Evaluating Bounds and Estimators for Constants of Random Polycrystals Composed of Orthotropic Elastic Materials

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Abstract

While the well-known Voigt and Reuss (VR) bounds, and the Voigt-Reuss-Hill (VRH) elastic constant estimators for random polycrystals are all straightforwardly calculated once the elastic constants of anisotropic crystals are known, the Hashin-Shtrikman (HS) bounds and related self-consistent (SC) estimators for the same constants are, by comparison, more difficult to compute. Recent work has shown how to simplify (to some extent) these harder to compute HS bounds and SC estimators. An overview and analysis of a subsampling of these results is presented here with the main point being to show whether or not this extra work (*i.e.*, in calculating both the HS bounds and the SC estimates) does provide added value since, in particular, the VRH estimators often do not fall within the HS bounds, while the SC estimators (for good reasons) have always been found to do so. The quantitative differences between the SC and the VRH estimators in the eight cases considered are often quite small however, being on the order of ±1%. These quantitative results hold true even though these polycrystal Voigt-Reuss-Hill estimators more typically (but not always) fall outside the Hashin-Shtrikman bounds, while the self-consistent estimators always fall inside (or on the boundaries of) these same bounds.

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1. Introduction

While the well-known Voigt [1] and Reuss [2] bounds, and the Voigt-Reuss-Hill [3] elastic constant estimators for random polycrystals are all easily calculated once the elastic constants of anisotropic crystals are known, the Hashin-Shtrikman bounds [4] and related self-consistent [5] estimators for the same constants are comparatively more difficult to compute. Some recent work [6,7] has shown how to simplify these harder to compute estimators to some extent. The present discussion gives an overview with the main point being to show that this extra work does provide added value, since — in particular — the well-known Voigt-Reuss-Hill estimators often do *not* fall within the Hashin-Shtrikman bounds, but the self-consistent estimators (for good reasons [8]) have always been found to do so.

Self-consistent estimators can take a variety of forms, and not all of these forms are equivalent or equally valid. In particular, Hill's version of self-consistency is not the same as the ones that are based on physical arguments and scatterng theory such as the ones that are sometimes called the "coherent potential approximation," including Soven [9], Taylor [10], Gubernatis and Krumhansl [11], Berryman [12], and Olsen and Avellaneda [13]. This class of approximations is one considered specifically by Willis [8], and is one that seems to give consistently good results – by which statement we mean that the results are consistent with the rigorous bounds. A related class of approximations, also called "self-consistent," is discussed by Kanaun and Levin [14].

The present work will concentrate on showing how rigorous bounds (especially of the Hashin-Shtrikman-type) are related to the "self-consistent" estimators. Most of the earlier work has concentrated on one or the other of these approaches, without making an effort to compare, contrast, and mutually validate them. Some recent work of the author [6,7] has addressed some of these issues, including the orthorhombic case that will be the main emphasis here.

Section 2 will introduce the orthotropic polycrystal problem. Section 3 presents the mathematical formulation needed to solve these problems. Section 4 presents results for eight examples, and includes comparisons among both the rigorous and the approximate methods. Section 5 gives an overview of the results obtained here. Section 6 describes some of the possible applications of the methods presented. Section 7 summarizes our results.

2. Polycrystals of Orthotropic Elastic Meterials

We will follow the common convention of reducing elastic tensors to 6×6 matrices using the Voigt prescription:

$$
\begin{pmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{33} \\ \sigma_{23} \\ \sigma_{13} \\ \sigma_{12} \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{13} & & & \\ c_{12} & c_{22} & c_{23} & & & \\ c_{13} & c_{23} & c_{33} & & & \\ & & & c_{44} & & \\ & & & & c_{55} & \\ & & & & & c_{66} \end{pmatrix} \begin{pmatrix} \epsilon_{11} \\ \epsilon_{22} \\ \epsilon_{33} \\ \epsilon_{23} \\ \epsilon_{13} \\ \epsilon_{12} \end{pmatrix}. \tag{1}
$$

As commonly formulated, the σ_{ij}'s are the stresses, and the ϵ_{ij}'s are the strains, for $i, j = 1, 2, 3$, corresponding respectively to spatial axes x, y, z. As shown, the elastic constants are symmetric, so $c_{21} = c_{12}$, etc. The case being considered here is that of materials having orthotropic symmetry, which is not the most general case, but is surely the most general case considered very often in practice. The elastic constants c_{44}, c_{55}, c_{66} are elastic moduli for the twisting shear strains: ϵ_{23}, ϵ_{13}, ϵ_{12}, and their related stresses. For isotropic elastic materials, $c_{11} = c_{22} = c_{33} = \lambda + 2\mu$, $c_{44} = c_{55} = c_{66} = \mu$, and $c_{12} = c_{13} = c_{23} = \lambda$, where λ and μ are the two Lamé constants, and the isotropic bulk and shear moduli are given (in this very special isotropic case) by $K = \lambda + 2\mu/3$ and $G = \mu$, respectively.

