Poisson Ratios of Polycrystals

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Poisson ratios of fcc and bcc polycrystals are calculated for a variety of atomic models and the theoretical results are compared with experiment. In contrast with previously reported results, it is found that an accurate description of polycrystalline Poisson ratios of metals is obtained from the model in which the binding energy E_{bind} consists of a structure dependent part E_{str} and a volume dependent part E_{vol}. Investigations are made of the general, inherent abilities of various subsets of this model to describe experimental polycrystalline Poisson ratios; these subsets include the Cauchy model (i.e. E_{vol} is neglected in E_{bind}) and the Milstein-Rasky model (i.e. the volume dependent contribution to the bulk modulus $\varkappa_{\text{vol}}$ is neglected). In addition, specific computations of polycrystalline Poisson ratios are made for the complete families of bcc and fcc Morse function (Cauchy) crystals and for (non-Cauchy) models (simplified forms of which are suggested by pseudopotential theory for the noble metals).

Introduction

This is a study of relationships between the Poisson ratios ν of polycrystalline aggregates and the nature of interatomic interactions within the constituent crystals. This topic has long been of theoretical interest; for example, Ledbetter [1] noted that many authors [2–5] "have cited the deviation of ν from 1/4 as proof that the interatomic potential has a non-central component". Ledbetter [1] computed theoretically the Poisson ratios of polycrystalline aggregates composed of randomly oriented body centered cubic (bcc) and face centered cubic (fcc) single crystals in which the atoms interact solely through pairwise, nearest neighbor, central forces. He used the Voigt [6] and Reuss [7] averages as the lower and upper bounds on ν and the Hill [8] arithmetic average as the "best" theoretical value. For these models, he determined that $\nu(\text{fcc}) = 0.261$ and $\nu(\text{bcc}) = 0.364$ (Hill averages) and concluded that "a nearest neighbor model can predict the Poisson's ratio of cubic solids reasonably well". Ledbetter also attempted to improve his calculations by adding volume-dependent energy terms to model the kinetic, exchange, and correlation energies of the electron gas; these were of the form $E_{\text{vol}} = \sum_j A_j \Omega^{n_j}$, where A_j and n_j are constants and Ω is the atomic volume. However, he found the general agreement between observed and calculated values of ν to be "unaffected or worsened by including the effects of these electron-electron interactions", and concluded that the model (consisting of central, pairwise interactions and the above form of E_{vol}), "although used frequently, is incorrect, at least for some of the elastic constants."

Here we examine several aspects of the problem of relating interatomic forces and bcc and fcc polycrystalline Poisson ratios. We begin by reviewing the expressions for the Voigt, Reuss, and Hill approximations of the Poisson ratios; these are formulated in terms of dimensionless ratios of the single crystal elastic moduli. This formulation facilitates investigation of the inherent ability of selected crystal models to describe accurately the Poisson ratios of polycrystals. (Following Ledbetter, we consider the Hill averages to be equivalent to the "best" theoretical values of ν.) We then review various model dependent relations among the single crystal elastic moduli and examine the implications of these relations for the polycrystalline Poisson ratios. For example, for a fcc crystal with given values of the shear moduli or with given values for a shear modulus and the bulk modulus, the central force model generally is constrained to produce a polycrystalline Poisson ratio that is too high (when compared with experiment), irrespective of the detailed form of interatomic potential or the number of neighboring atoms included in the summing

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procedure. On the other hand, we find (in contrast with Ledbetter [1]) very good agreement between experimental and theoretical polycrystalline Poisson ratios wherein the latter are determined from the model in which the binding energy per atom E_{bind} consists of a structure dependent part E_{str} (i.e. a summation over pairwise energies Φ depending only upon interatomic separation r) and a volume dependent part E_{vol} (depending only upon the volume per atom Ω),

$$E_{\text{bind}} = E_{\text{str}} + E_{\text{vol}} . \tag{1}$$

This agreement is demonstrated for specific forms [9] of the E_{str} and E_{vol} contributions to (1). We also examine the role of more distant interatomic interactions (i.e. beyond nearest neighbors) in the central force model (i.e. with the E_{vol} contribution in (1) absent); we find that adding such interactions also improves the agreement between theory and experiment, but not to the extent of adding the E_{vol} contribution. Simplified models for crystal binding (such as those considered in the present paper) are widely used in studies of the solid state; thus it is important to determine the extent to which such models can reflect experimentally observed behavior.

Polycrystalline Poisson Ratios from Single Crystal Moduli

The Voigt [6] and Reuss [7] calculations of the elastic moduli of a polycrystal are the respective averages, over all possible lattice orientations, of the relations expressing the stress in a single crystal in terms of the given strain (Voigt) and of the strain in terms of the given stress (Reuss). For an aggregate that is macroscopically isotropic, Hill [8] showed that

$$K_{\text{R}} \leqq K \leqq K_{\text{V}} \quad \text{and} \quad G_{\text{R}} \leqq G \leqq G_{\text{V}} , \tag{2}$$

where K and G are the actual polycrystalline bulk and shear moduli, respectively, and the subscripts V and R denote the values calculated in the Voigt and Reuss approximations, respectively. The Poisson ratio ν of the polycrystal can be written in terms of a ratio of two elastic moduli, say

$$G/K \equiv \alpha ; \tag{3}$$

then

$$\nu = \tfrac{1}{2} - \tfrac{3}{2}[1/(1+3/\alpha)] . \tag{4}$$

The Voigt and Reuss values of α are obtained by substituting the corresponding values of G and K into (3); the resulting α values are substituted into (4) to obtain the Voigt and Reuss values of ν.

