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Bounds and Self-Consistent Estimates for Elastic Constants of Random Polycrystals with Hexagonal, Trigonal, and Tetragonal Symmetries

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Abstract

Peselnick, Meister, and Watt have developed rigorous methods for bounding elastic constants of random polycrystals based on the Hashin-Shtrikman variational principles. In particular, a fairly complex set of equations that amounts to an algorithm has been presented previously for finding the bounds on effective elastic moduli for polycrystals having hexagonal, trigonal, and tetragonal symmetries. The more analytical approach developed here, although based on the same ideas, results in a new set of compact formulas for all the cases considered. Once these formulas have been established, it is then straightforward to perform what could be considered an analytic continuation of the formulas (into the region of parameter space between the bounds) that can subsequently be used to provide self-consistent estimates for the elastic constants in all cases. These self-consistent estimates are easily shown (essentially by construction) to lie within the bounds for all the choices of crystal symmetry considered. Estimates obtained this way are quite comparable to those found by the Gubernatis and Krumhansl CPA (coherent potential approximation), but do not require any computations of scattering coefficients.

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I. INTRODUCTION

Polycrystalline materials such as water ice and quenched volcanic melts occur in nature and such as powder compacts have been developed extensively by industry. So, for both scientific and engineering purposes, it is important to be able to characterize the mechanical behavior of the very great variety of polycrystalline solid media of interest. Estimates of elastic constants came first [1, 2], to be followed later by Hill's discovery [3] that the same estimates were in fact rigorous, if somewhat crude, bounds on the constants. The Hashin-Shtrikman bounds [4] were then developed using some new variational principles to provide improved bounds for polycrystals of cubic solids. These variational methods were subsequently used to provide improved rigorous bounds for many of the most important crystal symmetry classes [5–7]. However, the main estimates used for polycrystals are still the Voigt-Reuss-Hill averages [8], as suggested by Hill in his original paper [3] on the subject. So the question arises now whether there are better estimates available, perhaps based on the information contained in the bounds themselves. One approach to the finding an answer to this question is the subject of the present work.

There have been previous efforts to obtain self-consistent estimates by (among others) Kroner [9] and Gubernatis and Krumhansl [10] of the elastic constants for polycrystals. In particular, Gubernatis and Krumhansl [10] derived a set of self-consistent formulas using scattering theory. Their results are in the same class of approximations as the CPA (coherent potential approximation) [11] used successsfully in estimating densities of states and band structures in disordered binary alloys. Although it is beyond our current scope to determine the relationship (if any) between the present work and the earlier approaches using the CPA, ultimately we will conjecture that the present results are probably numerically equivalent to CPA, at least in the symmetry classes studied so far. (In fact, the numerical evidence so far shows that they are roughly equivalent.) Furthermore, it has been shown in another context [12] that two such approaches to the problem of estimating elastic constants for two-component random composites are exactly equivalent. Nevertheless, the present approach gives a quite different insight into the polycrystal analysis and coefficient estimation problem, and we believe it therefore has inherent merit based on this criterion alone. Furthermore, since the estimates obtained are derived from the bounds, there is obviously little need to check to see if the bounds are being satisfied. There is also no need to compute scattering

coefficients with the present methods.

The next section presents the stress-strain relations for the hexagonal, trigonal, and tetragonal symmetries to be considered here. Appendices A and B review known bounds, including the Voigt [1] and Reuss [2] bounds as well as the Peselnick-Meister-Watt (PMW) bounds [4–7], based on the Hashin-Shtrikman variational principles. The third section in the main text uses the results of these two Appendices to reformulate the PMW bounds and arrive at the desired analytic formulas for them. The fourth section then uses these formulas to construct self-consistent estimates for random polycrystals. The fifth section presents some examples making use of both bounds and estimates. The sixth section summarizes our conclusions.

II. STRESS-STRAIN RELATIONS FOR THE THREE SYMMETRY CLASSES

The members of the class of crystal symmetries considered here have their stress-strain relations given in the form:

$$\begin{pmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{33} \\ \sigma_{23} \\ \sigma_{31} \\ \sigma_{12} \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{13} & c_{14} & & \\ c_{12} & c_{11} & c_{13} & -c_{14} & & \\ c_{13} & c_{13} & c_{33} & & & \\ c_{14} & -c_{14} & & c_{44} & & \\ & & & & c_{44} & c_{14} \\ & & & & c_{14} & c_{66} \end{pmatrix} \begin{pmatrix} e_{11} \\ e_{22} \\ e_{33} \\ e_{23} \\ e_{31} \\ e_{12} \end{pmatrix}, \tag{1}$$

where σ_{ij} are the usual stress components for $i, j = 1 - 3$ in Cartesian coordinates, with 3 (or z) being the axis of symmetry. Displacement u_i is then related to strain component e_{ij} by $e_{ij} = \partial u_i/\partial x_j + \partial u_j/\partial x_i$, when $i \neq j$, and $e_{ii} = \partial u_i/\partial x_i$ when $i = j$. For trigonal symmetry all of these constants shown are nonzero, but $c_{66} = (c_{11} - c_{12})/2$. Both hexagonal and tetragonal symmetries have $c_{14} = 0$, while hexagonal again has $c_{66} = (c_{11} - c_{12})/2$, but tetragonal symmetry does not share this restriction.

III. ELASTIC CONSTANT BOUNDS FOR THE MODEL

Voigt and Reuss bounds [1, 2] for the three crystal symmetry classes studied in this paper are reviewed in Appendix A. These bounds also help to motivate a pair of product formulas

that will be used extensively in the following discussion.

A. SIMPLIFIED BOUNDS ON BULK MODULUS

The formulas for the Hashin-Shtrikman-type bounds on polycrystals [4] of grains having hexagonal, trigonal, and tetragonal symmetries are summarized in Appendix B. These bounds were derived originally by Peselnick and Meister [5] and Meister and Peselnick [6] with some corrections appended later by Watt and Peselnick [7]. The presentation of these bounds is fairly complex, and so we will describe them as being expressed "algorithmically" – rather than as formulas. What we mean by this statement is that this way of presenting the results is sufficiently opaque that it is not at all obvious how to use such bounds to produce – for example – a set of self-consistent effective medium approximations based on them. So, in order to gain the insight needed to deduce (in an operational sense) effective medium approximations based on such bounds, it is most helpful to have analytical formulas. Indeed, the usual self-consistency conditions basically require an analytic continuation of a formula (or in elasticity a pair of coupled formulas) in order to achieve a successful approximation. Thus, it will be our goal to find appropriate analytic formulas for bulk modulus here and, in the next subsection, also for shear modulus.

