STRUCTURAL BONDING CONTRIBUTIONS AND THE ELASTIC RESPONSE OF B.C.C. AND F.C.C. CRYSTALS

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Abstract—The anisotropic elastic response of body centered cubic (b.c.c.) and face centered cubic (f.c.c.) crystals is reviewed within the framework of general elasticity and particular model dependent relations. It is found that important trends in the observed behavior of specific groups of crystals can be reproduced by models that include only structural contributions to crystal binding. In fact, a very simple model, consisting of only nearest and next nearest neighbor interactions, reproduces the salient behavior, including the algebraic signs of Poisson's ratios and the orderings of the shear moduli, Young's moduli, and Poisson's ratios associated with major crystallographic symmetries. The analysis provides insight into the differences between the b.c.c. transition metals and the b.c.c. alkali metals.

Résumé—On étudie la réponse élastique anisotrope de cristaux cubiques centrés (c.c.) et cubiques à faces centrées (c.f.c.) dans le cadre de relations dépendant de l'élasticité générale et d'un modèle particulier. On trouve que les principales tendances du comportement observé de groupes spécifiques de cristaux peuvent être décrites par des modèles qui n'incluent que les contributions structurales à la liaison du cristal. En fait, un modèle très simple faisant intervenir seulement les interactions entre premiers et seconds proches voisins décrit l'essentiel de ce comportement, y compris les signes algébriques des coefficients de Poisson et les ordres de grandeurs du module de cisaillement, du module de Young et du coefficient de Poisson associés aux symétries cristallographiques majeures. Cette analyse permet de comprendre les différences entre les métaux de transition c.c. et les métaux c.c. alcalins.

Zusammenfassung—Die anisotropischen elastischen Eigenschaften von kubischen raumentrierten (k.f.z.) und kubischen flächenzentrierten (k.r.z.) Kristallen werden im Rahmen der allgemeinen Elastizitätstheorie und bestimmter modellabhänger Beziehungen diskutiert. Es stellt sich heraus, daß wichtige Trends in dem beobachteten Verhalten spezifischer Gruppen von Kristallen von Modellen wiedergegeben werden, die nur strukturabhängige Beiträge zur Bindungskraft berücksichtigen. In der Tat gibt ein einfaches Modell, das nur die Wechselwirkungen nächster und übernächster Nachbaren berücksichtigt, die wichtigsten Eigenschaften wieder, einschließlich der Vorzeichen der Poissonschen Querdehnungsziffern und der Anordnung der Schermodule, Youngschen Elastizitätsmodule und Poissonischer Querdehnungsziffern, die man in Verbindung mit wichtigen kristallographischen Symmetrien findet. Die Analyse verschafft einen Einblick in die Unterschiede zwischen den k.r.z. Übergangsmetallen und den k.r.z. Alkalimetallen.

1. INTRODUCTION

The elastic behavior of body centered cubic (b.c.c.) crystals under uniaxial loads in the principal symmetry directions has been analyzed, based on theoretical symmetry and bifurcation considerations, by Milstein and Marschall [1]. They noted that the alkali metals and various β-brasses behave, as a group, in agreement with a "standard" model of a b.c.c. crystal, in which (i) Young's moduli are ordered according to $E_{111} > E_{110} > E_{100}$ (the subscripts indicate the crystallographic direction of loading), (ii) the initial portion of the stress–strain curve is concave downwards in [100] and [111] loading but concave upwards in [110] loading, and (iii) Poisson's ratio $v_{110}^{1\bar{1}0}$ is negative. (For a crystal loaded uniaxially in the [hkl] direction, Poisson's ratio $v_{hkl}^{h'k'l'} \equiv -\epsilon_{h'k'l'}/\epsilon_{hkl}$, where ϵ_{hkl} and $\epsilon_{h'k'l'}$ are, respectively, the axial and transverse strains; the superscript on v is omitted if the transverse strain is isotropic.) Milstein and Marschall also observed that the elastic properties of the group V and VI b.c.c. transition metals are not consonant with the "standard" model of a b.c.c. crystal, but are rather more typical of the theoretical behavior that might be expected for a stable, simple cubic (sc) crystal; i.e. $v_{110}^{1\bar{1}0}$ is positive and the usual ordering of Young's moduli is $E_{100} > E_{110} > E_{111}$. Furthermore, available experimental data (for Nb) show that the initial stress–strain curve is concave upwards in [111] loading, which is inconsistent with the "expected behavior" of a b.c.c. crystal but consistent with that of an sc crystal. It was suggested [1] that differences between the elastic behaviors of these groups of metals can be attributed to the presence of much stronger second nearest neighbor interactions (relative to nearest neighbor interactions) in the b.c.c.