For a bcc or a fcc crystal [6–8],

$$K_{\text{R}} = K_{\text{V}} = \varkappa \tag{5}$$

$$5 G_{\text{V}} = 2\mu + 3\mu' , \tag{6}$$

and

$$G_{\text{R}} = \frac{5\mu\mu'}{3\mu + 2\mu'} , \tag{7}$$

where $\varkappa$ is the single crystal bulk modulus and μ and μ' are the single crystal shear moduli (which are related to the single crystal elastic constants C_{ij} by $\varkappa = \frac{1}{3}(C_{11} + 2C_{12})$, $\mu = \frac{1}{2}(C_{11} - C_{12})$ and $\mu' = C_{44}$). From relations (2), (3), and (5), it follows that

$$\alpha_{\text{R}} \leqq \alpha \leqq \alpha_{\text{V}} .$$

Since ν is a monotonically decreasing function of α for $\alpha > -3$, and material stability requires $\alpha > 0$, it also follows that

$$\nu_{\text{V}} \leqq \nu \leqq \nu_{\text{R}} . \tag{8}$$

This inequality is evident from Hill's discourse [8]; it was also employed by Ledbetter [10]. The Voigt and Reuss approximations of the polycrystalline Poisson ratio of a cubic crystal can be written in terms of any pair of the ratios

$$\xi \equiv \mu/\varkappa , \quad \zeta \equiv \mu'/\varkappa , \quad \text{or} \quad \eta \equiv \mu/\mu' . \tag{9}$$

For example, ν_{V} and ν_{R} are determined as functions of ξ and ζ by use of

$$\alpha_{\text{V}} = \tfrac{2}{5}\xi + \tfrac{3}{5}\zeta \tag{10}$$

and

$$\alpha_{\text{R}} = 5\xi\zeta/(3\xi + 2\zeta) \tag{11}$$

in (4).

Since G_{V} and G_{R} are upper and lower limits on G, Hill [8] suggested

$$G_{\text{H}} \equiv \tfrac{1}{2}(G_{\text{R}} + G_{\text{V}}) \quad \text{and} \quad G_{\text{h}} \equiv (G_{\text{R}} G_{\text{V}})^{1/2} \tag{12}$$

as good approximations to G. It then follows from (3), (5), and (12) that the corresponding Hill approximation of the Poisson ratio of the poly-

crystalline aggregate of a bcc or fcc crystal can be obtained by use of

$$\alpha_H = \tfrac{1}{2}(\alpha_V + \alpha_R) \quad \text{and} \quad \alpha_h = (\alpha_V \alpha_R)^{1/2} \tag{13}$$

in (4).

If there exists a relationship (among the three fcc or bcc single crystal elastic moduli) that reduces the number of independent single crystal moduli from three to two, then the Poisson ratios in the Voigt, Reuss, and Hill approximations can be written in terms of a single ratio of the single crystal elastic moduli (i.e. ξ, ζ, or η). Examples of such relations are considered in the following sections.

Crystal Models and Single Crystal Moduli

For a cubic crystal with its binding energy given by (1), the total external pressure P and the elastic moduli $\varkappa$, μ, and μ' are obtained by summing the individual contributions of E_{str} and E_{vol}. (These contributions are denoted by the respective subscripts str and vol; for example, $P_{vol} = -\,\mathrm{d}E_{vol}/\mathrm{d}\Omega$ and $\varkappa_{vol} = -\,\Omega\,\mathrm{d}P_{vol}/\mathrm{d}\Omega$ are the contributions of E_{vol} to P and $\varkappa$, respectively.) However, at a given atomic volume Ω, the term E_{vol} does not contribute to the shear moduli μ or μ'. Thus

$$P = P_{vol} + P_{str}\,, \quad \varkappa = \varkappa_{vol} + \varkappa_{str}\,, \tag{14}$$

$$\mu = \mu_{str}\,, \qquad \mu' = \mu'_{str}\,. \tag{15}$$

(Note that it is inaccurate to state that varying E_{vol} will not affect the value of μ and μ', since a variation of E_{vol}, in general, will affect Ω (for a given P), which in turn affects μ and μ').

Milstein and Hill [11, 12] derived the following expressions for the structure-dependent contributions to $\varkappa$, μ, and μ':

$$3\,\varkappa_{str} = \frac{n\,a}{2^3} \sum [(m_1^4 + 2\,m_1^2\,m_2^2)\,\Phi''(r^2)] + P_{str}\,, \tag{16}$$

$$\mu_{str} = \frac{n\,a}{2^4} \sum [(m_1^4 - m_1^2\,m_2^2)\,\Phi''(r^2)] - P_{str}\,, \tag{17}$$

$$\mu'_{str} = \frac{n\,a}{2^3} \sum [m_1^2\,m_2^2\,\Phi''(r^2)] - P_{str}\,, \tag{18}$$

where a is the lattice parameter; n is the number of atoms in a conventional cubic cell; the summations are over the m_i which are integers appropriate to the particular cubic lattice; and $\Phi''(r^2)$ is the second derivative of the pairwise interatomic potential Φ with respect to the square of interatomic distance r^2. Combination of (14–18) yields [9]

$$\varkappa_{vol} - 2\,P_{vol} = \varkappa - 2\,P - \mu' - \tfrac{2}{3}\mu\,. \tag{19}$$

For a Cauchy solid (central, pairwise forces only), $\varkappa_{vol}$ and P_{vol} are zero. If the external pressure P is also zero, (19) reduces to the well known Cauchy relation

$$\varkappa = \mu' + \tfrac{2}{3}\mu\,, \tag{20}$$

which is of course equivalent to $C_{12} = C_{44}$.

