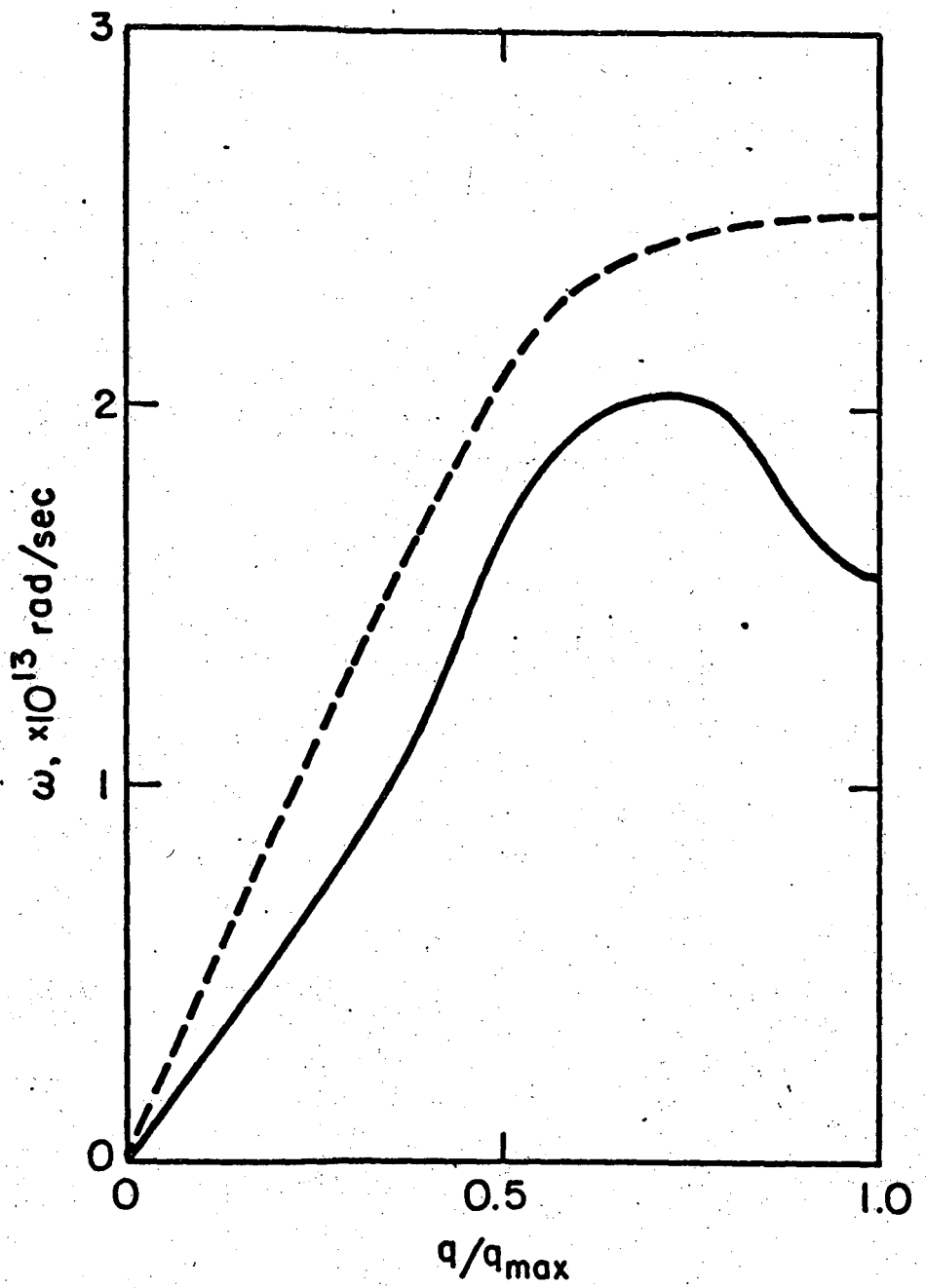

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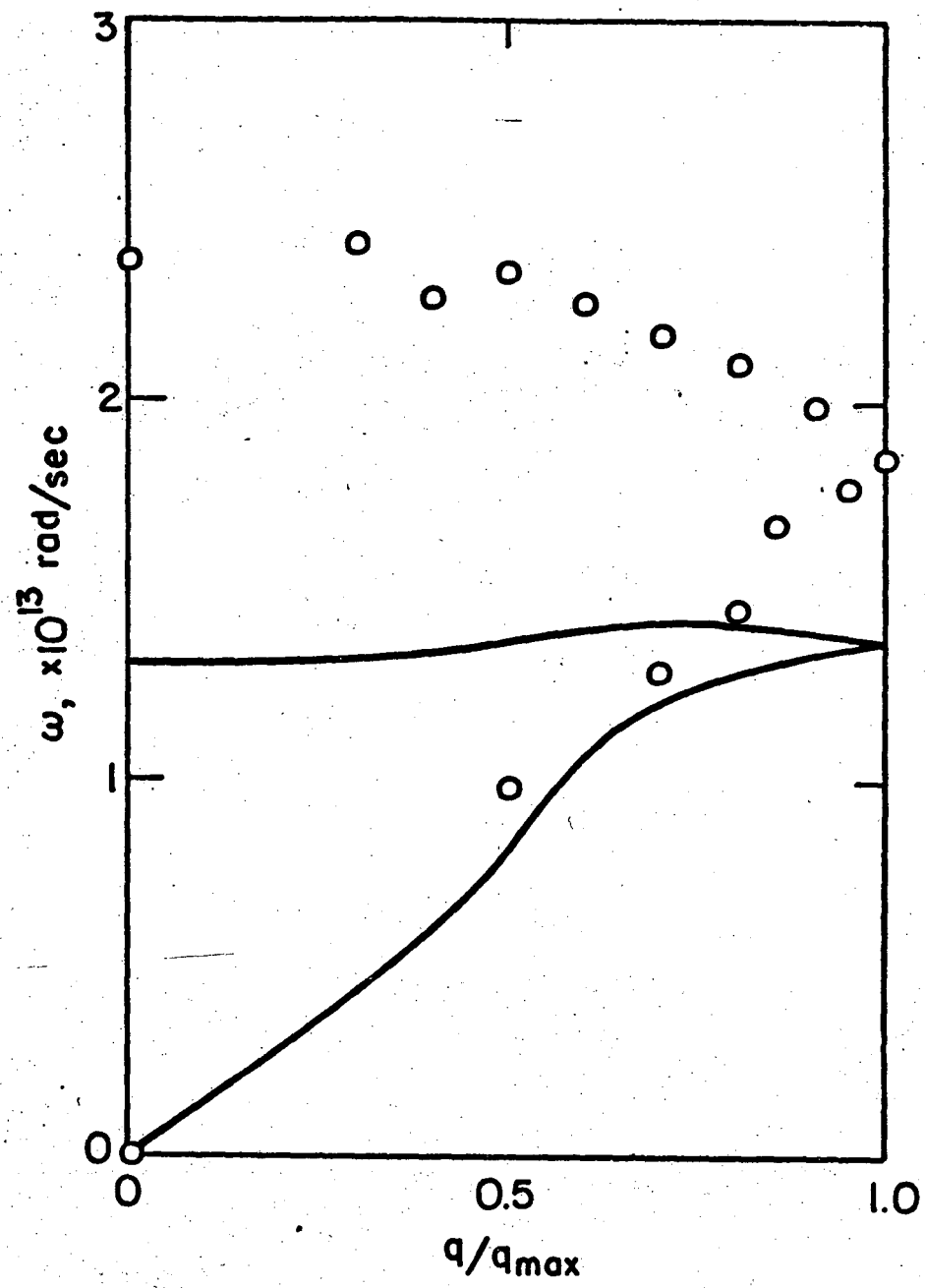

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FIG. 1. Phonon dispersion curves for: (a) Aluminum (Z = 3), $\langle 111 \rangle_T$ mode and (b) Magnesium (Z = 2), $\langle 001 \rangle_T$. The solid curve is the calculated relation. The dashed curve (Al) and discrete points (Mg) represent experimental data.