transition metals than in the alkali metals or β-brasses. These considerations have prompted us to examine the linear elastic response of b.c.c. crystals in terms of purely structural contributions to atomic binding, in general, and of the relative strengths of the first and second nearest neighbor interactions, in particular. We have also similarly examined f.c.c. crystals. Milstein and Rasky [2] previously analyzed the elastic behavior of face centered cubic (f.c.c.) crystals from the viewpoint of lattice symmetry and load path branching. In the "standard" model of an f.c.c. crystal, (i) $E_{111} > E_{110} > E_{100}$, (ii) a downward curvature occurs in the initial portion of the stress–strain curve in [111] and [110] uniaxial loading and an upward curvature in [100] loading, and (iii) Poisson's ratio $v_{110}^{1\bar{1}0}$ is negative [3, 4]. There is generally good agreement between this "standard" model of f.c.c. crystals and experimental observation; the only apparent exceptions are Al (for which $v_{110}^{1\bar{1}0} > 0$ and the [100] loading curve is concave downward), Pt and Ir ($v_{110}^{1\bar{1}0} > 0$) and Pd ($v_{110}^{1\bar{1}0} < 0$ except at low temperatures).

Various theoretical studies have been made of the elastic response of cubic crystals loaded uniaxially along the principal symmetry crystallographic axes [5–17]. Such studies have employed relatively simple crystal models containing only structurally dependent, pairwise, interatomic interactions as well as more complex quantum mechanically based pseudo-potential models of crystal binding. One surprising feature of this body of work is that computational results based on the simpler empirical models and on the quantum mechanical models are often indistinguishable, and where differences occur, there are often striking qualitative similarities [15–17]; agreement with experiment is likewise excellent [1–3]. This suggests that crystal symmetries and structural effects (which are contained in both the simpler and more complex models) play a key role in determining the elastic response of crystals to uniaxial and shear loadings. Although the simpler models neglect contributions to atomic binding that are known to be important (e.g. volumetric dependent energies, many body effects, etc.), such contributions seem to be relatively more important to the establishment of the *total* binding energy than to the very small *changes* in energy that occur during elastic deformations associated with principal symmetries. For example, at a given atomic volume, purely volumetric contributions to the bonding energy do not contribute to the shear moduli of a crystal [18]; as an extreme case, a crystal with volumetric energy alone would be unable to resist shear loading, since small shear strains conserve volume. Yet, as we show here, the ratios of the shear moduli μ/μ' of most cubic crystals are excellent indicators of linear elastic responses associated with principal symmetry axes.

In the present study it is found that a very simple model of crystal binding, which consists of purely structure dependent interatomic interactions summed over only the first and second nearest neighbor atoms, reproduces the salient trends in the observed linear elastic response of a given crystal, including the algebraic signs of Poisson's ratios and the orderings of the shear moduli, Young's moduli, and Poisson's ratios associated with the major symmetry axes and/or planes. Additionally, numerical agreement between experimental and theoretical values of various ratios of elastic properties is surprisingly good, wherein the theoretical values are computed by this very simple model. This analysis provides further insight into the differences between the b.c.c. alkali and transition metals and also into the high degree of elastic isotropy of tungsten; it also underscores the importance of structure dependent contributions to crystal binding in determining the elastic response of cubic crystals to uniaxial and shear loads.

2. MODEL INDEPENDENT ELASTICITY RELATIONS

For a cubic crystal, Young's moduli, in the relations between uniaxial stresses and the corresponding axial strains in the main symmetry directions, are known to be related to the bulk modulus κ and the shear moduli μ and μ' by

$$E_{100} = \frac{9\kappa\mu}{3\kappa + \mu},$$

$$E_{110} = \frac{36\kappa\mu\mu'}{9\kappa\mu + 3\kappa\mu' + 4\mu\mu'},$$

$$E_{111} = \frac{9\kappa\mu'}{3\kappa + \mu'}.$$

The elastic moduli κ, μ, and μ' are related to the usual elastic constants C_{ij} by $\kappa = (C_{11} + 2C_{12})/3$, $\mu = (C_{11} - C_{12})/2$ and $\mu' = C_{44}$. For the purpose of examining the relative magnitudes of the Young moduli, it is useful to form "Young's moduli ratios" in terms of dimensionless "Elastic moduli ratios", defined by $\xi \equiv \mu/\kappa$, $\zeta \equiv \mu'/\kappa$, and $\eta \equiv \mu/\mu'$; Young's moduli ratio can then be written in terms of any two elastic moduli ratios, e.g.

$$E_{111}/E_{100} = \frac{3 + \xi}{3\eta + \xi}, \tag{1a}$$

and

$$E_{110}/E_{100} = \frac{4(3 + \zeta)}{9\eta + 3 + 4\xi}. \tag{1b}$$

For an elastically stable crystal with finite bonding energy, the numerical values of ξ, ζ, and η must be finite and positive. Although the magnitudes of the Young moduli ratios depend upon two independent elastic moduli ratios, the ordering of the Young moduli depends only upon η, i.e.