The main observation that helps us to find such formulas in this case is based on the easily verified facts (using the notation from Appendix B) that

$$1 + 2\beta_{\pm}G_{\pm} = -2\beta_{\pm}\zeta_{\pm} \tag{2}$$

where $\beta_{\pm}$ are defined in (38) and $\zeta_{\pm}$ are defined by

$$\zeta_{\pm} = \frac{G_{\pm}}{6}\left(\frac{9K_{\pm} + 8G_{\pm}}{K_{\pm} + 2G_{\pm}}\right). \tag{3}$$

In (3), the values $G_{\pm}$ and $K_{\pm}$ are those given in Appendix B, having the significance of the shear and bulk moduli of the isotropic comparison material used in the Hashin-Shtrikman bounds. As one example, consider hexagonal symmetry: for the values in (3) and Appendix B, we typically have $G_{-} = c_{44}$ and $G_{+} = c_{66}$. Then, the values of $K_{\pm}$ are computed from (44)-(48).

To obtain the desired result for bulk modulus, first rearrange (36) into the form

$$K_{PM}^{\pm} = \frac{K_V + K_{\pm}2\beta_{\pm}(G_{\pm} - G_{\text{eff}}^{v})}{1 + 2\beta_{\pm}(G_{\pm} - G_{\text{eff}}^{v})}, \tag{4}$$

where $G^v_{\rm eff}$ ($G^v_{\rm eff}$) is the uniaxial shear energy per unit volume for a unit applied shear strain (stress). [See [13, 14] and/or Appendix A for more discussion.] Then, making use of (44), we have

$$K^{\pm}_{PM} = \frac{K_V[1 + 2\beta_{\pm}(G_{\pm} - G^r_{\rm eff})]}{1 + 2\beta_{\pm}(G_{\pm} - G^v_{\rm eff})}. \tag{5}$$

And, finally, substituting (2) into (5), we obtain the desired result:

$$K^{\pm}_{PM} = \frac{K_V(G^r_{\rm eff} + \zeta_{\pm})}{(G^v_{\rm eff} + \zeta_{\pm})}. \tag{6}$$

These formulas are the simplified versions of the Peselnick-Meister-Watt (PMW) bounds, which are rigorous bounds derived from the Hashin-Shtrikman variational principles for random polycrystals. The same results for bulk modulus are valid for all three symmetry classes considered here. Also, note that, for cubic symmetry [4], $K_V = K_R$ implies $G^r_{\rm eff} = G^v_{\rm eff}$, so $K^{\pm}_{PM} \equiv K_V$.

The functional $\zeta(G_{\pm}, K_{\pm}) \equiv \zeta_{\pm}$ is monotonic in both arguments $G_{\pm}$ and $K_{\pm}$. As $K_{\pm}$ ranges from 0 to ∞ for fixed $G_{\pm}$, $\zeta_{\pm}$ lies in the bounded range $\frac{2}{3}G_{\pm} \le \zeta_{\pm} \le \frac{3}{2}G_{\pm}$. As $G_{\pm}$ varies from 0 to ∞, $\zeta_{\pm}$ also ranges from 0 to ∞. In particular, when $\zeta_{-} = 0$, (6) shows that

$$K^{-}_{PM} = K_R, \tag{7}$$

which follows from the product formula $K_V G^r_{\rm eff}/G^v_{\rm eff} = K_R$. When $\zeta_{+} = \infty$, (6) shows that

$$K^{+}_{PM} = K_V. \tag{8}$$

These two expressions are obviously the lower and upper bounds on K given by Reuss and Voigt, respectively. Thus, this analytical formula parameterizes the bounds in terms of the $\zeta_{\pm}$, which are still determined by the formulas given for $G_{\pm}$ and $K_{\pm}$ in Appendix B. But, as we will soon see, the formula (6) has the advantage that it is also easy to use as the basis for an effective medium approximation.

B. SIMPLIFIED BOUNDS ON SHEAR MODULUS

To find the simplified version of (37) for the overall shear modulus, we first shift $G_{\pm}$ to the left hand side, then multiply by $-2\beta_{\pm}$, and finally add unity to both sides of the result. We find that

$$[1 + 2\beta_{\pm}(G_{\pm} - \mu^{\pm}_{PM})] = \frac{1}{1 + 2\beta_{\pm}B^{\pm}_2}. \tag{9}$$

Using (2) to simplify the left hand side, we then have

$$\mu_{PM}^{\pm} + \zeta_{\pm} = -\frac{1}{2\beta_{\pm}(1 + 2\beta_{\pm}B_2^{\pm})}. \tag{10}$$

The right hand side of (10) can be greatly simplified for all three symmetry classes, but unlike the bulk modulus, the resulting formulas are distinct — *i.e.*, depending on the symmetry class. When this (rather tedious algebra) has been completed for hexagonal symmetry, the formula (10) can be inverted to give

$$\frac{1}{\mu_{\rm hex}^{\pm} + \zeta_{\pm}} = \frac{1}{5}\left[\frac{1 - \alpha_{\pm}(K_V - K_{\pm})}{G_{\rm eff}^{v} + \zeta_{\pm} + \frac{\alpha_{\pm}}{2\beta_{\pm}}(K_V - K_{\pm})} + \frac{2}{c_{44} + \zeta_{\pm}} + \frac{2}{c_{66} + \zeta_{\pm}}\right]. \tag{11}$$

For the hexagonal case, the formula (11) reduces correctly to (21) as $\zeta_+ \to \infty$ and to (24) as $\zeta_- \to 0$, *i.e.*, the Voigt and Reuss bounds on the polycrystal's overall shear modulus. The result for $\zeta_+ \to \infty$ is obtained from a standard limiting process. Some extra steps in the $\zeta_- \to 0$ calculation are: $K_- \to K_R$, $\alpha_- \to -1/K_R$, and $\beta_- \to \infty$. The expected result (24) is then obtained because $K_V/G_{\rm eff}^{v}K_R = 1/G_{\rm eff}^{r}$ follows from the product formulas. Terms identical to the complicated first one here on the right hand side appear in the formulas for all symmetry classes. This form cannot be simplified further because the Voigt and Reuss bounds depend on the (usually distinct) factors $G_{\rm eff}^{v}$ and $G_{\rm eff}^{r}$, respectively. This term provides the essential link, or interpolation formula if you like, between these limits.