Milstein and Rasky [13] suggested that the elastic properties of cubic crystals can be more accurately described by a model that allows arbitrary contributions to the pressure (including P_{str} and P_{vol}, as well as more complicated pressure terms, as, e.g., are included in pseudopotential or other more sophisticated models), but in which the bulk modulus $\varkappa$ is determined by (16) [as well as μ and μ' by (17) and (18)]. The difference between the Milstein-Rasky crystal and the Cauchy crystal is that the total pressure $P = P_{str}$ in the latter crystal, but not in the former. They also suggested that, for many fcc crystals, it is reasonable to assume that the leading $\Phi''(r^2)$ term dominates the $\Phi''(r^2)$ summations of (16–18). The leading terms [11, 12] in (16–18) are, for fcc crystals,

$$\begin{aligned}
3\,\varkappa_{str} &= 8\sqrt{2}\,R_1\,[\Phi''(R_1^2) + 2\,\Phi''(2\,R_1^2) \\
&\qquad + 18\,\Phi''(3\,R_1^2) + \ldots] + P_{str}\,, \\
\mu_{str} &= \sqrt{2}\,R_1\,[\Phi''(R_1^2) + 8\,\Phi''(2\,R_1^2) \\
&\qquad + 18\,\Phi''(3\,R_1^2) + \ldots] - P_{str}\,, \\
\mu'_{str} &= 2\sqrt{2}\,R_1\,[\Phi''(R_1^2) + 0\,\Phi''(2\,R_1^2) \\
&\qquad + 18\,\Phi''(3\,R_1^2) + \ldots] - P_{str}\,,
\end{aligned} \tag{21}$$

and are, for bcc crystals,

$$\begin{aligned}
3\,\varkappa_{str} &= 4\sqrt{3}\,R_1\,[\Phi''(R_1^2) + \tfrac{4}{3}\,\Phi''(\tfrac{4}{3}\,R_1^2) \\
&\qquad + \tfrac{32}{3}\,\Phi''(\tfrac{8}{3}\,R_1^2) + \ldots] + P_{str}\,, \\
\mu_{str} &= \frac{8\,R_1}{\sqrt{3}}\,[0\,\Phi''(R_1^2) + \Phi''(\tfrac{4}{3}\,R_1^2) \\
&\qquad + 2\,\Phi''(\tfrac{8}{3}\,R_1^2) + \ldots] - P_{str}\,, \\
\mu'_{str} &= \frac{4\,R_1}{\sqrt{3}}\,[\Phi''(R_1^2) + 0\,\Phi''(\tfrac{4}{3}\,R_1^2) \\
&\qquad + 8\,\Phi''(\tfrac{8}{3}\,R_1^2) + \ldots] - P_{str}\,,
\end{aligned} \tag{22}$$

where R_1 is the nearest neighbor distance in the crystal. If just the $\Phi''(R_1^2)$ term is included in the Φ''-sums of (21), elimination of P_{str} yields [13]

$$\varkappa = \tfrac{1}{3}(9\,\mu' - 10\,\mu) \tag{23}$$

for the Milstein-Rasky model of a fcc crystal. This relation has been shown [13] to be in better agreement with experimental data for fcc metals and inert gas solids than the Cauchy relation (20). Within the framework of the model represented by (1), (23) is equivalent to assuming that $\varkappa_{vol}$ is zero, since (21) (with only the $\Phi''(R_1^2)$ term included in the Φ''-sums) can be combined with (14) and (15) to yield [9]

$$\varkappa - \varkappa_{vol} = \tfrac{1}{3}(9\,\mu' - 10\,\mu)\,, \tag{24}$$

although (1) is not a necessary assumption in the derivation of (23). Milstein and Rasky [9] computed $\varkappa_{vol}$ for a number of fcc metals, using (24) with experimental values of the elastic moduli, and found that $\varkappa_{vol}$ is frequently small compared with $\varkappa$. A notable exception is Al, for which $\varkappa_{vol} \approx \varkappa$ so that

$$\mu/\mu' \approx 0.9\,. \tag{25}$$

(For Al at 0 and 300 K, respectively, $\mu/\mu' = 0.83$ and 0.82.) The large contribution of $\varkappa_{vol}$ to $\varkappa$ in Al can be understood qualitatively from aluminum's relatively high valence and small, closed-shell ionic core; i.e. the nearest-neighbor ionic cores are well separated, and the bulk modulus of Al is mainly determined, not by interactions between neighboring ion cores, but by the distribution of the valence electrons which are scattered by the lattice of ion cores in the crystal. This evidently causes the elastic behavior of Al to be anomalous, when compared with most other fcc crystals [9].

Crystal Models and Polycrystalline Poisson Ratios

We consider next the utility of the model, represented by (1), in describing the Poisson ratios of polycrystals. This model can be considered to contain various "subsets", two of which, reviewed in the prior section, are the Cauchy solid, in which E_{vol} is neglected and the single crystal elastic moduli are related by (20), and the Milstein-Rasky model, in which $\varkappa_{vol}$ is neglected and (23) holds. For the latter case, (9) and (23) combine to yield $\zeta = (10\,\xi + 3)/9$, and thus (10) and (11) become

$$\alpha_V = (16\,\xi + 3)/15 \tag{26}$$

and

$$\alpha_R = 5\,\xi\,(10\,\xi + 3)/(47\,\xi + 6)\,; \tag{27}$$

the Hill values of α are obtained from (13), and the Voigt, Reuss, and Hill values of ν are readily computed by substituting the corresponding value of α into (4). For this model, Fig. 1 shows the theoretical ξ-dependencies of ν_H and ν_h (indicated respectively as $\nu_{H(M-R)}$ and $\nu_{h(M-R)}$). Figure 1 also shows the theoretical ξ-dependencies of the Hill values of ν for the Cauchy model (i.e. $\nu_{H(C)}$ and $\nu_{h(C)}$), as well as fcc experimental values of polycrystalline Poisson ratios ν, plotted versus experimental values of the single crystal elastic moduli ratios ξ. First, it is interesting to note that, although (in principle) the experimental values of ν should depend upon two of the ratios defined by (9), there is a definite tendency for the experimental values of ν for the fcc metals to decrease with increasing ξ. In fact, it is possible to draw a smooth, monotonically decreasing curve through all of the experimental data except those of Al, Pt (which would lie above the curve) and Th (which would be below the curve). Over the range of ξ-values of interest for fcc metals (i.e. $\xi \lesssim 0.5$), the theoretical ν values in Fig. 1 also de-