$$E_{111} > E_{110} > E_{100} \quad \text{if} \quad \eta < 1 \tag{2a}$$

and

$$E_{100} > E_{110} > E_{111} \quad \text{if} \quad n > 1. \tag{2b}$$

If $\eta = 1$, the crystal is isotropic and $E_{100} = E_{110} = E_{111}$. The relationship between the ordering of the Young moduli and the shear moduli is well known and has been remarked on, for example, by Boas and Mackenzie [19], Nye [20], Chung and Buessem [21], and Reid [22], although these authors apparently did not relate the specific orderings observed in various materials to physical attributes such as crystal structure or interatomic interactions.

Shear moduli $G_{(HKL)[hkl]}$ (in the relations between pure shear stresses and the corresponding shear strains) for shear stresses that act upon major crystallographic planes (HKL) in important symmetry directions $[hkl]$ of a cubic crystal are

$$G_{(110)[001]} = G_{(100)} = \mu', \qquad (3a)$$

$$G_{(110)[\bar{1}10]} = \mu, \qquad (3b)$$

and

$$G_{(110)[\bar{1}11]} = G_{(111)} = \frac{3\mu\mu'}{\mu + 2\mu'}. \qquad (3c)$$

The shear moduli on (100) and (111) planes are independent of the direction of loading and thus the $[hkl]$ subscript is omitted. (The first equalities in equations (3a) and (3c) are readily evident from crystal symmetry and the condition $G_{(HKL)[hkl]} = G_{(hkl)[HKL]}$ [22].) Ratios of the shear moduli depend only upon η, e.g.

$$G_{(111)}/G_{(100)} = \frac{3\eta}{(\eta + 2)} \qquad (4a)$$

and

$$G_{(110)[\bar{1}10]}/G_{(100)} = \eta. \qquad (4b)$$

If $\eta < 1$ the ordering of the shear moduli is

$$G_{(110)[001]} = G_{(100)} > G_{(110)[\bar{1}11]} = G_{(111)} > G_{(110)[\bar{1}10]}$$

and if $\eta > 1$ the ordering is reversed.

For a cubic crystal, Poisson's ratios for the principal symmetry directions may be expressed in terms of the elastic moduli ratios as follows

$$v_{110}^{001} = \frac{2(3 - 2\xi)}{9\eta + 3 + 4\xi}, \qquad (5a)$$

$$v_{100} = \frac{3 - 2\xi}{6 + 2\xi}, \qquad (5b)$$

$$v_{111} = \frac{3 - 2\zeta}{6 + 2\zeta}, \qquad (5c)$$

$$v_{110}^{1\bar{1}0} = \frac{9\eta - 3 - 4\xi}{9\eta + 3 + 4\xi}, \qquad (5d)$$

v_{100} depends upon only one elastic moduli ratio, i.e. ξ; v_{111} depends only upon ζ; v_{110}^{001} and $v_{110}^{1\bar{1}0}$ each depend upon two elastic moduli ratios. The orderings of Poisson's ratios are readily established from equations (5); the four possible

orderings are

$$v_{110}^{001} > v_{100} > v_{111} > v_{110}^{1\bar{1}0}$$
$$\text{if} \quad \eta < 1 \quad \text{and} \quad \zeta < \tfrac{3}{2}, \quad (6a)$$

$$v_{110}^{1\bar{1}0} > v_{111} > v_{100} > v_{110}^{001}$$
$$\text{if} \quad \eta > 1 \quad \text{and} \quad \zeta < \tfrac{3}{2}, \quad (6b)$$

$$v_{100} > v_{110}^{001} > v_{111} > v_{110}^{1\bar{1}0}$$
$$\text{if} \quad \eta < 1 \quad \text{and} \quad \zeta > \tfrac{3}{2}, \quad (6c)$$

and

$$v_{110}^{1\bar{1}0} > v_{111} > v_{110}^{001} > v_{100}$$
$$\text{if} \quad \eta > 1 \quad \text{and} \quad \zeta > \tfrac{3}{2}. \quad (6d)$$

If $\eta = 1$, all Poisson's ratios are of course equal; if $\zeta = 3/2$, $v_{110}^{001} = v_{100} = 0$. The condition $\zeta \geqslant 3/2$ (or equivalently $C_{12} \leqslant 0$) evidently has not been observed in cubic crystals, thus the orderings (6c) and (6d) are hypothetical.