The analogous steps carried through for the trigonal case give:

$$\frac{1}{\mu_{\rm trig}^{\pm} + \zeta_{\pm}} = \frac{1}{5}\left[\frac{1 - \alpha_{\pm}(K_V - K_{\pm})}{G_{\rm eff}^{v} + \zeta_{\pm} + \frac{\alpha_{\pm}}{2\beta_{\pm}}(K_V - K_{\pm})} + \frac{2}{\mu_1 + \zeta_{\pm}} + \frac{2}{\mu_2 + \zeta_{\pm}}\right], \tag{12}$$

where μ_1 and μ_2 are defined in equations (27) and (28).

For tetragonal symmetry, the result is:

$$\frac{1}{\mu_{\rm tetr}^{\pm} + \zeta_{\pm}} = \frac{1}{5}\left[\frac{1 - \alpha_{\pm}(K_V - K_{\pm})}{G_{\rm eff}^{v} + \zeta_{\pm} + \frac{\alpha_{\pm}}{2\beta_{\pm}}(K_V - K_{\pm})} + \frac{1}{\mu_3 + \zeta_{\pm}} + \frac{2}{c_{44} + \zeta_{\pm}} + \frac{1}{c_{66} + \zeta_{\pm}}\right], \tag{13}$$

where $\mu_3 \equiv (c_{11} - c_{12})/2$.

Cubic symmetry requires $c_{11} = c_{22} = c_{33}$, $c_{12} = c_{13} = c_{23}$, $c_{44} = c_{55} = c_{66}$. This symmetry class may therefore be viewed as a special case of the tetragonal symmetry class. As such, we can immediately write the results for the bounds. It was already noted that $K_{PM}^{\pm} = K_{\pm} \equiv K_V$ for cubic symmetry. Furthermore, $G_{\rm eff}^{v} = G_{\rm eff}^{r} = \mu_3 = \frac{1}{2}(c_{11} - c_{12})$. So (13) becomes

$$\frac{1}{\mu_{\rm cub}^{\pm} + \zeta_{\pm}} = \frac{1}{5}\left[\frac{2}{G_{\rm eff}^{v} + \zeta_{\pm}} + \frac{3}{c_{44} + \zeta_{\pm}}\right]. \tag{14}$$

It is not difficult to verify that these bounds are identical to those found originally by Hashin and Shtrikman [4] for this case.

The uniaxial shear energies $G^v_{\rm eff}$ and $G^r_{\rm eff}$ play a strong role (and essentially the same role) in all these formulas even though only rarely are they simply related to eigenvalues of the elastic system equations.

IV. SELF-CONSISTENT ESTIMATES OBTAINED FROM THE BOUNDS

We are now in position to create some useful effective medium approximations based on the formulas for the rigorous bounds (6) and (11)-(14) derived in the previous section. In each case the choices to be made seem quite apparent based both on the form of these bounds, and on prior experiences with other bounds and self-consistent estimates [12]. The resulting formulas obtained this way will be called the "self-consistent" or SC estimates based on these bounds from the Hashin-Shtrikman variational principles.

We take the self-consistent estimate for bulk modulus to be

$$K^* = \frac{K_V(G^r_{\rm eff}+\zeta^*)}{(G^v_{\rm eff}+\zeta^*)} = \frac{(G^v_{\rm eff}K_R+\zeta^* K_V)}{(G^v_{\rm eff}+\zeta^*)}, \tag{15}$$

where

$$\zeta^* = \frac{\mu^*}{6}\left(\frac{9K^*+8\mu^*}{K^*+2\mu^*}\right). \tag{16}$$

In (16), K^* is determined by (15), μ^* is determined by the self-consistent expression for the shear modulus to follow, and ζ^* is then determined by (16). The formulas (15) and (16) are true for all three symmetry classes, but the final results will differ by symmetry because the formulas for μ^* to follow differ. In fact, for hexagonal symmetry μ^* is obtained similarly from (11) and we have

$$\frac{1}{\mu^*_{\rm hex}+\zeta^*} = \frac{1}{5}\left[\frac{1-\alpha^*(K_V-K^*)}{G^v_{\rm eff}+\zeta^*+\frac{\alpha^*}{2\beta^*}(K_V-K^*)} + \frac{2}{c_{44}+\zeta^*} + \frac{2}{c_{66}+\zeta^*}\right]. \tag{17}$$

Then, for trigonal symmetry, (12) gives:

$$\frac{1}{\mu^*_{\rm trig}+\zeta^*} = \frac{1}{5}\left[\frac{1-\alpha^*(K_V-K^*)}{G^v_{\rm eff}+\zeta^*+\frac{\alpha^*}{2\beta^*}(K_V-K^*)} + \frac{2}{\mu_1+\zeta^*} + \frac{2}{\mu_2+\zeta^*}\right]. \tag{18}$$

Finally, for tetragonal symmetry, we have from (13):

$$\frac{1}{\mu^*_{\rm tetr}+\zeta^*} = \frac{1}{5}\left[\frac{1-\alpha^*(K_V-K^*)}{G^v_{\rm eff}+\zeta^*+\frac{\alpha^*}{2\beta^*}(K_V-K^*)} + \frac{1}{\mu_3+\zeta^*} + \frac{2}{c_{44}+\zeta^*} + \frac{1}{c_{66}+\zeta^*}\right]. \tag{19}$$

As pointed out previously, cubic symmetry is a special case of tetragonal symmetry and so the self-consistent formulation for cubic does not require separate treatment.

In all cases, these formulas are obtained by replacing the terms in the bounds everywhere so that $K_\pm \to K^*$ and $G_\pm \to \mu^*$. The result is a set of coupled equations that are most conveniently solved by numerical iteration.