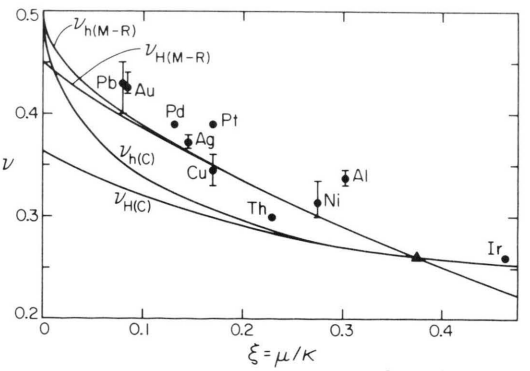

Fig. 1. Polycrystalline Poisson ratios ν versus single crystal shear moduli ratio ξ. Each (circular) datum point represents the average of experimentally based values of ν found in the literature [23–27] for fcc elements; the limits on the "error bars" denote the highest and lowest of the experimental values of ν for the respective elements. The theoretical curves are the Hill averages in the Milstein-Rasky model, $\nu_{H(M-R)}$ and $\nu_{h(M-R)}$, and in the Cauchy model, $\nu_{H(C)}$ and $\nu_{h(C)}$. The triangle in the lower right hand region designates the values of ν_H and ν_h for an fcc Cauchy crystal with nearest neighbor interactions only.

crease with increasing ξ. For the Milstein-Rasky model, the agreement between the theoretical Hill relations for ν and the experimental data is quite good in general, but the experimental ν values are typically much higher than the theoretical Hill values in the Cauchy model. In particular, among the fcc metals, Al exhibits the worst fit to the Milstein-Rasky model (whereas the majority of the fcc metals have even worse fits to the Cauchy model). Only Ir and Th agree with the Cauchy model better than with the Milstein-Rasky model (whereas the agreement in the latter model is satisfactory for these elements). The theoretical values of ν in the Cauchy model were calculated in a manner analogous to the calculation of the theoretical values of ν in the Milstein-Rasky model; i.e., from (9) and (20), $\zeta = 1 - 2\,\xi/3$; thus, (10) becomes

$$\alpha_V = \tfrac{3}{5}\,, \tag{28}$$

from which

$$\nu_V = \tfrac{1}{4} \tag{29}$$

for the Cauchy solid, independent of the values of the single crystal elastic moduli; (11) becomes

$$\alpha_R = 5\,\xi\,(3 - 2\,\xi)/(5\,\xi + 6)\,, \tag{30}$$

and ν_R, ν_H, and ν_h for the Cauchy solid are computed as a function of ξ using (4), (13), (28), and (30).

Equation (29) was noted "in passing" by Hill [8], and according to Ledbetter [10], "Schmid and Boas realized, as did Voigt, that Voigt's average for the case $C_{12} = C_{44}$ predicts inevitably that $\nu = 1/4$ for polycrystals. However, Schmid and Boas believed wrongly that other averaging methods would also predict $\nu = 1/4$".

Figure 2 compares the Voigt lower limits, $\nu_{V(C)}$ and $\nu_{V(M-R)}$, and the Reuss upper limits, $\nu_{R(C)}$ and $\nu_{R(M-R)}$, of the polycrystalline Poisson ratios in the respective Cauchy and Milstein-Rasky models. The principal difference between the two models is in the ν_V values. For a given value of ξ in the range $0 < \xi < 3/8$ (i.e. the range of interest for most fcc metals), $\nu_{R(C)}$ is bounded by $\nu_{R(M-R)}$ and $\nu_{V(M-R)}$, and thus the plot of $\nu_{R(C)}$ vs ξ does not differ markedly from the plots of $\nu_{H(M-R)}$ and $\nu_{h(M-R)}$ versus ξ.

The various theoretical polycrystalline Poisson ratios in the Cauchy and Milstein-Rasky models are also readily expressed uniquely as functions of ζ or

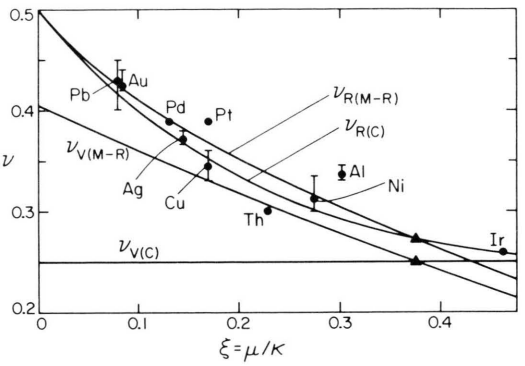

Fig. 2. Dependencies upon ξ of the theoretical Voigt and Reuss polycrystalline Poisson ratios, ν_V and ν_R, in the Milstein-Rasky (M−R) and Cauchy (C) models. The experimental data are the same as in Fig. 1; the triangles show the values for an fcc Cauchy crystal with nearest neighbor interactions only.

η by use of

$$\alpha_V = 3\,(8\,\zeta - 1)/25 = 3\,(2\,\eta + 3)/[5\,(9 - 10\,\eta)] \tag{31}$$

and

$$\begin{aligned}\alpha_R &= 5\,\zeta\,(9\,\zeta - 3)/(47\,\zeta - 9)\\ &= 15\,\eta/[(9 - 10\,\eta)\,(3\,\eta + 2)]\end{aligned} \tag{32}$$

for the Milstein-Rasky solid and

$$\begin{aligned}\alpha_R &= 15\,\zeta\,(\zeta - 1)/(5\,\zeta - 9)\\ &= 15\,\eta/[(3\,\eta + 2)\,(2\,\eta + 3)]\end{aligned} \tag{33}$$

for the Cauchy solid. Equations (31)−(33) were also used to compute the theoretical polycrystalline fcc Poisson ratios as functions of ζ and η. Plots of ν versus ζ and η (not shown, for the sake of brevity) exhibit the following characteristics. The experimental values of ν tend to decrease with increasing ζ, as they do with increasing ξ. There is more scatter in the plot of the experimental ν-values versus the experimental η-values, with no general pattern appearing. The fit between the experimental data and the theoretical $\nu_{H(C)}$ and $\nu_{H(M-R)}$ curves also tends to be worse for the cases where ζ and η are the independent variables, rather than ξ. For all of the fcc metals, the experimental values of ν are greater than the values calculated in the Cauchy model (irrespective of whether the experimental values of ξ, ζ or η are used in the calculations), mainly owing to the very low, constant value of ν_V. Particularly poor agreement between the experimental values of ν and