The allowed ranges of values of Poisson's ratios, based upon elastic stability and finite bond strength, are $-1 < v_{110}^{001} < 2$, $-1 < v_{100} < 1/2$, $-1 < v_{111} < 1/2$, and $-1 < v_{110}^{1\bar{1}0} < 1$. The denominators of all of equations (5) are positive and thus the algebraic sign of each Poisson's ratio is that of the corresponding numerator. In particular, the condition $\zeta < 3/2$ implies that v_{100} and v_{110}^{001} are positive (both would be negative if ζ were greater than 3/2); v_{111} is positive if $\zeta < 3/2$ (and would be negative if ζ were greater than 3/2). Since available experimental data indicate that the ratios ξ and ζ are less than unity for b.c.c. and f.c.c. crystals, v_{110}^{001}, v_{100}, and v_{111} are observed to be positive. Zener [23] noted the dependence of the algebraic signs of v_{100} and v_{111} upon the magnitudes of ξ and ζ, respectively; he cited β-brass as a material for which $\zeta > 3/2$; more recent experimental data indicate that ζ is apparently in the range 0.65–0.75 [24, 25]. The algebraic sign of $v_{110}^{1\bar{1}0}$ depends, in general, upon two elastic moduli ratios; a necessary and sufficient condition for

$$v_{110}^{1\bar{1}0} < 0 \quad \text{is} \quad \eta < \frac{1}{3} + \frac{4\xi}{9},$$

although a sufficient condition is $\eta \leqslant 1/3$ (since ξ must be positive). Likewise a sufficient condition for $v_{110}^{1\bar{1}0} < 0$ is $\zeta > 9/4$ although, as indicated above, such large values of ζ are not observed experimentally. We note in passing that Chung and Buessem [21, 26] have defined the *degree* of elastic anisotropy (in percent) as $A^* \equiv 300(A - 1)^2/[3(A - 1)^2 + 25A]$, where the Zener anisotropy ratio [23] $A \equiv \mu'/\mu$; thus e.g. for both $A = 3$ and $A = 1/3$, $A^* = 13.8\%$. However, with $A = 3$ ($\eta = 1/3$) $v_{110}^{1\bar{1}0} < 0$ while $A = 1/3$ ($\eta = 3$) leads to $v_{110}^{1\bar{1}0} > 0$ (for any reasonable value of ξ); thus crystals with the same *degree* of elastic anisotropy A^* may have markedly different elastic responses.

Various other relations among the moduli and Poisson's ratios may be derived. For example, from

the known condition [20] that the volume change of a cubic crystal under a uniaxial stress is independent of the direction of stress, it is readily shown that

$$\frac{1 - 2v_{100}}{E_{100}} = \frac{1 - v_{110}^{1\bar{1}0} - v_{110}^{001}}{E_{110}} = \frac{1 - 2v_{111}}{E_{111}}$$

which, when combined with relation (2), yields

$$v_{100} > \tfrac{1}{2}(v_{110}^{1\bar{1}0} + v_{110}^{001}) > v_{111} \quad \text{for} \quad \eta < 1$$

and

$$v_{111} > \tfrac{1}{2}(v_{110}^{1\bar{1}0} + v_{110}^{001}) > v_{100} \quad \text{for} \quad \eta > 1.$$

3. MODEL DEPENDENT ELASTICITY RELATIONS

In order to illustrate the deterministic effect of structural contributions upon the observed trends in cubic crystal elastic response, we begin by examining the considered elasticity relations for the crystal model consisting of pairwise, structural interactions only. We then further simplify the model to the case of first and second nearest neighbor interactions only; this is the simplest structure dependent model of crystal binding which yields stable b.c.c. and f.c.c. crystals. For such models, the total binding energy of an atom in the lattice is determined solely through a pairwise summation of interatomic potential energies ϕ; no volumetric or non-central (e.g. many-body) contributions to the binding energy are considered; the line of action of attractive or repulsive force between any two atoms (at arbitrarily large separation) passes through both atomic centers (and thus these models are also termed "central force").

A well known "consequence" of the central force approximation is the Cauchy symmetry of the elastic moduli of cubic crystals, which may be expressed as

$$3\kappa = 3\mu' + 2\mu. \tag{7}$$

As a result, the models cannot, in general, accurately reproduce all three independent elastic moduli of a given cubic crystal (although this can be accomplished by adding volume dependent terms (see e.g. Milstein and Rasky [18] or Johnson [27]) or non-pairwise interactions—as in the N-body potentials of Finis and Sinclair [28]). However, our purpose here is not to model a particular crystal quantitatively, but rather to demonstrate the systematic "essential role" of structure-dependent interactions in determining observed *trends* in elastic response. Thus, although the considered models represent a major simplification of the complexities of atomic binding in most crystals, they are adequate for the present purpose; they retain important features which are included in more substantiated, quantum based models (structure dependence) and are particularly important to anisotropic elastic behavior (near neighbor interactions). This viewpoint is supported by various quantum mechanically based calculations, wherein the determining contributions to the elastic moduli were found to come from structure dependent

interactions; e.g. Suzuki et al. [29], Thomas [30], and Swartz et al. [25]. Furthermore, structure dependent contributions to the elastic moduli are often dominated by the interactions of closely neighboring atoms. This was seen, for example, in the work of Thomas [30] who computed the second and third order elastic constants of Cu and Ag, and found them determined almost completely by a d-band overlap energy which had been represented by a Born–Mayer potential summed over the 12 nearest neighbors only.