This iteration process is expected to converge rapidly to definite unique answers for both K^* and μ^*, and especially so when it can be shown that the individual formulas are monotonic functionals of their arguments. It is well-known that $\zeta^* = \zeta(\mu^*, K^*)$ is a monotonic functional of both arguments [12]. It is also quite easy to check using (15) that K^* is a monotonic functional of ζ^*. Since $K^* \leq K_V$ will always be satisfied, μ^* is easily shown for all three crystal symmetries to be a monotonic functional of ζ^*. The only remaining issue to check is whether μ^* is also a monotonic functional of K^*. A rather tedious analysis (which will therefore not be shown here) indicates that μ^* is indeed a monotonic functional of K^* as long as $\mu^* \leq G^v_{\text{eff}}$. However, since G^v_{eff} is not the overall Voigt average of the shear modulus (but rather the energy per unit volume of the uniaxial shear component), this relationship does not have to be obeyed. (Note: Trigonal arsenic and all the cubic materials considered here are examples admitting violation of the condition $\mu^* \leq G^v_{\text{eff}}$. Hexagonal and tetragonal materials tend to obey this condition, while the results for trigonal symmetry are mixed.) The examples show that in fact convergence is very quick when this condition is satisfied, but it is not always satisfied. When it is not, then the convergence may be much slower, but nevertheless convergence has always been attained in all the examples computed. For comparison purposes, we display the values of G^v_{eff} in all the following examples in order to provide quantitative verification of these comments.

V. EXAMPLES AND DISCUSSION

A. Examples

The theoretical ideas in the preceding text will be tested now using laboratory data in this section. All the data presented here were taken at nominal room temperature or at 300 K unless otherwise stated.

For hexagonal symmetry (Tables 1 and 2), we present examples for water ice, magne-

sium, cobalt, and graphite. The single-crystal data for ice (at 257 K) are from Jona and Scherrer [15] and Huntington [16]. (Comparable, but somewhat smaller, values for ice are found in Kneer [17] and Hearmon [18].) The single-crystal data for magnesium and cobalt are from Hearmon [18]. The data for graphite A are from Blakslee *et al.* [19], who quote a range of values for $c_{44} = 0.18$ to 0.35 GPa. The data for graphite B are from Hearmon *et al.* [18], who quotes exactly the same values except for $c_{44} = 4$ GPa. (We use this case as an example of how data uncertainty propagates through the equations in the *Discussion* subsection.) Data for polycrystalline ice shown in the TABLE 2 are from Gammon *et al.* [20, 21]. Earlier data on polycrystalline ice lie in the same range [22, 23]. Data for polycrystalline magnesium are from Krautkrämer [24].

For trigonal symmetry (TABLES 3 and 4), we present examples for bismuth, antimony, arsenic, calcite, and corundum. The single-crystal data for bismuth, antimony, and barsenic were taken from Pace *et al* [25]. Single-crystal data for calcite were taken from Hearmon [18]. Single-crystal data for corundum were taken from Anderson and Isaak [26]. Data for polycrystalline bismuth are from Krautkrämer [24]. Polycrystal data for corundum were found in Thomsen [8] (high values) and in Mavko *et al.* [27] (low values). Mavko *et al.* [27] list five different values for the polycrystal data on calcite; of these, we show the two highest values for both bulk and shear modulus.

For tetragonal symmetry (TABLES 5 and 6), we present examples for urea, mercurous chloride, tin, and titanium dioxide (rutile). The single-crystal data for urea are from Fischer and Zarembowitch [28]. The single-crystal data for mercurous chloride were from Sil'vestrova *et al.* [29], and are very similar to the data in Hearmon [18]. The single-crystal data for tin and for titanium dioxide are from Hearmon [18]. Data for polycrystalline tin are from Krautkrämer [24]. Polycrystal data for titanium dioxide (rutile) were found in Thomsen [8] (low values) and in Mavko *et al.* [27] (high values).

For cubic symmetry (TABLES 7 and 8), we present examples for aluminum, gold, copper, germanium, α-iron, magnesium oxide (magnesia), and spinel. The single-crystal data and polycrystal data for copper, gold, and α-iron were taken from the original Hashin and Shtrikman paper [4], so direct comparisons could be made to their results. Single-crystal data for gold and α-iron are the same as in Kneer [17]. Single-crystal data for aluminum were taken from Valin *et al.* [30]. Single-crystal data for germanium and magnesium oxide were taken from Huntington [16]. Single crystal data for spinel ($MgAl_2O_4$) were taken from

Hearmon [18]. For bulk modulus the first value listed is the same as K_V, since this is a measured value based on the measured single crystal values. Primary polycrystal data for magnesium oxide and secondary for spinel were found in Thomsen [8]. Secondary polycrystal data for aluminum, germanium, α=iron, and magnesium oxide, and spinel are from Anderson [31]. Secondary values of polycrystal data for gold and copper are from Krautkrämer [24].

Results quoted by Gubernatis and Krumhansl [10] for Al and Cu agree well with the present results, but were not identical. Agreement was precise for the bulk modulus, but the results obtained here were not quite as stiff in shear as those obtained by Gubernatis and Krumhansl [10]. Although we conjecture that the present self-consistent method should be equivalent to the CPA, so far the results only confirm that they are roughly equivalent. Observed differences may be due to slightly different single-crystal input values, to errors in the computations (such as using insufficient precision or failure to iterate to convergence), or to some more fundamental difference between the two approaches.

TABLE 1. Elastic stiffness constants of the hexagonal crystals for water ice (at 257 K), magnesium, cobalt, and graphite. Units for all constants are GPa.

	H_2O	Mg	Co	Graphite A	Graphite B
c_{11}	13.84	59.3	295.	1060.	1060.
c_{12}	7.07	25.7	159.	180.	180.
c_{13}	5.81	21.4	111.	15.0	15.0
c_{33}	14.99	61.5	335.	36.5	36.5
c_{44}	3.19	16.4	71.	0.26	4.0

TABLE 2. Measured and estimated elastic stiffness constants for polycrystalline aggregates of the hexagonal crystals of water ice, cobalt, magnesium, and graphite. Single-crystal constants used in the calculations are found in TABLE 1. Units for all constants are GPa.