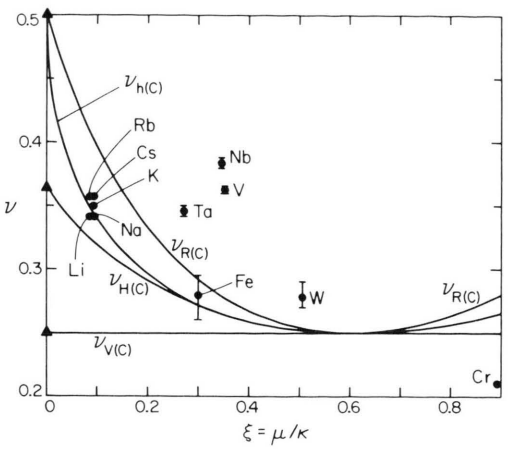

Fig. 3. Polycrystalline Poisson ratios ν versus ξ. For the bcc transition metals, each circular datum point represents the average of experimentally based values found in the literature [23–27]; the "error bars" denote the highest and lowest values. For the bcc alkali metals, the circular data points mark the experimental values of ξ and experimentally based values of ν_H (computed using the experimental values of $\varkappa$, μ, and μ' [28]) at 78 K. The theoretical curves are the Voigt, Reuss, and Hill averages in the Cauchy model; the triangles on these curves mark the values for a bcc Cauchy crystal with nearest neighbor interactions only.

the theoretical Cauchy values of ν_H is found for the elements Pb, Au, Pd, Ag, Cu, and Pt when ζ is chosen as the independent variable and for the elements Pb, Au, Pd, Ag, Pt, and Al when η is the independent variable. In comparing the experimental values of ν with $\nu_{H(M-R)}$, when ζ is the independent variable, good agreement is found for Pb, Pd, Ag, Cu, Ni, and Ir and poor agreement only for Au, Pt, and Al; when η is the independent variable, poor agreement is found for these latter three elements and Ir.

Figure 3 compares the theoretical behavior of the Poisson ratios in the general bcc Cauchy model with experiment. Again there is a tendency for the experimental values of ν to decrease with increasing ξ, but there is more "scatter" in this "relationship" for the bcc than for the fcc metals. In principle, the Cauchy model is reasonably well-suited to correlating ν and ξ for Fe, W, and the alkali metals. The condition for isotropy in the Cauchy model of cubic crystals is $\zeta = \xi = 0.6$ ($\eta = 1$); when this occurs $\nu_V = \nu_R$, of course (as seen in Figure 3). For bcc crystals, the second nearest neighbor $\Phi''(4/3\,R_1^2)$ terms in (22) make relatively large contributions to the elastic moduli μ and $\varkappa$, and thus Milstein and Rasky [9, 13] did not attempt to determine a relation among the elastic moduli of bcc crystals (analogous to (23) for fcc crystals), independent of the particular form of Φ.

Figures 1–3 show the values of ν in the Cauchy and Milstein-Rasky models for crystals with given values of ξ, but the results shown do not ensure that any *particular* forms of E_{vol} and/or E_{str} will yield crystals capable of possessing the appropriate values of ξ. For example, for the Cauchy model at zero pressure, with nearest neighbor interactions only, for fcc crystals (from (21))

$$\xi = \sqrt{2}\,R_1\,\Phi''(R_1^2)/(8\sqrt{2}\,R_1\,\Phi''(R_1^2)/3) = 3/8$$

(similarly $\zeta = 3/4$), and for bcc crystals (from (22)), $\xi = 0$ (and $\zeta = 1$). Thus, with α_V and ν_V given by (28) and (29), (4), (28), and (30) yield, for the fcc case

$$\alpha_R = 0.536,\ \alpha_H = 0.568, \quad \text{and} \quad \alpha_h = 0.567,$$

from which

$$\nu_R = 0.273,\ \nu_H = 0.261, \quad \text{and} \quad \nu_h = 0.262,$$

and for the bcc structure,

$$\alpha_R = 0,\ \alpha_H = 0.300, \quad \text{and} \quad \alpha_h = 0,$$

from which

$$\nu_R = 0.500,\ \nu_H = 0.364, \quad \text{and} \quad \nu_h = 0.500,$$

thereby reproducing the values of ν_V, ν_R, and ν_H obtained by Ledbetter. The behavior of Cauchy crystals with nearest neighbor interactions is thus seen to be described by single points on the respective ν vs ξ curves. These points are indicated as "triangles" for the fcc structure in Figs. 1 and 2 and for the bcc structure in Figure 3. Ledbetter [1] observed that the fcc ν value calculated in the nearest neighbor Cauchy model is smaller than experimental values of ν for fcc crystals. In Fig. 1 we see this to be associated with the fact that the value of ξ for the nearest neighbor fcc Cauchy crystal is too high (when compared with experiment) for all of the fcc metals except Ir. Ledbetter [1] also noted that the "agreement with a central force value of ν is much better in the bcc case than in the fcc case." Figure 3 indicates that this result (which was based on the nearest neighbor model) is evidently "fortuitous," and not an indication that the general elastic properties of bcc crystals are reasonably described

by a nearest neighbor Cauchy model. In fact, quite the contrary is true, since $\mu = 0$ (and hence the bcc crystal is unstable for this model) [14]. Ledbetter [1] claimed that his "results are contrary to MacDonald's contention that 'general properties of a crystal may not necessarily be realized on a nearest neighbor model.'" For Cauchy crystals, our results support "MacDonald's [15] contention."

In the nearest neighbor approximation, the Milstein-Rasky and the Cauchy models are identical if the total pressure P is equal to the structural contribution P_{str} (i.e. $P_{vol} = 0$); if $P = 0$, this occurs for fcc crystals where $\xi = 3/8$ ($\zeta = 3/4$, $\eta = 1/2$) (see (21) in [9]). Thus, the respective theoretical M−R and C curves cross at $\xi = 3/8$ in Figs. 1 and 2. If $\xi < 3/8$ ($\eta < \frac{1}{2}$) in the Milstein-Rasky model, then $P_{vol} < 0$ (i.e. the E_{vol} contribution to E_{bind} "forces the atoms together" while the E_{str} part "pushes them apart," when the total applied pressure is zero); conversely, if $\xi > 3/8$, $P_{vol} > 0$.