When only structurally dependent pairwise interactions are present, the identities $\zeta = 3\eta/(2\eta + 3)$ and $\zeta = 3/(2\eta + 3)$ follow from equation (7), and thus the dimensionless elastic property ratios of equations (1) and (5), as well as (4), may be written as functions of a single elastic moduli ratio. An appropriate choice for this independent variable is η; Table 1 lists the dimensionless ratios of equations (1), (4), and (5) for this case. The last two columns of Table 1 list the bounds on the physically acceptable values of these ratios, based on crystal stability and finite bond strength in any central force model. The formulae of Table 1 are not *rigorously* obeyed by most crystals (with the exception of the formulae for the shear moduli ratios); thus the inherent ability of such models to describe the considered trends in elastic response depends upon how well experimentally determined values of the elastic property ratios of column 1 agree with the corresponding theoretical values calculated with the formulae of column 2 (wherein experimentally determined values of η are employed). This agreement turns out to be very good, in general, as is discussed in the following paragraphs.

It is also interesting to note that the central force model disallows certain elastic phenomena that are not found experimentally, but are not precluded by general elasticity considerations. For example, the relation $\zeta = 3/(2\eta + 3)$ implies that $\zeta < 1$ (for all bounded values of η), which apparently agrees with experimental observation; similar considerations yield $\zeta < 3/2$, which eliminates the possible orderings given by equations (6c) and (6d), which, as previously noted, are not observed experimentally. Additionally v_{100}, v_{110}^{001}, and v_{111} are required to be positive (as is observed experimentally) and the conditions governing the sign of $v_{110}^{1\bar{1}0}$ are simplified to $v_{110}^{1\bar{1}0} < 0$ if $\eta < 1/2$ and $v_{110}^{1\bar{1}0} > 0$ if $\eta > 1/2$. These inequalities agree with the *experimentally based* observation of Kitagawa et al. [4] that $v_{110}^{1\bar{1}0}$ "is positive when (the) anisotropy factor $(1/\eta)$ is less than about 2, but is negative when (the) anisotropy factor is more than about 2".

Further insight can be gained by examining the approximation of b.c.c. and f.c.c. crystals with nearest and next nearest neighbor interactions only. Explicit expressions for the structure-dependent contributions to μ and μ' of cubic crystals at arbitrary pressure have been derived by Milstein and Hill [31]. At zero pressure, to first and second nearest neighbor

Table 1. The dimensionless elastic property ratios of equations (1), (4), and (5) in terms of η for central force models of atomic binding; the physically realizable upper and lower limits of these ratios, which occur as $\eta \to 0$ and $\eta \to \infty$, are also listed

Property ratio	η-dependence of property ratio	Physical limits on property ratio as	
		$\eta \to 0$	$\eta \to \infty$
E_{110}/E_{100}	$\dfrac{4(\eta + 1)}{(2\eta^2 + 5\eta + 1)}$	4	0
E_{111}/E_{100}	$\dfrac{3(\eta + 1)}{2\eta(\eta + 2)}$	∞	0
$\dfrac{G_{(110)[1\bar{1}0]}}{G_{(100)}}$	η	0	∞
$\dfrac{G_{111}}{G_{(100)}}$	$\dfrac{3\eta}{(\eta + 2)}$	0	3
v_{110}^{001}	$\dfrac{2}{(2\eta^2 + 5\eta + 1)}$	2	0
v_{100}	$\dfrac{1}{2(\eta + 1)}$	1/2	0
v_{111}	$\dfrac{(2\eta + 1)}{4(\eta + 2)}$	1/8	1/2
$v_{110}^{1\bar{1}0}$	$\dfrac{(2\eta^2 + \eta - 1)}{(2\eta^2 + 5\eta + 1)}$	-1	1

terms only, for f.c.c. crystals

$$\mu = \sqrt{2}R_1[\phi''(R_1^2) + 8\phi''(R_2^2)] \qquad (8a)$$

$$\mu' = 2\sqrt{2}R_1[\phi''(R_1^2) + 0\phi''(R_2^2)] \qquad (8b)$$

from which

$$\eta = \tfrac{1}{2}[1 + 8\phi''(R_2^2)/\phi''(R_1^2)] = \tfrac{1}{2}[1 + 8\delta] \qquad (8c)$$