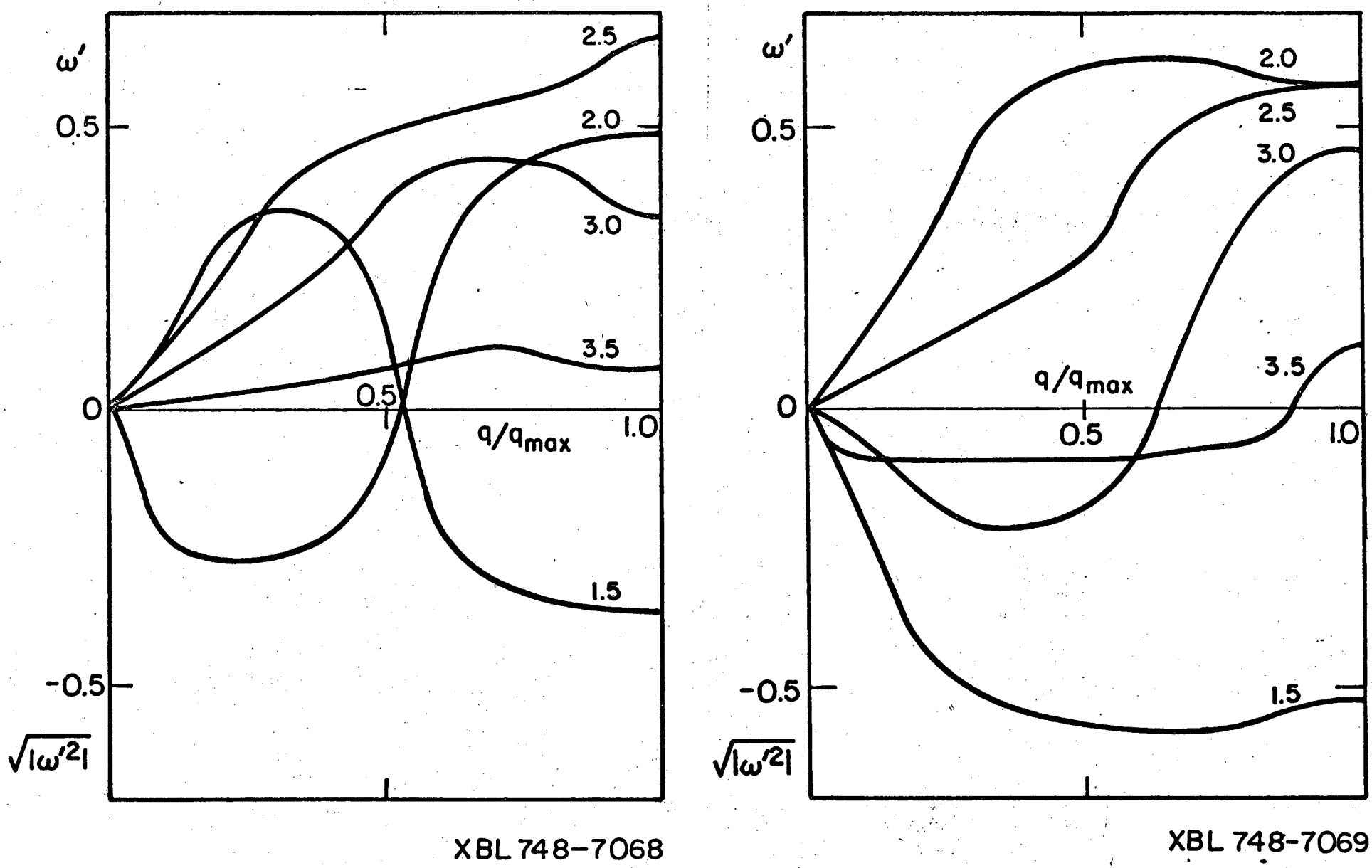

FIG. 2. Phonon dispersion curves as a function of valence (Z) for (a) the $\langle 111 \rangle_T$ mode in an FCC lattice, (b) the $\langle 001 \rangle_T$ acoustic mode in an HCP lattice. Where the frequency ω' is imaginary the curve has been continued by plotting the quantity $-\sqrt{(\omega')^2}$.