Figures 1−3 suggest that the description of the single crystal elastic moduli and polycrystalline Poisson ratios in the Cauchy model can be improved significantly (when compared with the nearest neighbor approximation) by employing particular forms of Φ and carrying the summations beyond just nearest neighbors in (16−18) or (21) and (22). As an example, we compute ν for fcc and bcc Cauchy crystals for the complete family of Morse functions,

$$\Phi(r) = D\{\exp[-2\omega(r - r_0)] - 2\exp[-\omega(r - r_0)]\}, \tag{34}$$

where D, ω, and r_0 are empirical parameters; $(d\Phi/dr) = 0$ at $r = r_0$; and $\Phi(r_0) = -D$, the dissociation energy of two atoms. In these computations of ν, the lattice summations are over a sufficiently large number of lattice sites to obtain convergence to at least 5 significant figures. In addition, in order to allow the roles of first and second neighbor interactions and the cumulative effect of more distant neighbor interactions to be examined explicitly, the computations of the single crystal elastic moduli and the polycrystalline Poisson ratios are also made for the complete Morse family of fcc and bcc crystals with just nearest and next nearest neighbor contributions.

The Morse function was selected for this example for the following reasons. It has been widely used in describing crystal elasticity, often with remarkably accurate results (numerous examples are given in the review article by Milstein [16]; see also [17] and [18]); specific parameters D, ω, and r_0 have been determined from experimental values of atomic volume and single crystal elastic moduli for a number of cubic crystals [19−21]; the general elastic properties, including stability, of the complete Morse family of bcc and fcc single crystals have been studied over wide ranges of pressure [11, 12, 14]. Another useful and interesting characteristic of the Morse function is that it conveniently permits the modeling of interatomic interactions that range from the "nearest neighbor" limit (for the case $\beta \equiv \exp(\omega r_0) \to \infty$) to the "continuum" limit (for $\beta \to 16$) [11]. Thus the parameter β serves as an effective potential range indicator; larger values of β mean shorter range and steeper functions $\Phi(r)$. That is, as β becomes large, the nearest neighbor distance in the unstressed crystal approaches the value that would exist in the limiting approximation of nearest neighbor interactions only. As β decreases, the ratio r_0/R_1 increases; thus, the distance from the origin to the potential minimum becomes larger, relative to R_1. In other words, the potential becomes "longer range" and "shallower." The intermediate values, say $\ln\beta \approx 3$ to 8, provide the most realistic models of actual crystals [19−21].

For the Morse model, the dimensionless ratio ξ (as well as ζ and η) depends uniquely upon the parameter $\ln\beta$, the applied pressure, and the crystal structure; this was demonstrated, and the dependencies were computed, by Milstein and Hill [11, 12]. It is therefore straightforward to use their zero pressure computations (see Fig. 11 in [12]) to determine the theoretical polycrystalline Poisson ratios as unique functions of $\ln\beta$ for the complete Morse family of fcc and bcc crystals. This was done and the results are shown in Figs. 4 and 5. The range of ξ for fcc Morse function crystals was found to be $0.067 \lesssim \xi \leqq 0.375$ (the lower limit is for small $\ln\beta$; the upper limit is for large $\ln\beta$ − i.e. the "nearest neighbor limit"). As is indicated in Fig. 4, the Morse function achieves the theoretically possible relations shown in Figs. 1 and 2 over the ranges of interest for most fcc crystals (Ir is the exception). For elastically stable (i.e. $\mu > 0$) bcc crystals with Morse function interactions between atoms, however, $0 < \xi \lesssim 0.2$ where $\xi > 0$ if and only if $\ln\beta < 4.517$; the upper limit corresponds to small $\ln\beta$. The very small range of positive ξ values in the

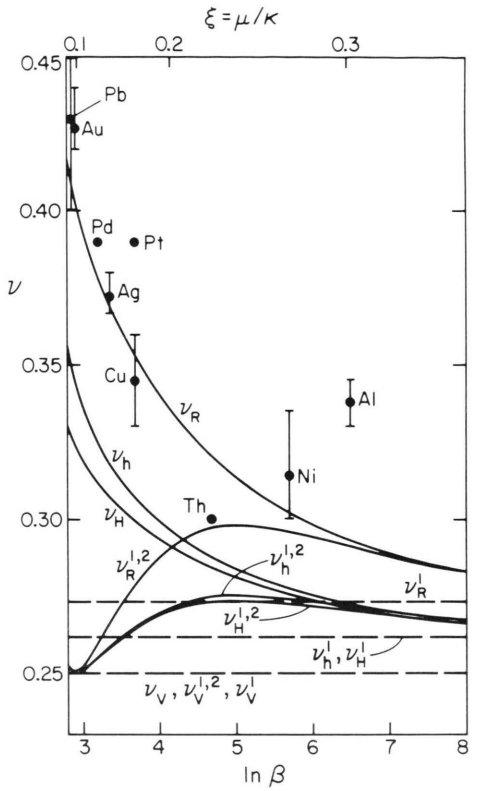

Fig. 4. Polycrystalline Poisson ratios for fcc crystals. The curves ν_R, ν_h, and ν_H represent the Reuss and the two Hill theoretical values for fcc Morse function crystals in which the Φ''-lattice summations are summed to convergence (and the pressure P_{str} is zero). The curves labeled $\nu_R^{1,2}$, $\nu_h^{1,2}$, and $\nu_H^{1,2}$ give the contributions to ν_R, ν_h, and ν_H, respectively, of the combined first and second nearest neighbor Φ''-interactions; the curves labeled with the superscript 1 give the respective contributions of the nearest neighbor interactions only. (ν_V is 1/4 irrespective of the summing details.) The experimental data are the same as in Figs. 1 and 2; the $\ln\beta$-abscissa scale applies to all of the theoretical curves (including the $\nu^{1,2}$ curves); the ξ-abscissa scale applies to the experimental data and to the ν_R, ν_h, and ν_V curves.