and for b.c.c. crystals

$$\mu = \frac{8R_1}{\sqrt{3}}[0\phi''(R_1^2) + \phi''(R_2^2)] \qquad (9a)$$

$$\mu' = \frac{4R_1}{\sqrt{3}}[\phi''(R_1^2) + 0\phi''(R_2^2)] \qquad (9b)$$

so that

$$\eta = 2\phi''(R_2^2)/\phi''(R_1^2) = 2\delta \qquad (9c)$$

where R_1 is the nearest neighbor distance, R_2 is the second nearest neighbor distance, and $\phi''(R^2)$ is the second derivative of the pairwise interatomic potential ϕ with respect to the square of the interatomic distance R. The ratio δ [defined as $\phi''(R_2^2)/\phi''(R_1^2)$] is a measure of the strength of the next nearest neighbor interaction compared with that of the nearest neighbor interaction. The allowed range of values of δ (in this simplified model) is evident from equations (8c) and (9c), i.e. since $0 < \eta < \infty$, for f.c.c. $-1/8 < \delta < \infty$, and for b.c.c. $0 < \delta < \infty$. [For b.c.c. both $\phi''(R_1^2)$ and $\phi''(R_2^2)$ must be positive for stability and thus δ must be greater than zero; for f.c.c. only $\phi''(R_1^2)$ must be positive while $\phi''(R_2^2)$ may take on positive or negative values so long as $\phi''(R_1^2) + 8\phi''(R_2^2) > 0$.]

Experimentally based values of δ are readily computed from equations (8c) and (9c) (independent of the form of ϕ) from experimental values of η; values of δ computed in this manner are listed in Table 2, along with a compilation of experimental values of κ, μ, and μ' for a large number of crystals. The magnitudes of δ vary over a much larger range in the b.c.c. group than in the f.c.c. (about 0.1 to 1.0 vs -0.06 to 0.08). Among the f.c.c. crystals only Al, Ir, and Pt have positive values of δ. Al has the largest relative second nearest neighbor contribution with $\delta = 0.0823$. Among the b.c.c. metals, the alkalis are seen to have very small second nearest neighbor contributions when compared with the transition metals. Fe has a value of δ about $3\frac{1}{2}$ times greater than those found in the alkali metals, while for Nb, δ is almost 19 times greater. The isotropy of W may be thought of as a consequence of second to first nearest neighbor contributions approaching 1/2.

Table 2. Experimentally based values of the bulk modulus κ and the two shear moduli μ and μ' (in units of 10^{11} N/m²), and the ratio $\delta \equiv \phi''(R_2^2)/\phi''(R_1^2)$, computed using the experimental values of $\mu/\mu' = \eta$ in equations (8c) and (9c)

b.c.c. Elements	κ	μ	μ'	δ	f.c.c. Elements	κ	μ	μ'	δ
Li	0.1410	0.0120	0.1170	0.0513	Ne	0.0112	0.0040	0.0095	-0.0192
Na	0.0767	0.0070	0.0630	0.0556	Ar	0.0238	0.0097	0.0234	-0.0219
K	0.0377	0.0040	0.0290	0.0690	Kr	0.0361	0.0115	0.0268	-0.0177
Rb	0.0317	0.0025	0.0220	0.0568	Xe	0.0228	0.0057	0.0156	-0.0345
Cs	0.0232	0.0021	0.0161	0.0652	Ir	3.6667	1.7200	2.7000	0.0343
Fe	1.7310	0.5250	1.2190	0.215	Ni	1.8760	0.5520	1.3170	-0.0202
V	1.5704	0.5652	0.4595	0.615	Pd	1.9543	0.2900	0.7120	-0.0232
Nb	1.7303	0.5975	0.3097	0.965	Pt	2.8840	0.5220	0.7740	0.0436
Ta	1.9421	0.5408	0.8736	0.310	Cu	1.4200	0.2565	0.8180	-0.0466
Cr	1.9007	1.5070	1.0320	0.730	Ag	1.0870	0.1710	0.5110	-0.0413
Mo	2.6529	1.3855	1.2503	0.554	Au	1.8033	0.1595	0.4540	-0.0372
W	3.1415	1.6380	1.6313	0.502	Al	0.7937	0.2620	0.3160	0.0823
					Pb	0.4877	0.0505	0.1940	-0.0599
					Ce	1.8177	0.5875	1.7300	-0.0401
					Th	0.5807	0.1480	0.5130	-0.0529