It is well-known that, for such orthorhombic media, there are three simple eigenvectors and eigenvalues, and these are the ones again associated again with the twisting shear modes and the stiffnesses, namely c_{44}, c_{55}, and c_{66}, corresponding to rotations about spatial axes x, y, z, respectively. There are also three eigenmodes associated with the 3×3 submatrix in the upper lefthand corner of the full elastic matrix. However, these modes are not generally related simply to pure compression/extension or pure shear modes. It follows that our understanding of effective moduli such as effective bulk and shear modulus of polycrystals requires a rather complex relationship to the simpler ideas of a bulk modulus for pure compression or extension, and a shear modulus for one of the five potentially distinct shear moduli of any elastic material. The resulting mixing of the modes is the cause of the problems we have with analyzing the average modal behavior of (by assumption) perfectly isotropic polycrystals (on average), and therefore necessitates the use of the methods being discussed. Theoretical studies of these systems are usually designed to quantify the behavior

of random polycrystals, where the use of the word "random" in this context normally implies that the polycrystals are composed of a sufficiently large number of small crystallites oriented randomly in space so the overall polycrystalline behavior is either isotropic or sufficiently close to isotropic for engineering purposes. The resulting effective isotropic constants can therefore be chosen to be effective bulk K and shear G moduli.

The goal of the paper is then to find ways of estimating these bulk and shear moduli of such an overall isotropic average medium. The means we use to quantify these constants are rigorous bounds, and approximate theoretical estimators.

3. Bounds and Estimators

Results of Watt [15] for bounds on bulk modulus $K_{HS}^{\pm}$ and those of Middya and Basu [16] for self-consistent estimates K_{SC}^{*} of bulk modulus can both be written in virtually the same form:

$$K_{HS}^{\pm} = K_{\pm} + \frac{3B_1^{\pm} + 2B_2^{\pm}}{3 + \alpha^{\pm}(3B_1^{\pm} + 2B_2^{\pm})}, \tag{2}$$

where

$$3B_1^{\pm} + 2B_2^{\pm} = \frac{9(K_V - K_{\pm}) + 2\beta_{\pm}(d^{\pm} + e^{\pm} - c^{\pm}) + 3\beta_{\pm}^2\Omega^{\pm}}{1 - a^{\pm}\beta_{\pm} - 9\gamma_{\pm}(K_V - K_{\pm}) + D_{\pm}}. \tag{3}$$

The coefficients $a_{\pm}$, $b_{\pm}$, $c_{\pm}$, $d_{\pm}$, $e_{\pm}$ are defined here in the Appendix. The coefficients $\alpha_{\pm}$, $\beta_{\pm}$, $\gamma_{\pm}$ are defined below following Eq. (10). $\Omega^{\pm}$ is defined in (16) and (17). For self-consistency, simply replace the subscripts or superscripts $\pm$ with either $*$'s or SC as desired, while also removing the HS (and/or PM) subscripts.

The denominator of expression (3) is the same as the denominator of the first term in

$$\begin{aligned} 15B_2^{\pm} = {}& \frac{a^{\pm} - b^{\pm} + \beta_{\pm}(2d^{\pm} - 2c^{\pm} - e^{\pm}) + 3\gamma_{\pm}(d^{\pm} - c^{\pm} + e^{\pm}) + \alpha_{\pm}\beta_{\pm}\Omega^{\pm}}{1 - a^{\pm}\beta_{\pm} - 9\gamma_{\pm}(K_V - K_{\pm}) + D_{\pm}} \\ & + 3(G_{\pm} + \zeta_{\pm})^2 \left(\frac{3}{G_{\pm} + \zeta_{\pm}} - \frac{1}{c_{44} + \zeta_{\pm}} - \frac{1}{c_{55} + \zeta_{\pm}} - \frac{1}{c_{66} + \zeta_{\pm}} \right), \end{aligned} \tag{4}$$

and $D_{\pm}$ is defined in

$$D_{\pm} = \beta_{\pm}(\beta_{\pm} + 2\gamma_{\pm})(c^{\pm} - d^{\pm}) - 2e^{\pm}\beta_{\pm}\gamma_{\pm} - \frac{\alpha_{\pm}\beta_{\pm}^2\Omega_{\pm}}{3}. \tag{5}$$

The Voigt average of the bulk modulus is

$$K_V = \frac{1}{9}\left[c_{11} + c_{22} + c_{33} + 2(c_{12} + c_{23} + c_{13}) \right]. \tag{6}$$

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Similarly, the Voigt average of the shear modulus is

$$G_V = \frac{1}{15} \left[c_{11} + c_{22} + c_{33} - c_{12} - c_{23} - c_{13} + 3(c_{44} + c_{55} + c_{66}) \right]. \tag{7}$$

For completeness, we also note that the corresponding Reuss averages [2] for orthorhombic crystals are determined by

$$\frac{1}{K_R} = (S_{11} + S_{22} + S_{33}) + 2 (S_{23} + S_{31} + S_{12}) \tag{8}$$

and

$$\frac{15}{G_R} = 4 (S_{11} + S_{22} + S_{33}) - 4 (S_{23} + S_{31} + S_{12}) + 3 (S_{44} + S_{55} + S_{66}), \tag{9}$$

where the S_{ij}'s are the compliance matrix elements, related to the stiffness matrix elements by the matrix equation $\mathbf{S} = \mathbf{C}^{-1}$.