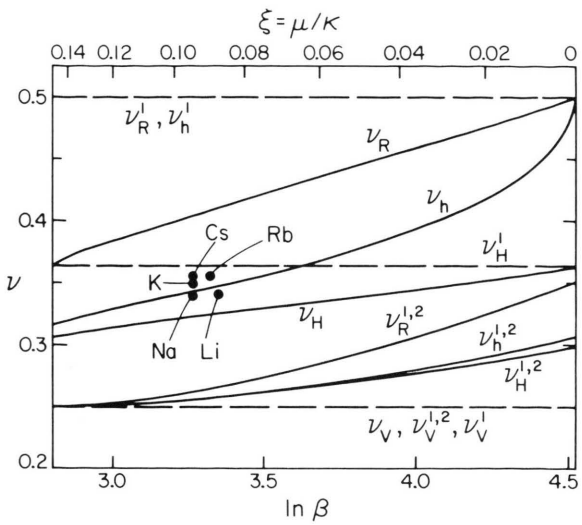

Fig. 5. Polycrystalline Poisson ratios for bcc crystals. The values indicated for the alkali metals are the same as in Figure 3. The caption of Fig. 4 explains the labeling of the curves and the applicability of the two abscissa scales.

Morse model of bcc crystals limits its applicability only to the far left portion of Fig. 3; i.e., among the bcc crystals, the Morse model provides a reasonable description of the alkali metals only. The difficulty in describing the shear moduli μ of bcc crystals in the framework of a purely central force model is characteristic of such models in general [22], not just the Morse model, owing to the zero coefficient of the leading term in the Φ''-summation for μ_{str} [see (22)]. Further insight can be obtained by examining explicitly the roles of nearest and next nearest neighbor interactions in bcc and fcc Cauchy crystals, as follows.

If ε represents the ratio of the second nearest neighbor Φ''-term to the first nearest neighbor Φ''-term in (21) and (22) (i.e. $\varepsilon = \Phi''(2R_1^2)/\Phi''(R_1^2)$ for fcc and $\varepsilon = \Phi''(4/3\,R_1^2)/\Phi''(R_1^2)$ for bcc), then for Cauchy crystals with first and second nearest neighbor interactions only,

$$\xi = (3/8 + 3\varepsilon)/(1 + 2\varepsilon) \tag{35}$$

for fcc, and

$$\xi = 2\varepsilon/(1 + 4\varepsilon/3) \tag{36}$$

for bcc. (Likewise $\eta = \frac{1}{2} + 4\varepsilon$ for fcc and $\eta = 2\varepsilon$ for bcc.) If ϱ represents the ratio of the second to first neighbor distances (i.e. $\varrho = \sqrt{2}$ for fcc and $\varrho = \sqrt{4/3}$ for bcc), from (34) and the definition of ε,

$$\varepsilon = \frac{\beta e^{2\omega R_1(1-\varrho)}(2\omega R_1\varrho + 1) - e^{\omega R_1(2-\varrho)}(\omega R_1\varrho + 1)}{[\beta(2\omega R_1 + 1) - e^{\omega R_1}(\omega R_1 + 1)]\varrho^3} \tag{37}$$

for the Morse function. For Morse function cubic crystals, the quantity ωR_1 depends uniquely upon β and the type of crystal structure (see Fig. 2 in [11]); thus, the value of ε depends uniquely upon β and crystal structure. The dependence of ε upon $\ln\beta$ (calculated from (37) with Milstein and Hill's [11]

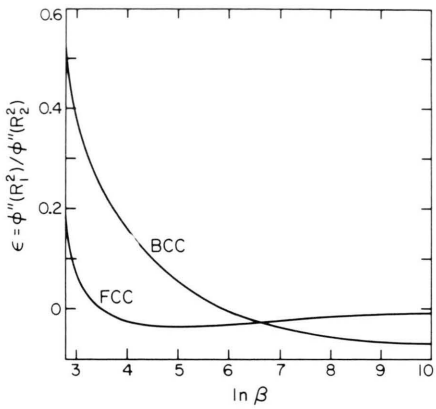

Fig. 6. Ratio of $\Phi''(R_1^2)/\Phi''(R_2^2)$ versus $\ln\beta$ for fcc and bcc crystals in which the atoms interact via the Morse function (34); Φ'' is the second derivative of Φ with respect to the square of interatomic distance (r^2) and R_1 and R_2 are the nearest and second nearest neighbor distances in the crystals.

computed values of ωR_1 vs $\ln\beta$) is shown in Fig. 6 for the fcc and bcc structures. (Throughout most of this plot, the magnitude of ε is greater for bcc than for fcc, thus illustrating the relatively greater importance of second nearest neighbor interactions in bcc crystals.) The values of ε shown in Fig. 6 are then used with (35) and (36) to compute ξ versus $\ln\beta$; the values of ξ are then used to compute the α-values ((13), (28), and (30)), which in turn are used to determine the theoretical ν-values (4); these (combined) nearest and next nearest neighbor Morse model computations of ν are also shown in Figs. 4 and 5 (i.e. the ν-values labeled with the superscripts 1, 2). For the fcc case (Fig. 4), for $\ln\beta \gtrsim 6$, the combined first and second nearest neighbor contributions to the theoretical ν values are very close to the values obtained when the lattice sums are taken to convergence; the combined first and second neighbor approximations to ν_R, ν_H, and ν_h tend to diverge from the "full summation" ν values for $\ln\beta \lesssim 5$; this is consistent with the interpretation of $\ln\beta$ as a potential range indicator. For most fcc metals, the agreement between the experimental values of ν and the theoretical values computed in the Morse model is best when the sums are taken to convergence. This is also the case for the bcc alkali metals shown in Fig. 5 (although, as mentioned earlier, the nearest neighbor Hill value ν_H^1 fortuitously agrees well with experiment).