	H_2O	Mg	Co	Graphite A	Graphite B
K_{meas}	8.90	35.5	–	–	–
K_R	8.89	35.2	187.4	35.8	35.8
K_{HS}^-	8.89	35.2	187.4	36.2	42.0
K_{SC}	8.89	35.2	187.4	91.0	100.0
K_{HS}^+	8.89	35.2	187.4	204.2	204.2
K_V	8.89	35.2	187.4	286.3	286.3
μ_{meas}	3.52	15.8	–	–	–
μ_R	3.48	17.2	75.3	0.65	9.2
μ_{HS}^-	3.52	17.3	76.6	1.21	14.8
μ_{SC}	3.52	17.3	76.6	56.9	71.2
μ_{HS}^+	3.52	17.3	77.0	146.2	148.9
μ_V	3.55	17.4	78.3	217.8	219.4
G_{eff}^v	4.61	20.4	113.3	208.8	208.8

TABLE 3. Elastic stiffness constants of the trigonal crystals for bismuth, antimony, arsenic, calcite, and corundum. All constants are in units of GPa.

	Bi	Sb	As	$CaCO_3$	Al_2O_3
c_{11}	63.22	99.4	123.6	144.	497.2
c_{12}	24.42	30.9	19.70	53.9	162.8
c_{13}	24.40	26.4	62.30	51.1	116.0
c_{14}	7.20	21.6	- 4.16	-20.5	-21.9
c_{33}	38.11	44.5	59.11	84.0	500.8
c_{44}	11.30	39.5	22.57	33.5	146.7

TABLE 4. Measured and estimated elastic stiffness constants for polycrystalline aggregates of the trigonal crystals of bismuth, antimony, arsenic, calcite, and corundum. Single-crystal constants used in the calculations are found in TABLE 3. Units of all constants are GPa.

	Bi	Sb	As	$CaCO_3$	Al_2O_3
K_{meas}	30.8	–	–	76.8/74.8	255.1/252.9
K_R	32.44	38.74	57.46	70.6	253.5
K_{HS}^-	33.37	41.60	60.63	73.0	253.7
K_{SC}	33.64	42.84	65.48	73.7	253.7
K_{HS}^+	33.89	43.82	65.77	74.4	253.7
K_V	34.55	45.63	66.10	76.0	253.9
μ_{meas}	11.9	–	–	32.0/30.6	163.2/162.1
μ_R	10.79	21.85	7.25	27.1	160.7
μ_{HS}^-	12.08	24.82	9.71	30.4	162.9
μ_{SC}	12.64	27.15	22.79	31.9	163.2
μ_{HS}^+	13.00	28.46	25.27	32.8	163.6
μ_V	14.49	33.27	30.22	36.8	165.5
G_{eff}^v	11.04	18.97	2.05	26.9	199.6
μ_1	23.61	58.61	52.53	60.6	181.1
μ_2	7.09	15.09	21.99	18.0	132.8

TABLE 5. Elastic stiffness constants of the tetragonal crystals for urea [$CO(NH_2)_2$], mercurous chloride, tin, and titanium dioxide (rutile). All constants in units of GPa.

	$CO(NH_2)_2$	Hg_2Cl_2	Sn	TiO_2
c_{11}	21.7	18.93	73.2	270.
c_{12}	8.9	17.19	59.8	176.
c_{13}	24.0	15.63	39.1	147.
c_{33}	53.2	80.37	90.6	480.
c_{44}	6.26	8.46	21.9	124.
c_{66}	0.45	12.25	23.8	193.

TABLE 6. Measured and estimated elastic stiffness constants for polycrystalline aggregates of the tetragonal crystals urea, mercurous chloride, tin, and titanium dioxide (rutile). Single-crystal constants used in the calculations are found in TABLE 5. All constants in units of GPa.

	$CO(NH_2)_2$	Hg_2Cl_2	Sn	TiO_2
K_{meas}	–	–	53.3	217.1/210.5
K_R	11.6	17.97	57.0	209.
K_{HS}^-	12.6	18.28	57.0	212.
K_{SC}	16.7	19.65	57.0	213.
K_{HS}^+	18.7	21.53	57.0	214.
K_V	23.4	23.90	57.0	218.
μ_{meas}	–	–	20.4	116.1/111.5
μ_R	1.67	3.26	15.6	99.5
μ_{HS}^-	2.51	4.93	17.7	110.0
μ_{SC}	4.33	7.82	18.7	115.0
μ_{HS}^+	4.33	9.11	19.0	117.0
μ_V	5.24	10.48	20.1	124.9
G_{eff}^v	6.83	22.39	26.3	136.3
μ_3	6.40	0.87	6.7	47.0

TABLE 7. Single-crystal elastic stiffness constants of the cubic crystals aluminum, gold, coper, germanium, α-iron, magnesium oxide (magnesia), and spinel. All constants in units of GPa.

	Al	Au	Cu	Ge	α-Fe	MgO	$MgAl_2O_4$
c_{11}	107.3	186.	171.0	128.9	237.	286.	282.
c_{12}	60.8	157.	122.0	48.3	141.	87.	154.
c_{44}	28.3	42.	69.1	67.1	116.	148.	154.

TABLE 8. Measured and estimated elastic stiffness constants for polycrystalline aggregates of the cubic crystals aluminum, gold, copper, germanium, α-iron, magnesium oxide (magnesia), and spinel. Single-crystal constants used in the calculations are found in TABLE 7. All constants in units of GPa.

	Al	Au	Cu	Ge	α-Fe	MgO	$MgAl_2O_4$
K_{meas}	76.3/74.0	167.0/165.6	138.0/136.0	75.2/75.1	173.0/159.	162.4/155.0	196.7/197.2
K_V	76.3	167.0	138.0	75.2	173.0	162.4	196.7
μ_{meas}	26.1/26.5	27.7/27.8	45.5/45.6	–	83.1/80.8	130.6/130.1	108.0/116.5
μ_R	26.0	23.9	40.0	53.0	74.0	123.9	98.6
μ_{HS}^-	26.2	27.0	44.8	54.6	80.5	126.1	106.9
μ_{SC}	26.2	28.1	46.3	54.8	82.1	126.3	109.0
μ_{HS}^+	26.2	28.6	47.2	54.9	83.1	126.4	110.3
μ_V	26.3	31.0	51.3	56.4	88.8	128.6	118.0
G_{eff}^v	23.3	14.5	24.5	40.3	48.0	99.5	64.0

B. Discussion

Convergence of the iteration scheme was monitored. Typically, a fixed number of 10 iterations was chosen, and the iterates were saved to a file. The results showed that the iterates converged to six figures in either three or four iterations in most cases. The only

exceptions noted were the two hexagonal graphite examples. Case B converged in about 30 iterations, while Case A required about 45 iterations to converge when the starting values were the lower Hashin-Shtrikman bounds.