The equation corresponding to (2) for the shear modulus is given by

$$G_{PM}^{\pm} = G_{\pm} + \frac{B_2^{\pm}}{1 + 2\beta_{\pm} B_2^{\pm}}, \tag{10}$$

where PM indicates the contribution of Peselnick and Meister [17], who were early evaluators of the HS bounds. The Hashin-Shtrikman bounds themselves are then given exactly by $K_{HS}^{\pm} \equiv K_{PM}^{\pm}$ and $G_{HS}^{\pm} \equiv G_{PM}^{\pm}$. Again K_V is the Voigt average of bulk modulus. Definitions of another useful shear factor G_{eff}^v depend on the specific crystal symmetry under consideration (see Refs. [6,7] for specifics).

In particular, $B_2^{\pm}$ itself was defined in (4).

Parameters $\alpha_{\pm}$ and $\beta_{\pm}$ that appear repeatedly above can be related to Eshelby [18] results by rewriting them in the form:

$$-\frac{1}{\alpha_{\pm}} = K_{\pm} + 4G_{\pm}/3 \tag{11}$$

and

$$-\frac{1}{2\beta_{\pm}} = G_{\pm} + \zeta_{\pm}. \tag{12}$$

Another combination of these two that also frequently appears in the formulas is

$$\gamma_{\pm} = \frac{\alpha_{\pm} - 3\beta_{\pm}}{9}. \tag{13}$$

Using these definitions, we find that:

$$\frac{1}{K_{HS}^{\pm} + 4G_{\pm}/3} = \frac{1 - (B_1^{\pm} + 2B_2^{\pm}/3)/(K_{\pm} + 4G_{\pm}/3)}{K_{\pm} + 4G_{\pm}/3}, \tag{14}$$

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which is valid for orthorhombic and some more symmetric crystal structures, such as hexagonal, tetragonal, and trigonal. Eq. (14) should be compared to the analogous shear formula given by

$$\frac{1}{G_{PM}^{\pm} + \zeta_{\pm}} = \frac{1 - B_2^{\pm}/(G_{\pm} + \zeta_{\pm})}{G_{\pm} + \zeta_{\pm}}, \tag{15}$$

which is valid for the same crystal symmetries, being analogous forms for the bulk and shear moduli respectively

As first noted, these equations are for the upper and lower bounds $K_{HS}^{\pm}$ on the bulk modulus. These bounds are found when the constraints are optimal. Then the determinant of the matrix $X^{\pm}$ is given by

$$\Omega^{\pm} \equiv \det\left(X^{\pm}\right) = X_{11}^{\pm} X_{22}^{\pm} X_{33}^{\pm} + 2 X_{12}^{\pm} X_{23}^{\pm} X_{13}^{\pm} - X_{11}^{\pm} \left(X_{23}^{\pm}\right)^2 - X_{22}^{\pm} \left(X_{13}^{\pm}\right)^2 - X_{33}^{\pm} \left(X_{12}^{\pm}\right)^2, \tag{16}$$

and we must have $\Omega^{\pm} = \det(X^{\pm}) \equiv 0$. Here $X^{\pm}$ is a 3×3 positive- or negative-semi-definite matrix, as defined by

$$\begin{aligned}
X_{11}^{\pm} &= c_{11} - K_{\pm} - \tfrac{4}{3}G_{\pm}, \ X_{12}^{\pm} = c_{12} - K_{\pm} + \tfrac{2}{3}G_{\pm}, \\
X_{22}^{\pm} &= c_{22} - K_{\pm} - \tfrac{4}{3}G_{\pm}, \ X_{13}^{\pm} = c_{13} - K_{\pm} + \tfrac{2}{3}G_{\pm}, \\
X_{33}^{\pm} &= c_{33} - K_{\pm} - \tfrac{4}{3}G_{\pm}, \ X_{23}^{\pm} = c_{23} - K_{\pm} + \tfrac{2}{3}G_{\pm}.
\end{aligned} \tag{17}$$

The required vanishing of $\det(X)$ is necessary because then, and only then, have we found either the greatest lower bound, or the smallest upper bound.

As already shown by Middya and Basu [16], these same equations can be used as well to determine the self-consistent estimates, as well as the bounds. These self-consistent values are determined instead specifically by the overall conditions: $B_2 = 0$ and $3B_1 + 2B_2 = 0$. Both conditions must apply simultaneously if the self-consistency conditions are to be satisfied. And so, it must also be true that $B_1 = 0$; but we never need to consider the condition on B_1 separately. The self-consistency conditions are therefore (obviously) given by:

$$K_{SC} = K^* \qquad \text{and} \qquad G_{SC} = G^*, \tag{18}$$

where the conditions that determine the values of K^* and G^* are exactly the ones that cause the two factors B_1 and B_2 to vanish simultaneously. Although this simultaneity condition might sound hard to achieve, it is really very easy to obtain by applying an iterative process wherein some initial K_0 and G_0 values are first chosen and substituted into (14) and (10) for the $K_{\pm}$ and $G_{\pm}$ values. The results that are next obtained for the left-hand-sides of both

these equations then become the new trial values for K_0 and G_0. Repeating this process has always been found to converge quickly as long as some reasonably intelligent choices are made for the initial values of K_0 and G_0. In any case, this part of the overall procedure is actually very easy in practice.