We return now to the more general model represented by (1). Figure 1 (i.e. $\nu_{H(M-R)}$ and $\nu_{h(M-R)}$) suggests that this model is capable of good agreement between theoretical and experimental elastic behavior, provided that appropriate forms of E_{vol} and E_{str} can be determined. As a specific example, we conider the forms proposed by Milstein and Rasky [9] for the noble metals, based upon concepts of pseudopotential theory. The volume-dependent part of the binding energy was written as

$$E_{vol} = E_{FE} + E_{es}^* + E_{CC}; \tag{38}$$

E_{FE} (which includes the kinetic, exchange, and correlation contributions to the energy of the free-electron gas) is given by a standard form, i.e.,

$$E_{FE} = z\,[5.742\,(z/\Omega)^{2/3} - 1.477\,(z/\Omega)^{1/3} - 0.031\ln(z/\Omega)^{1/2} - 0.130]. \tag{39}$$

(The units are rydbergs and Bohr radii a_0 for energies and lengths, respectively; z is the valence.) The electrostatic energy of interaction of a lattice of positive ion cores (treated as point ions) with the valence electrons (treated as a uniform negative background) was written as

$$E_{es}^* = -\delta z^2/\Omega^{1/3}, \tag{40}$$

and the effect of the finite-ion core size on the electrostatic attraction between the ion cores and valence electrons was taken into account by a core correction term of the form

$$E_{CC} = \gamma z^2/\Omega. \tag{41}$$

The parameters δ and γ are treated as adjustable constants; for Cu, Ag, and Au, respectively, [9] $\delta = 4.1859$, 7.4018, and 20.638 Ry a_0 and $\gamma = 5.3344$, 36.823, and 144.26 Ry a_0^3. The structural part of the binding energy was taken as a sum over Born-Mayer interactions,

$$E_{str} = \tfrac{1}{2}\sum_r A\,e^{-B(r/R_1-1)}, \tag{42}$$

where the r values are the distances between the origin atom and its neighbors, A and B are adjustable parameters, and R_1 is the nearest-neighbor distance. [Although three constants A, B, and R_1 appear in the Born-Mayer interaction (as it is normally written), there are of course only two "real" adjustable parameters, $A' \equiv A\,e^B$ and $B' \equiv B/R_1$.] For Cu, Ag, and Au, respectively, [9], $A = 6.6397\times10^{-3}$, 4.6598×10^{-3}, and 3.2660×10^{-3} Ry and $B = 13.167$, 14.697, and 16.297. Although the model has only four adjustable constants (δ, γ, A, B), it was able to fit the experimental values of the OK elastic moduli $\varkappa$, μ, and μ' and atomic volumes Ω

(at zero pressure); it also yielded good agreement between experimental and computed $P-\Omega$ relations and the pressure derivatives of $\varkappa$, μ, and μ' [9]. In particular, the elastic moduli (in units of 10^{12} dyn/cm^2) of Cu, Ag, and Au, described by the above model, are (respectively) $\varkappa = 1.420$, 1.087, and 1.803, $\mu = 0.2565$, 0.171, and 0.1595, and $\mu' = 0.818$, 0.511, and 0.454. Substituting these values into (9–11) and (13) yields (for Cu, Ag, and Au, respectively) $\alpha_V = 0.418$, 0.345, and 0.186, $\alpha_R = 0.307$, 0.262, and 0.145, $\alpha_H = 0.363$, 0.303, and 0.166, and $\alpha_h = 0.358$, 0.301, and 0.164, from which $\nu_V = 0.317$, 0.345, and 0.412, $\nu_r = 0.361$, 0.380, and 0.431, $\nu_H = 0.338$, 0.362, and 0.422, and $\nu_h = 0.340$, 0.363, and 0.422. Upon comparing the above theoretical values of ν_H or ν_h with the experimental values of ν for Cu, Ag, and Au (i.e. 0.345, 0.372, and 0.427, respectively – see Fig. 1), we note that there is excellent agreement. This of course is not surprising since the particular model describes the general elastic behavior of the single crystal noble metals very well [9]. Our main purpose in carrying out these computations for the noble metals is to demonstrate explicitly the efficacy of the model represented by (1) in the description of polycrystalline Poisson ratios, particularly in view of Ledbetter's [1] finding to the contrary; the differences are likely owing to the detailed nature of the specific forms of E_{str} and E_{vol}. (Some forms of E_{str} and E_{vol} no doubt will give worse agreement between theory and experiment than those employed above.) Milstein and Rasky [9] also found that the models of Cu and Ag (discussed above) agreed well with (23) (i.e. $\varkappa_{vol}$ in (24) is small compared with $\varkappa$); but for Au, $\varkappa_{vol}$ and $\varkappa_{str}$ are comparable in magnitude. Thus, in Fig. 1, the experimental Cu and Ag data are closer to the theoretical $\nu_{H(M-R)}$ curve than are the Au data.

Finally, we note that in the model for Al mentioned in the previous section, $\varkappa_{vol} \approx \varkappa$ (and thus the experimental value of ν for Al is relatively distant from the theoretical $\nu_{H(M-R)}$ curve in Figure 1). The theoretical values of ν_V and ν_R of a fcc crystal with $\varkappa_{vol} = \varkappa$ in (24) are readily computed as functions of ξ or ζ; i.e. from (9) and (25), $\xi = 0.9\,\zeta$, so (10) and (11) become

$$\alpha_V = 0.960\,\zeta \quad \text{and} \quad \alpha_R = 0.957\,\zeta \tag{43}$$

or

$$\alpha_V = 1.067\,\xi \quad \text{and} \quad \alpha_R = 1.064\,\xi\,. \tag{44}$$

With the experimental value of ζ for Al equal to 0.398, (43) and (4) yield 0.331 for both ν_V and ν_R; with the experimental value of ξ for Al of 0.330, (44) and (4) then yield $\nu_V = 0.342$ and $\nu_R = 0.343$. These computed values are all very close to the "average" experimental value of ν for Al in Fig. 1 (i.e. $\nu = 0.338$).

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