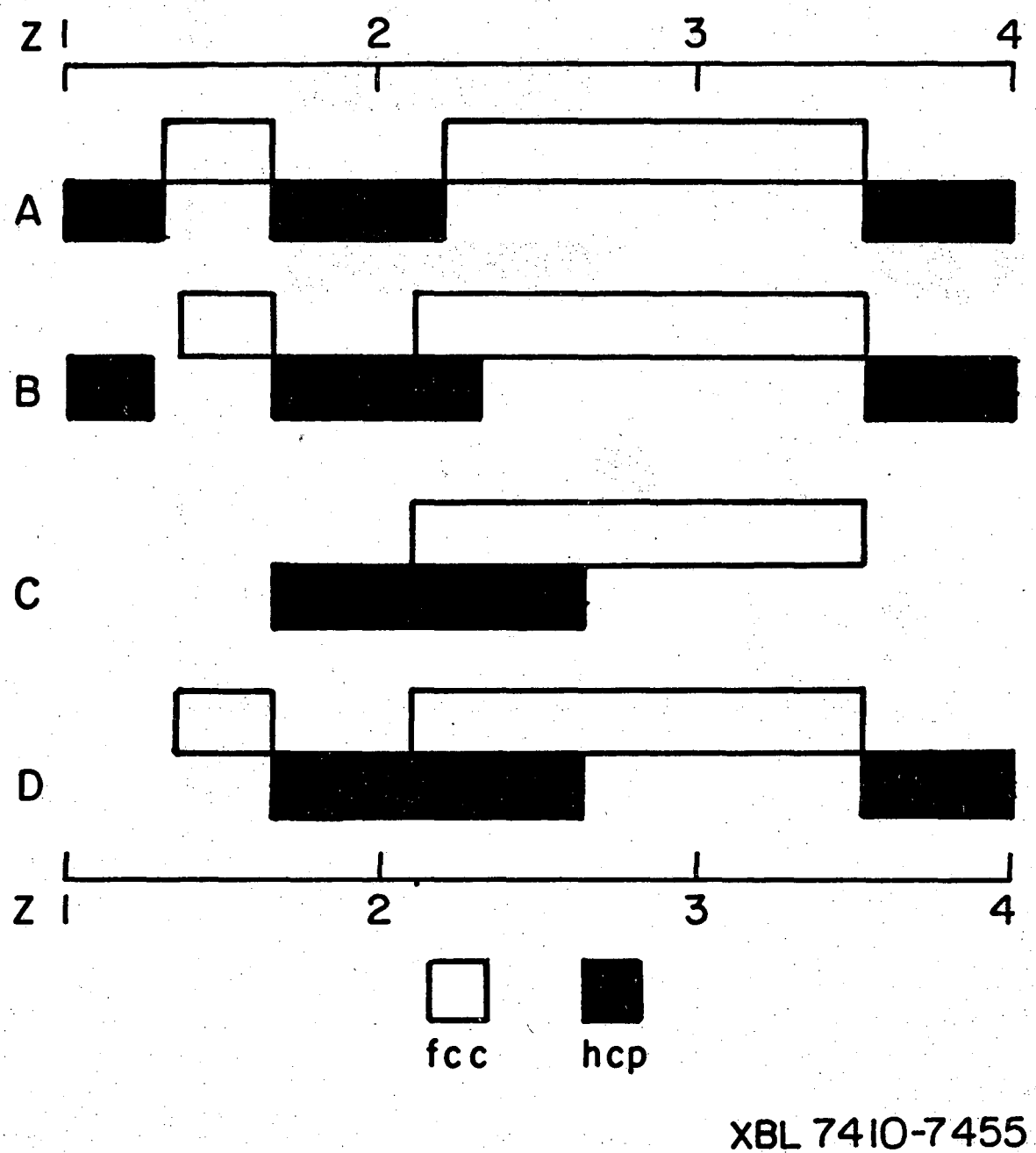

FIG. 3. Ranges of electron to atom ratio Z over which various stability criteria are satisfied for the FCC and HCP structures: A) relative cohesive energy at 0°K; B) stability against faulting; C) real phonon frequency; D) positive elastic constants.

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