Determining the HS bounds from this same set of equations is comparatively harder, but some tricks were developed in previous work of the author [7] that made the computational process easier. This work will be elaborated only briefly in the following discussion. In particular, a useful "shooting method of optimization" (which makes use of the computed values of the self-consistent estimates in order to speed up the search for HS bounds) was developed previously to streamline the algorithm used to produce the Hashin-Shtrikman bounds [4, 6, 7, 19]. We refer the interested reader to [7] for the details of this approach. The basic idea is this: Having already computed the pertinent self-consistent values, and knowing the Reuss and Voigt bounds on both K and G, we scan from the simple bounding values towards the SC point. We take care to observe where sign changes in these functionals occur. In this way, the optimal bounds (those closest) to the SC estimates can be quickly determined.

4. Discussion of Bounds and Estimators

A variety of other bounds and estimators can be found in the literature [20-23] in addition to the ones that we discuss here in detail.

4.1 Examples

Although (in this section) we consider only eight specific examples in the following analysis of the bounds and estimates, we are nevertheless able to show that a number of rather plausible hypotheses about possible relationships between and among the various bounds and estimates can be quickly excluded via specific counterexamples. The numerical values of the various bounds and estimates for the cases considered are summarized in TABLE 1.

First, we correctly anticipate that the self-consistent (SC) estimates always lie inside the Hashin-Shtrikman (HS) bounds. This expectation follows from the form of the equations for the self-consistent approximation, being based as they are — here for orthorhombic

materials only — on essentially the same equations as those for the HS bounds. However, a further hypothesis (which might seem reasonable) that the SC estimates could always lie at or near the center of the HS bounding region is quickly disproven. Of the eight orthorhombic examples considered, six produce results close to an edge of the HS bounding box. Only for Danburite and OsN_2 (LDA) among the examples shown do the SC estimates appear to be nearly centered in the HS bounding box. In all six of the other cases, the SC estimates lie either on or very near to a boundary of the HS bounding box.

Another possible simplification often contemplated is whether or not the VRH estimator always (or ever) lies inside the HS bounds, or alternatively that the HS bounds might be centered (or at least close to being centered) inside the Voigt-Reuss (VR) bounding box. We see that this possibility is excluded (as a general rule) by the cases computed for Aragonite, Forsterite, and Sulfur. Data are from [24], [26], [27], and [7].

In five of these eight cases (Danburite, Enstatite, OsN_2-LDA, Topaz, and α-U), it is true that the Voigt-Reuss-Hill (VRH) point lies inside the HS bounds, but the HS bounds are not well-centered around the VRH point in any of these five cases.

The case of Danburite is the only one among these eight having the SC point well-centered within the HS bounding box, although OsN_2-LDA and α-U have their SC points nearly centered. In the other five cases, the SC point is either close to one boundary, or to the intersection of two boundaries.

For mixtures of isotropic elastic materials, it is often observed that the VRH estimates tend to be consistently high when compared to SC estimates or the HS bounds. However, for the orthotropic cases considered here, this is true for three cases (Aragonite, Forsterite, and Sulfur), but false for five cases (Danburite, Enstatite, OsN_2-LDA, Topaz, and α-U). Furthermore, for the same five examples, the VRH estimator actually lies inside the HS bounding box. For Danburite and Enstatite, both the shear and bulk modulus VRH estimators are nearly equal to (but slightly smaller than) the SC estimates. For α-U, the VRH estimators are nearly equal to (but slightly larger than) the corresponding SC estimates.

Another general observation is that the *relative differences* between the SC estimates and the VRH estimates for these five orthorhombic materials are quantitatively small, *i.e.*, being fractions of 1%. This fact suggests that, for applications not requiring very high precision estimates, the VRH estimates will be of continuing value.

Of the cases considered, only Danburite and OsN_2 have the SC point well-centered within

the HS bounding box.

4.2 Geometric mean

As a final point of discussion, we considered another potential estimator, where instead of using the more standard choice of arithmetic mean for the VRH estimator, we considered a geometric mean of the Reuss and Voigt estimators for both bulk and shear modulus:

$$K_{GM} = (K_R K_V)^{1/2} \tag{19}$$

and

$$G_{GM} = (G_R G_V)^{1/2}. \tag{20}$$

We also considered other combinations of K_R and K_V (and similarly for G) such as combining $K_1 \equiv \frac{1}{2}(K_R + K_V)$ and $\frac{1}{K_2} \equiv \frac{1}{2}(\frac{1}{K_R} + \frac{1}{K_V})$ into a different geometric mean, given by: $K_3 = (K_1 K_2)^{1/2}$ – and similarly for the shear modulus. However, it turns out that these choices simply reproduce exactly the means already shown in (19) and (20). So the possibilities (perhaps surprisingly) do *not* proliferate.

4.3 Figures

Figures 1 through 8 illustrate the same examples covered in TABLE 1. In each case, the Voigt-Reuss bounds are identified by the larger black rectangle, while the Hashin-Shtrikman bounds are located by the smaller blue rectangle. The Voigt-Reuss-Hill estimator (arithmetic mean) is shown with a green plus sign; this point is always exactly at the center of the VR bounding rectangle. The self-consistent (SC) estimator is shown as a red asterisk. This estimator is always somewhere inside, or on the boundary, of the HS bounding rectangle. The remaining point illustrated with a black diamond is the geometric mean (GM), again based on the Voigt-Reuss bounds. This geometric mean tends to be a little closer in these examples to the Hashin-Shtrikman and SC results, but in general is about as good an estimator (and also about as easy to compute) as the VRH arithmetic mean.