κ, μ, and μ' were computed from elastic constants found in Simmons and Wang [32] for Ir, Pt, Fe, and the b.c.c. transition metals, in Rasky and Milstein [16] for the alkali metals, in Greiner et al. [33] for Ce, and in Milstein and Rasky [34] for the remaining f.c.c. metals; all values are for 0 K except Ne (5 K), Ar (4.2 K), Kr (10 K), Xe (151 K), Ce (room temperature), Fe (4.2 K), Nb (4.2 K), and Cr (77.0 K).
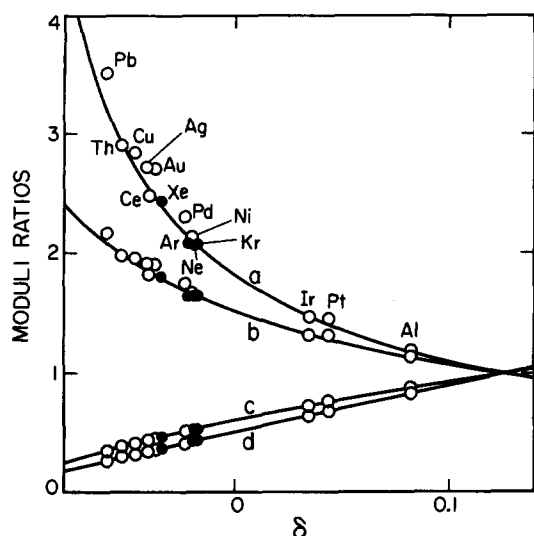
Fig. 1. Young's and shear moduli ratio data points (experimental) and curves (theoretical) for f.c.c. crystals: (a) E_{111}/E_{100}; (b) E_{110}/E_{100}; (c) $G_{(111)}/G_{(100)}$; (d) $G_{(110)[\bar{1}10]}/G_{(100)}$. The rare gas crystals are labeled as solid points.

Fig. 3. Poisson ratio data points (experimental) and curves (theoretical) for f.c.c. crystals: (a) v_{110}^{001}; (b) v_{100}; (c) v_{111}; (d) $v_{110}^{1\bar{1}0}$. Experimental values of the $v_{hkl}^{h'k'l'}$ are plotted using the following symbols: v_{110}^{001}, △ (for metals), ▲ (for rare-gas crystals); v_{100}, ● (metals), ◆ (rare-gases); v_{111}, ○ (metals), ◇ (rare-gases); $v_{110}^{1\bar{1}0}$, ▽ (metals), ▼ (rare-gases).

In order to illustrate the inherent ability of simple models (i.e. those containing only structurally dependent crystal binding contributions) to reproduce important anisotropy trends in the elastic behavior of specific cubic crystals, as well as examine the dependence of these trends upon δ, values of the Young moduli ratios E_{111}/E_{100} and E_{110}/E_{100}, the shear moduli ratios $G_{(111)}/G_{(100)}$ and $G_{(110)[\bar{1}10]}/G_{(100)}$, and the Poisson ratios v_{110}^{001}, v_{100}, v_{111}, and $v_{110}^{1\bar{1}0}$ were calculated using equations (1), (4), and (5), respectively, with the experimental data listed in Table 2. These experimentally determined ratios are represented as the ordinate-values of the individual data points plotted in Figs 1–4; the abscissa-values of
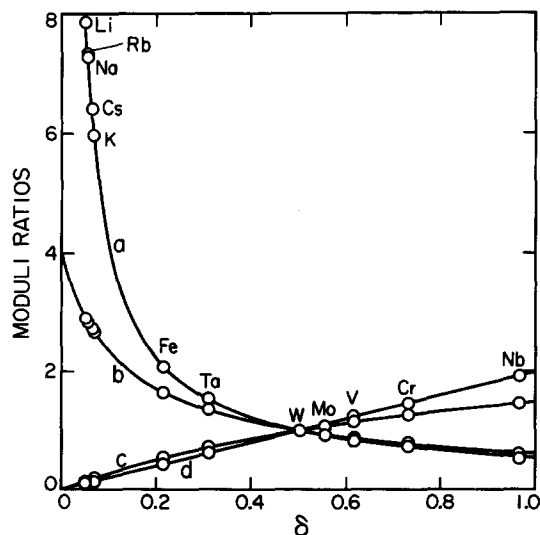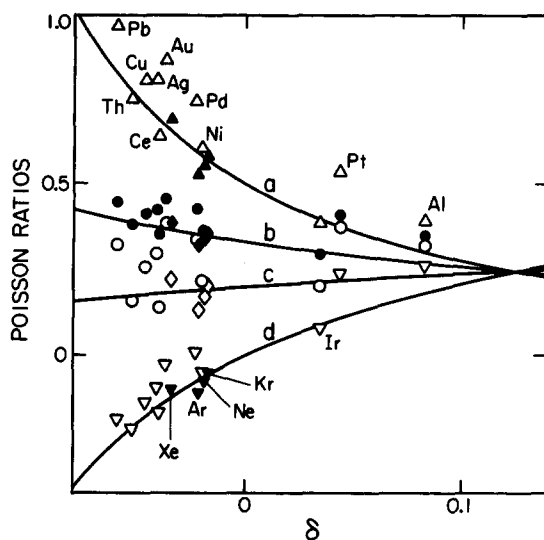
these data points in Figs 1–4 are the corresponding values of δ listed in Table 2. (Analogous plots can be made using the experimental values of η as the independent abscissa variable, since there is a one-to-one correspondence between η and δ for each of these crystals.) For comparison with theory, values of the elastic property ratios were calculated, as functions of η, using the formulae in Table 1, and as functions of δ, using the formulae in Table 1 together with equations (8c) and (9c); these values are also plotted vs δ as the "solid-line", theoretical curves in Figs 1–4.
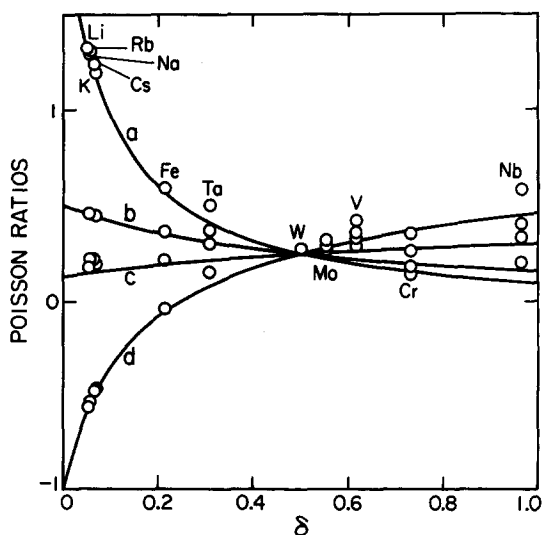