Data have been quoted here without specifying measurement uncertainty. Clearly, knowledge of the single-crystal data uncertainty and error propagation through the formulas presented is important, but such studies are beyond our current scope. We provide one example (hexagonal graphite) where this issue is addressed for just one of the elastic constant input variables (c_{44}) in order to provide some indication of how results might depend on these uncertainties. Bulk modulus and the two upper bounds on shear modulus of graphite were largely insensitive to the changes in c_{44}, while the two lower bounds were quite sensitive to them. These senitivities were also reflected in the self-consistent estimates for shear, but not as strongly as in the lower bounds.

VI. CONCLUSIONS

The main technical accomplishment of the paper has been the reworking of the Peselnick-Meister-Watt bounds into analytical formulas, thereby making the older work on bounding elastic constants for polycrystals more accessible and easier to interpret. The motivation for this work was, in part, the desire to obtain self-consistent estimates of the bulk and shear moduli of random polycrystals. This goal was achieved quite easily once the new analytical formulas were found.

Although we have not dwelled upon them here, there are examples of Hashin-Shtrikman upper and lower bounds – as obtained from the work of Peselnick, Meister, and Watt [5–7] on random polycrystals – that are so close together that no other estimates are needed for practical purposes. Since the self-consistent estimates have the advantage that they are always trapped between the bounds, they do just as well as the bounds in all such cases. But it is clearly not these easy circumstances that have motivated the present work.

In contrast there are other cases where the bounds are far apart and, furthermore, the Voigt-Reuss-Hill average [3] (*e.g.*, $\mu_{VRH} \equiv \frac{1}{2}[\mu_V + \mu_R]$) also does not fall between them. (Trigonal arsenic is one example.) So, it would be helpful to have some other means of producing an estimate. Clearly, some direct average (mean or geometric mean) of the Hashin-Shtrikman bounds could be used in these circumstances, but it would perhaps be

more helpful to have some estimate that is better motivated than such a quasi-Hill direct average either of the formulas or of the algorithmically derived curves. The self-consistent estimates obtained here were motivated in part by the desire to learn whether or not such estimates might be found. The (now apparent) conclusion is that they can.

The resulting new formulas for both the bounds and the estimates also provide some useful insight into what factors are important in determining both the bounds and the estimates for each symmetry class. In particular, the eigenvalues of the elastic tensor always appear prominently in these formulas. Furthermore, for those parts of the energy stored in shear that do not relate simply to eigenvalues, the product formulas ([13] and Appendix A) relating uniaxial shear energies to the Voigt and Reuss bounds on bulk modulus play a particularly strong role in determining the results in all three of the symmetry classes considered here. The physical reason why this must happen is that typically two of the eigenvalues are for mixed modes — *i.e.*, quasi-compressional and quasi-shear modes. The quantities G^v_{eff} and G^r_{eff} specify those remaining parts of the shear energy that determine the rigorous upper and lower bounds — both for the Voigt and Reuss bounds, which were the sources of their definitions, and also those for the Hashin-Shtrikman bounds derived by Peselnick, Meister and Watt, as has been shown here.

One complication not treated here concerns the very common occurrence of porosity between grains in polycrystalline aggregates [8, 32, 33]. When the volume fraction of void space is on the order of 0.5% or greater [32], the analysis presented here should be modified to take into account the expected reduction in values of both bulk and shear moduli [33]. Whenever measured values of the effective overall constants of polycrystals are lower than those expected/predicted by the Hashin-Shtrikman and Peselnick-Meister-Watt bounds, it will often be reasonable to assume that the cause might be due to unaccounted for porosity in the laboratory samples.

Future studies include (1) completing the analysis for the remaining crystal symmetry classes, (2) doing a more careful comparison between these self-consistent estimates and those of Gubernatis and Krumhansl [10], and (3) some more detailed measurement error analyses.

APPENDIX A: VOIGT AND REUSS BOUNDS AND A PRODUCT FORMULA IN ELASTICITY

Hexagonal symmetry

For hexagonal symmetry, the nonzero stiffness constants are: c_{11}, c_{12}, $c_{13} = c_{23}$, c_{33}, $c_{44} = c_{55}$, and $c_{66} = (c_{11} - c_{12})/2$.

The Voigt average for bulk modulus of hexagonal systems is well-known to be

$$K_V = \left[2(c_{11} + c_{12}) + 4c_{13} + c_{33}\right]/9. \tag{20}$$

Similarly, for the shear modulus we have

$$\mu_V = \frac{1}{5}\left(G^v_{\text{eff}} + 2c_{44} + 2c_{66}\right), \tag{21}$$

where the new term appearing here is essentially defined by (21) and given explicitly by

$$G^v_{\text{eff}} = (c_{11} + c_{33} - 2c_{13} - c_{66})/3. \tag{22}$$

The quantity G^v_{eff} is the energy per unit volume in a grain when a pure uniaxial shear *strain* of unit magnitude is applied to the grain along its axis of symmetry [13].

The Reuss average for bulk modulus is determined by $1/K_R = 2(s_{11} + s_{12}) + 4s_{13} + s_{33}$, which can also be written as

$$\frac{1}{K_R - c_{13}} = \frac{1}{c_{11} - c_{66} - c_{13}} + \frac{1}{c_{33} - c_{13}} \tag{23}$$

in terms of stiffness coefficients. The Reuss average for shear is

$$\mu_R = \left[\frac{1}{5}\left(\frac{1}{G^r_{\text{eff}}} + \frac{2}{c_{44}} + \frac{2}{c_{66}}\right)\right]^{-1}, \tag{24}$$

which again may be taken as the definition of G^r_{eff} – *i.e.*, the energy per unit volume in a grain when a pure uniaxial shear *stress* of unit magnitude is applied to a grain along its axis of symmetry.