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5. Quantifying Degree and Type of Anisotropy

There have been efforts in recent years to arrive at a universal means of quantifying the degree and type of anisotropy in elastic media [28]. One example of such a measure of anisotropy found in [28] is given by

$$A^U \equiv 5\frac{G_V}{G_R} + \frac{K_V}{K_R} - 6 \geq 0, \tag{21}$$

in our notation. Since $G_V \geq G_R$ and $K_V \geq K_R$, the inequality in (21) must always hold. And since the Voigt and Reuss averages can be easily computed for any elastic material once its stiffness or compliance tensor/matrix is known, the formula is certainly both simple and universal. However, it seems that this choice may be too simple for some applications, since it is surely also of interest to arrive at a formulation that provides more specific information, and in particular allows some more specific information to be incorporated into the scheme.

For applications involving wave propagation through orthorhombic (and therefore anisotropic) media, it is common to use certain parameters that arise naturally in studies of seismic waves. For example, certain dimensionless coefficients having forms (see [25] and [26]) arise, including:

$$\delta^{(2)} = \frac{(c_{13} + c_{55})^2 - (c_{33} - c_{55})^2}{2c_{33}(c_{33} - c_{55})}, \tag{22}$$

$$\epsilon^{(2)} = \frac{c_{11} - c_{33}}{2c_{33}}, \tag{23}$$

$$\gamma^{(2)} = \frac{c_{66} - c_{44}}{2c_{44}}, \tag{24}$$

as well as other permutations of indices resulting in six more ratios labelled similarly by (1) and (3). These coefficients arise in the context of measuring deviations from isotropy for wave propagation in particular directions within these orthorhombic elastic media. The same set of coefficients could also be used to measure deviations from isotropy for other purposes as well, such as quantitative classification of degree and type of anisotropy. The existence of up to nine distinct choices provides more information about where the anisotropy is coming from within the elastic tensor/matrix values.

6. Some Practical Applications of the Methods Presented

The range of possible applications of the methods presented is large and we will not attempt to enumerate them all here. One good example of a typical application to earth materials arises from the known fact [29] that among typically composite earth materials such as igneous rock, shale, sandstone, and limestone, there are only a relatively small number of materials constituting most of them, including: SiO_2 (trigonal), TiO_2 (tetragonal), Al_2O_3 (trigonal), Fe_2O_3 (trigonal), FeO (non-stoichiometric, but nearly cubic), MgO (cubic), and CaO (cubic). Of these seven materials, all but CaO and FeO were treated previously by the author [6], and these two are also very easily treated using the same methods since they are cubic symmetry materials — thus being the easiest of all to compute.

We have not shown any details here, but it is also quite straightforward to introduce porosity as another constituent into the self-consistent scheme [12]. This fact greatly expands the number of practical applications of the methods discussed to a large variety of porous materials of practical interest, including earth materials and many important engineering materials such as concrete.

Another relatively straightforward application of the methods presented is to obtain accurate elastic moduli in applications to so-called digital rocks, resulting from scans (*e.g.*, x-ray CT images) of rocks, or other composite materials — thus displaying the detailed microstructure in 3D for further computer analysis. Such information can provide both volume fraction and orientation information (important for the anisotropic constituents considered here), to be used to estimate the elastic response of the composite from known properties of its constitutents.

7. Summary and Conclusions

To summarize: Once the full set of elastic constants for an orthorhombic material constituting the random elements of the composite is known, the easiest isotropic estimators to compute are always the Voigt and Reuss averages for both bulk and shear moduli. Among the typical estimators most workers might consider computing, the next easiest quantities to compute are the self-consistent estimates. These SC estimates can then be used to speed up the computation of the Hashin-Shtrikman bounds as shown previously [7], and confirmed

again here. The self-consistent estimators themselves are very closely related to the HS bounds, and knowledge of the SC values is therefore useful in pinning down the optimal zeroes of the functionals used to determine these best bounds.

The Voigt-Reuss-Hill arithmetic averages often provide reasonable estimators of the effective constants, and are of the same level of difficulty to compute as the Voigt and Reuss averages themselves (which is to say, they are easy to compute). Finally, we have also considered the geometric-mean estimators, which are based again on the same Voigt and Reuss averages. These estimates are of the same level of difficulty to compute as the VRH estimators, but it has been found that they tend to lie closer to the self-consistent estimators, and therefore also either closer to or inside the HS bounds. The limited results presented here (only eight cases so far) suggest that this alternative should be studied further in order to evaluate how universal this observed behavior may be for a much wider study of orthorhombic and more symmetric elastic materials.