Fig. 2. Young's and shear moduli ratio data points (experimental) and curves (theoretical) for b.c.c. crystals: (a) E_{111}/E_{100}; (b) E_{110}/E_{100}; (c) $G_{(111)}/G_{(100)}$; (d) $G_{(110)[\bar{1}10]}/G_{(100)}$.

Fig. 4. Poisson ratio data points (experimental) and curves (theoretical) for b.c.c. crystals: (a) v_{110}^{001}; (b) v_{100}; (c) v_{111}; (d) $v_{110}^{1\bar{1}0}$.

The curves of the theoretical Young moduli and shear moduli ratios are compared with the experimental values for f.c.c. and b.c.c. crystals in Figs 1 and 2, respectively. With the computational procedure employed, the experimental shear moduli ratios are, of course, in exact agreement with the shear moduli ratio curves in Figs 1 and 2, since equations (4) depend on η only. What is remarkable, however, is the excellent quality of the fit obtained between the experimental and theoretical Young's moduli ratios (since experimental values of κ are required for the calculation of the former but are not included in the latter). The experimental data for the b.c.c. crystals match the theoretical curves almost exactly, while for the f.c.c. crystals the maximum discrepancy found in Fig. 1 is only about 9% (E_{111}/E_{100} for Au). This demonstrates that, while central force models of cubic crystals do not generally accurately reproduce all three independent elastic moduli (κ, μ, and μ'), such models are capable of matching all three Young's moduli (E_{111}, E_{110}, and E_{100}) well. Figures 3 and 4 compare the theoretical Poisson's ratio curves to experimental values for f.c.c. and b.c.c. materials, respectively. Again, the theoretical curves capture the "sense" of the Poisson's ratio variations quite well, though the agreement between theory and experiment is not as close as for the Young moduli ratios. In general the b.c.c. metals are in closer numerical agreement with the theoretical Poisson ratio curves than the f.c.c. metals. The b.c.c. crystals that fit the theoretical curves especially well include Fe, W, Cr, and the alkali metals; the f.c.c. crystals that best fit the theoretical curves include Ni, Ir, Ce, Th, Ne, Kr, and Ar while the worst fits are for Pb, Au, Pd, Pt, and Al.

4. SUMMARY

Important trends in the anisotropic elastic characteristics of cubic crystals may be described in surprising detail by models of crystal binding that include only structural contributions to atomic binding (omitting, e.g. purely volumetric dependent energy terms or many-body effects). This is made explicit by computations dependent upon only the ratio of second to first nearest neighbor atom contributions to the second order elastic moduli. Not only trends in elastic behavior but, in many cases, even rather accurate numerical agreement can be found by utilizing this extremely simple model. The present work underscores the central role of structure dependent interatomic contributions to crystal binding, in determining the elastic properties and behaviors of cubic crystals.

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