We will use the following product formula as the formal definition of G^r_{eff}. For each grain having hexagonal symmetry, two product formulas hold [13]: $3K_R G^v_{\text{eff}} = 3K_V G^r_{\text{eff}} = \omega_+\omega_-/2 = c_{33}(c_{11} - c_{66}) - c_{13}^2$. The symbols $\omega_\pm$ stand for the quasi-compressional and quasi-uniaxial-shear eigenvalues for the crystalline grains. Thus, $G^r_{\text{eff}} = K_R G^v_{\text{eff}}/K_V$ – a general formula that holds for all three of the crystal symmetry types considered here, treating (21) and (24) [or their equivalents for other symmetries] as the fundamental defining equations for G^v_{eff} and G^r_{eff}, respectively.

Trigonal symmetry

For trigonal symmetry (restricted to classses 32, $\bar{3}m$, $3m$ – see Nye [34]), the nonzero stiffness constants are: c_{11}, c_{12}, $c_{13} = c_{23}$, $c_{14} = c_{56} = -c_{24}$, c_{33}, $c_{44} = c_{55}$, and again $c_{66} = (c_{11} - c_{12})/2$.

For trigonal symmetry, the Voigt averages for bulk and shear moduli are again given by (20) and (21). The Reuss average for bulk modulus can be expressed in terms of the product formulas as

$$K_R = \frac{\omega_+\omega_-}{6G^v_{\text{eff}}}, \tag{25}$$

where G^v_{eff} is again given by (22). And we find that

$$\mu_R = \left[\frac{1}{5}\left(\frac{1}{G^r_{\text{eff}}} + \frac{2}{\mu_1} + \frac{2}{\mu_2}\right)\right]^{-1}, \tag{26}$$

where

$$\mu_1 = \frac{1}{2}\left[c_{44} + c_{66} + \left([c_{44} - c_{66}]^2 + 4c_{14}^2\right)^{\frac{1}{2}}\right], \tag{27}$$

$$\mu_2 = \frac{1}{2}\left[c_{44} + c_{66} - \left([c_{44} - c_{66}]^2 + 4c_{14}^2\right)^{\frac{1}{2}}\right], \tag{28}$$

and

$$G^r_{\text{eff}} = \frac{\omega_+\omega_-}{6K_V}. \tag{29}$$

It is also instructive (and useful to the discussion in the main text) to note that (21) can also be written for trigonal symmetry as

$$\mu_V = \frac{1}{5}\left(G^v_{\text{eff}} + 2\mu_1 + 2\mu_2\right). \tag{30}$$

Tetragonal symmetry

For tetragonal symmetry (restricted to classses $4mm$, $\bar{4}2m$, 422, $4/mmm$ – see Nye [34]), the nonzero stiffness constants are: c_{11}, c_{12}, $c_{13} = c_{23}$, c_{33}, $c_{44} = c_{55}$, and c_{66} (which is not coupled to c_{11} and c_{12} as it was in the other two cases).

For tetragonal symmetry, the Voigt average for bulk modulus is again given by (20), while the Voigt average for shear modulus is given now by

$$\mu_V = \frac{1}{5}\left(G^v_{eff} + \mu_3 + 2c_{44} + c_{66}\right), \tag{31}$$

where $\mu_3 \equiv (c_{11} - c_{12})/2$ and

$$G^v_{\text{eff}} = (c_{11} + c_{12} - 4c_{13} + 2c_{33})/6. \tag{32}$$

(Note that the formulas for G^v_{eff} for both hexagonal and trigonal symmetry could have also been written this way — but not vice versa.) The Reuss average for bulk modulus is again given by (25), using the new definition of G^v_{eff}. Alternatively, we have

$$\frac{1}{K_R - c_{13}} = \frac{2}{c_{11} + c_{12} - 2c_{13}} + \frac{1}{c_{33} - c_{13}}, \tag{33}$$

a form which is also valid for hexagonal and trigonal symmetries, whereas (23) is not valid for tetragonal symmetry. The Reuss average for shear modulus is

$$\mu_R = \left[\frac{1}{5}\left(\frac{1}{G^r_{\text{eff}}} + \frac{1}{\mu_3} + \frac{2}{c_{44}} + \frac{1}{c_{66}}\right)\right]^{-1}, \tag{34}$$

where we again have

$$G^r_{\text{eff}} = \frac{\omega_+\omega_-}{6K_V}, \tag{35}$$

and where, for tetragonal symmetry, $\omega_+\omega_- = [(c_{11} + c_{12})c_{33} - 2c_{13}^2]$.

APPENDIX B: PESELNICK-MEISTER-WATT BOUNDS FOR HEXAGONAL, TRIGONAL, AND TETRAGONAL SYMMETRIES

Hashin-Shtrikman-style bounds [35, 36] on the bulk and shear moduli of isotropic random polycrystals composed of hexagonal, trigonal, and tetragonal grains have been derived by Peselnick and Meister [5], with later corrections by Watt and Peselnick [7]. Notation used is similar to that in the original Hashin-Shtrikman paper on random polycrystals of grains having cubic symmetry [4]. We will use a silightly modified notation here, taking into account the product formulas ([13] and Appendix A) in order to simplify the satatement of the results. Derivations are found in the references, and therefore not repeated here.

Parameters used to optimize the Hashin-Shtrikman bounds are $K_\pm$ and $G_\pm$, which have the significance of being the bulk and shear moduli of two ($\pm$) isotropic comparison materials. G_+, K_+ are the values used in the formulas for the upper bounds, and G_-, K_- for the lower bounds. Formulas for the bounds are:

$$K^\pm_{PM} = K_\pm + \frac{K_V - K_\pm}{1 + 2\beta_\pm(G_\pm - G^v_{\text{eff}})}, \tag{36}$$

and

$$\mu_{PM}^{\pm} = G_{\pm} + \frac{B_2^{\pm}}{1 + 2\beta_{\pm} B_2^{\pm}}, \tag{37}$$

where

$$\alpha_{\pm} = \frac{-1}{K_{\pm} + 4G_{\pm}/3}, \qquad \beta_{\pm} = \frac{2\alpha_{\pm}}{15} - \frac{1}{5G_{\pm}}, \qquad \gamma_{\pm} = \frac{1}{9}(\alpha_{\pm} - 3\beta_{\pm}). \tag{38}$$

The form of $B_2^{\pm}$ depends on the crystal symmetry.