Acknowledgments

Appendix: Coefficients $a^{\pm} - e^{\pm}$

The remaining constants appearing in (4) are given by

$$
\begin{aligned}
a^{\pm} &= X_{11}^{\pm} + X_{22}^{\pm} + X_{33}^{\pm}, \qquad b^{\pm} = X_{12}^{\pm} + X_{23}^{\pm} + X_{13}^{\pm}, \\
c^{\pm} &= X_{11}^{\pm} X_{22}^{\pm} + X_{22}^{\pm} X_{33}^{\pm} + X_{33}^{\pm} X_{11}^{\pm}, \qquad d^{\pm} = \left(X_{12}^{\pm}\right)^2 + \left(X_{23}^{\pm}\right)^2 + \left(X_{13}^{\pm}\right)^2, \\
e^{\pm} &= X_{12}^{\pm} X_{13}^{\pm} + X_{13}^{\pm} X_{23}^{\pm} + X_{23}^{\pm} X_{13}^{\pm} - X_{11}^{\pm} X_{23}^{\pm} - X_{22}^{\pm} X_{13}^{\pm} - X_{33}^{\pm} X_{12}^{\pm},
\end{aligned}
\tag{25}
$$

where the $X^{\pm}$ matrix elements were defined in (17). [Note: The symbol $\pm$ always appears as a subscript for scalar quantities, except for the scalar Hashin-Shtrikman bounds themselves, where the bound label is used as a subscript. The symbol $\pm$ appears as a superscript for all quantities that are themselves matrix elements (therefore having additional subscripts), and for quantities that are combinations only of such matrix elements. For scalar quantities that

are themselves combinations of scalars and also quantities derived from matrix elements, the subscript version is again used – except as already noted for the scalar bounds themselves.]

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TABLE 1. Comparisons of bounds and estimates for the bulk (K) and shear moduli (G) of polycrystals (composites of randomly oriented crystals of uniform type) for eight orthorhombic elastic materials: Aragonite ($CaCO_3$), Danburite ($CaB_2Si_2O_8$), Enstatite ($MgSiO_3$), Forsterite (Mg_2SiO_4), OsN$_2$-LDA, Sulfur (S), Topaz ($Al_2(F,OH)_2SiO_4$), and α-Uranium. Estimators shown are: Reuss lower bound (R), Hashin-Shtrikman lower bound (HS^-), Self-consistent estimate (SC^*), Geometric Mean (GM),Voigt-Reuss-Hill average (VRH), Hashin-Shtrikman upper bound (HS^+), and Voigt (V) upper bound, respectively, for both the bulk (K) and shear moduli (G). All effective constants are in units of GPa (gigapascal).

	K, G	R	HS^-	SC^*	GM	VRH	HS^+	V
Aragonite	K	44.71	45.56	46.36	46.83	46.88	46.41	49.04
	G	36.62	37.56	38.31	38.47	38.52	38.35	40.41
Danburite	K	90.52	91.37	91.89	91.70	91.71	92.40	92.89
	G	62.47	63.50	64.27	64.15	64.17	65.06	65.87
Enstatite	K	107.29	107.65	107.83	107.79	107.79	107.83	108.29
	G	75.18	75.52	75.70	75.66	75.67	75.71	76.15
Forsterite	K	127.27	128.49	128.49	129.45	129.47	128.49	131.67
	G	79.54	80.35	80.35	81.05	81.06	80.89	82.58
OsN$_2$-LDA	K	412.6	417.9	418.6	418.30	418.34	419.6	424.07
	G	225.6	243.6	246.2	246.3	247.2	250.1	268.8
Sulfur	K	17.56	18.76	18.85	19.02	19.08	18.87	20.60
	G	6.17	6.61	6.64	6.67	6.70	6.66	7.22
Topaz	K	166.19	167.37	167.46	167.43	167.43	167.73	168.67
	G	113.54	114.73	115.06	114.76	114.77	115.09	116.00
α-Uranium	K	111.3	112.5	112.7	112.94	112.95	113.1	114.6
	G	80.7	83.6	84.1	84.2	84.3	84.9	87.9
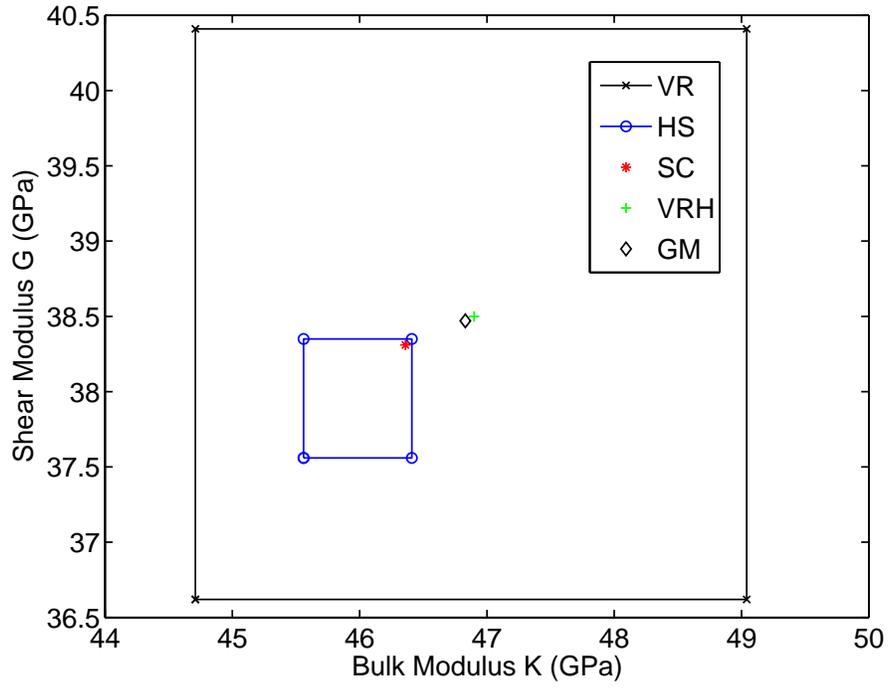
FIG. 1: Voigt-Reuss (VR) and Hashin-Shtrikman (HS) bounding boxes, and Self-Consistent (SC), Voigt-Reuss-Hill (VRH), and Geometric Mean (GM) estimates for effective elastic constants of polycrystalline Aragonite.
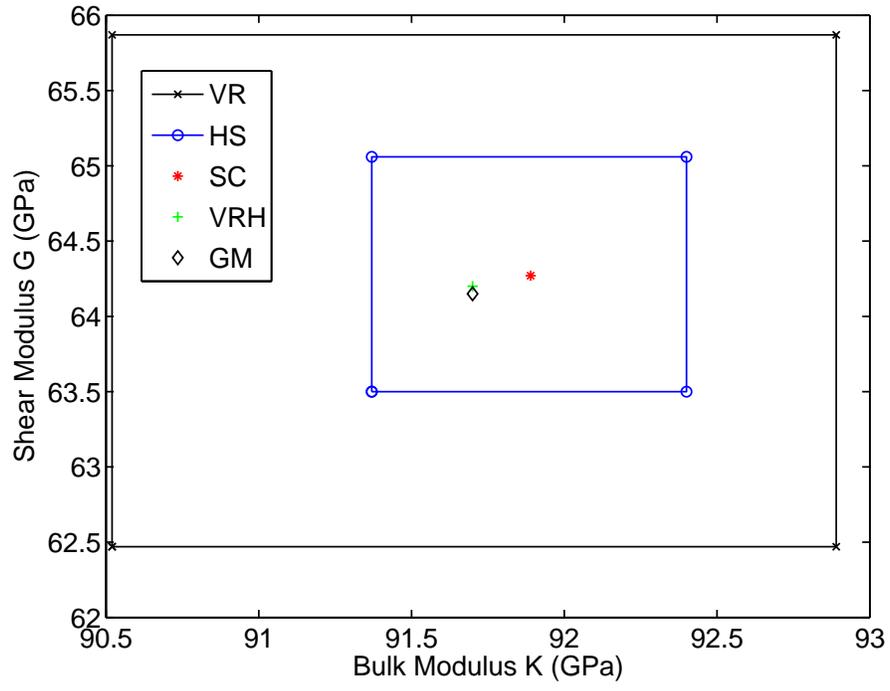
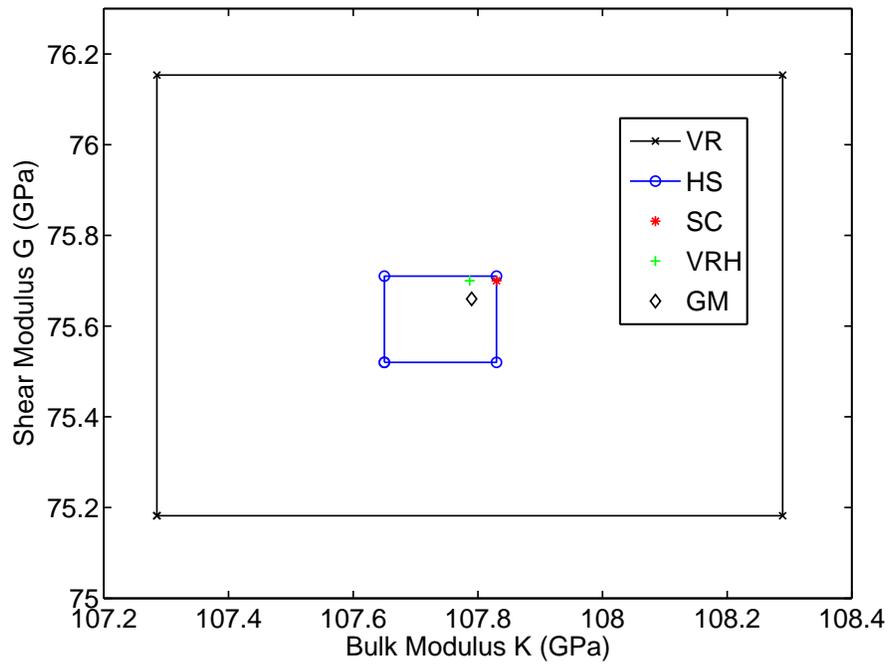FIG. 2: Same as Fig. 1 for polycrystalline Danburite.