For hexagonal symmetry, we have

$$B_2^{\pm} = \frac{1}{5}\Big[\frac{G_{\text{eff}}^{v} - G_{\pm}}{\mathcal{D}_{\pm}} + \frac{2(c_{44} - G_{\pm})}{1 - 2\beta_{\pm}(c_{44} - G_{\pm})} + \frac{2(c_{66} - G_{\pm})}{1 - 2\beta_{\pm}(c_{66} - G_{\pm})}\Big], \tag{39}$$

with

$$\mathcal{D}_{\pm} = 1 - \beta_{\pm}(c_{11} + c_{12} + c_{33} - 3K_{\pm} - 2G_{\pm}) - 9\gamma_{\pm}(K_V - K_{\pm}). \tag{40}$$

Using the product formulas, (40) can be simplified to

$$\mathcal{D}_{\pm} = 1 - 2\beta_{\pm}(G_{\text{eff}}^{v} - G_{\pm}) - \alpha_{\pm}(K_V - K_{\pm}). \tag{41}$$

For trigonal symmetry, we have

$$B_2^{\pm} = \frac{1}{5}\Big[\frac{G_{\text{eff}}^{v} - G_{\pm}}{\mathcal{D}_{\pm}} + \frac{2(\mu_1 - G_{\pm})}{1 - 2\beta_{\pm}(\mu_1 - G_{\pm})} + \frac{2(\mu_2 - G_{\pm})}{1 - 2\beta_{\pm}(\mu_2 - G_{\pm})}\Big], \tag{42}$$

where $\mathcal{D}_{\pm}$ is defined as in (41), but using the definitions of K_V and G_{eff}^{v} appropriate for the trigonal symmetry.

For tetragonal symmetry, we have

$$B_2^{\pm} = \frac{1}{5}\Big[\frac{G_{\text{eff}}^{v} - G_{\pm}}{\mathcal{D}_{\pm}} + \frac{(\mu_3 - G_{\pm})}{1 - 2\beta_{\pm}(\mu_3 - G_{\pm})} + \frac{2(c_{44} - G_{\pm})}{1 - 2\beta_{\pm}(c_{44} - G_{\pm})} + \frac{(c_{66} - G_{\pm})}{1 - 2\beta_{\pm}(c_{66} - G_{\pm})}\Big], \tag{43}$$

where $\mathcal{D}_{\pm}$ is defined as in (41), but using the definitions of K_V and G_{eff}^{v} appropriate for the tetragonal symmetry.

Optimum values of the moduli for the comparison materials have been shown to be (in the present notation)

$$K_{\pm} = \frac{K_V(G_{\text{eff}}^{r} - G_{\pm})}{(G_{\text{eff}}^{v} - G_{\pm})}, \tag{44}$$

where, for K_{-},

$$0 \le G_{-} \le \min(c_{44}, G_{\text{eff}}^{r}, c_{66}) \qquad \text{(hexagonal)}, \tag{45}$$

$$0 \le G_{-} \le \min(\mu_2, G_{\text{eff}}^{r}) \qquad \text{(trigonal)}, \tag{46}$$

$$0 \le G_{-} \le \min(c_{44}, \mu_3, G_{\text{eff}}^{r}, c_{66}) \qquad \text{(tetragonal)}. \tag{47}$$

Similarly, for the K_+ formula,

$$\max(c_{44}, G^v_{\text{eff}}, c_{66}) \leq G_+ \leq \infty \qquad \text{(hexagonal)}, \tag{48}$$

$$\max(G^v_{\text{eff}}, \mu_1) \leq G_+ \leq \infty \qquad \text{(trigonal)}, \tag{49}$$

$$\max(c_{44}, \mu_3, G^v_{\text{eff}}, c_{66}) \leq G_+ \leq \infty \qquad \text{(tetragonal)}, \tag{50}$$

Note that, when $G_- = 0$, $K_- = K_R$, because $K_R = K_V G^r_{\text{eff}}/G^v_{\text{eff}}$ from the product formulas [13]. When $G_+ \to \infty$, $K_+ \to K_V$.

Peselnick and Meister [5] had originally obtained all the results for hexagonal symmetry, except for the additional condition in (45) that permits c_{44} to be replaced in some circumstances by G^r_{eff}. This new condition was added later by Watt and Peselnick [7]. For trigonal symmetry, the general results $\mu_2 \leq \min(c_{44}, c_{66})$ and $\max(c_{44}, c_{66}) \leq \mu_1$, permitted simplification of these expressions. For tetragonal symmetry, the conditions depending on μ_3 were also added by Watt and Peselnick [7].

Implementation issues

Equation (44) has an obvious singularity if it ever happens that $G_+ = G^v_{\text{eff}}$. (The case $G_- = G^v_{\text{eff}}$ will never occur except in the most trivial cases, where bounding methods are not really required.) Since this does happen in practice (hexagonal cobalt, trigonal corundum, and both tetragonal urea and mercurous chloride are four examples), it is necessary to modify the numerical algorithm for the bounds slightly. To avoid this problem, it is sufficient (and also consistent with spirit of the variational bounding methods) to make the replacement in these cases $G_+ = G^v_{\text{eff}} + \delta$, where is δ is a small positive shift. This choice guarantees that the result is still an upper bound, but avoids the singularity. Any positive shift on the order of the experimental error in the crystalline elastic stiffness data should be sufficient to eliminate this purely numerical difficulty, but the choice made will then be reflected directly in the upper bounds on both bulk and shear modulus – so results presented here (for the upper bounds in these cases) may differ slightly from those of Watt and Peselnick [7]. However, this issue does not affect the final results for self-consistent estimates at all. It also means the preferred choices of the starting values for the self-consistent iteration scheme are the values for the lower PMW bounds on bulk and shear modulus, since these are unaffected by this issue.

The graphical structure of the algorithm for computing these bounds has been illustrated previously by Watt and Peselnick [7] and more recently by Berryman [14].

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