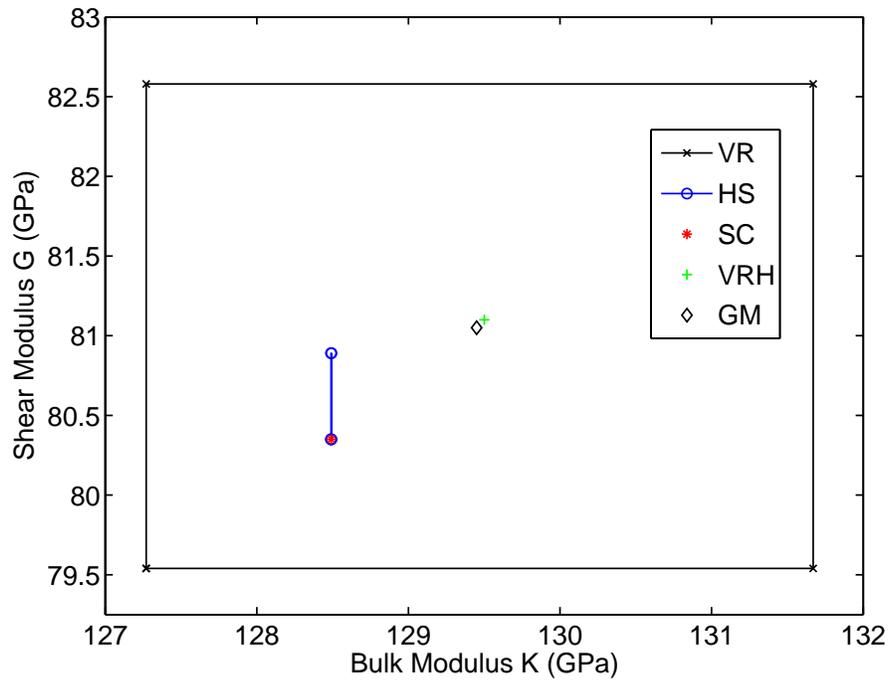FIG. 3: Same as Fig. 1 for polycrystalline Enstatite.

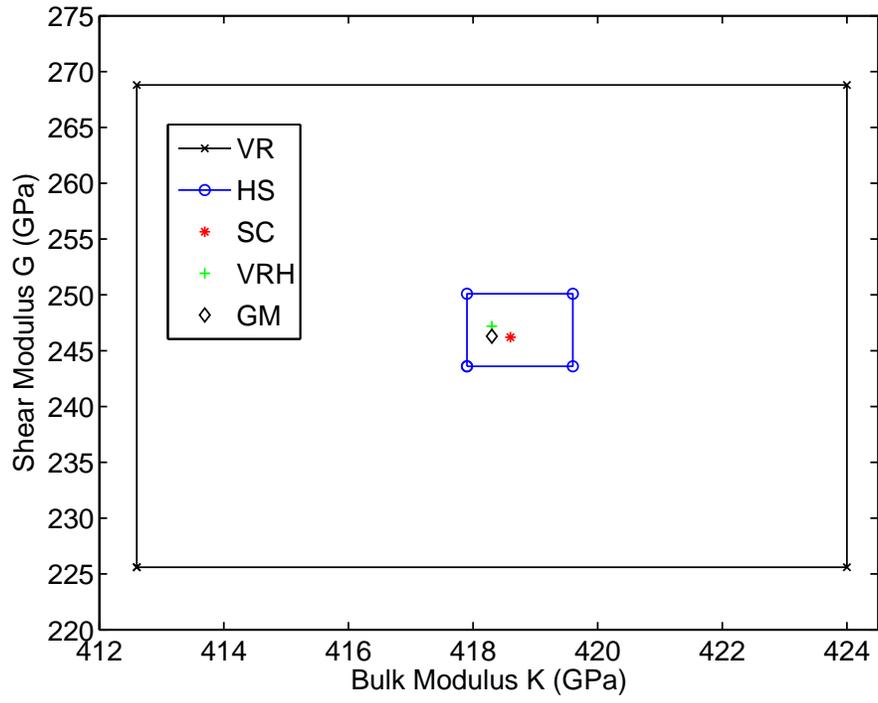FIG. 4: Same as Fig. 1 for polycrystalline Forsterite.

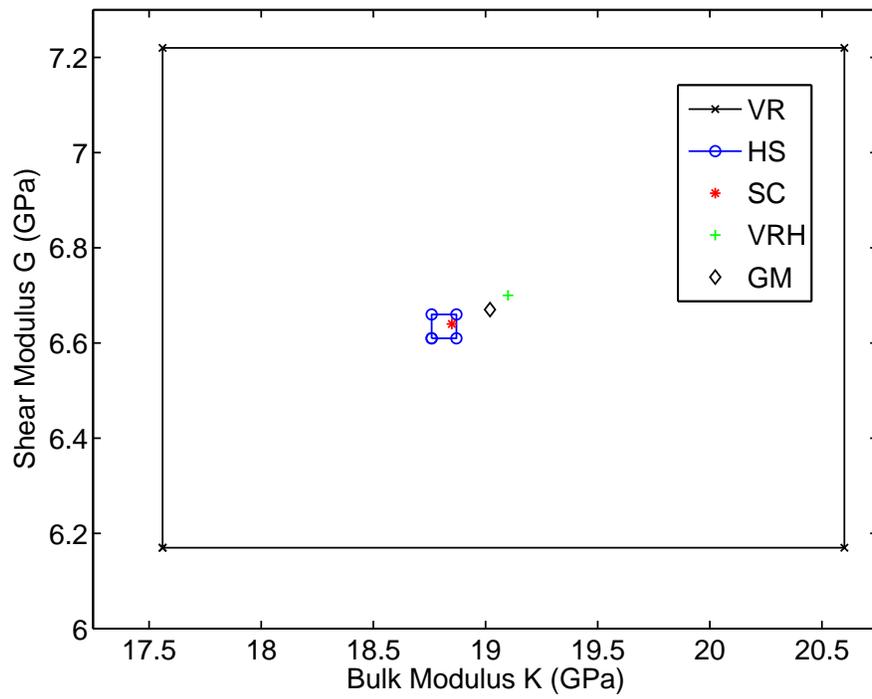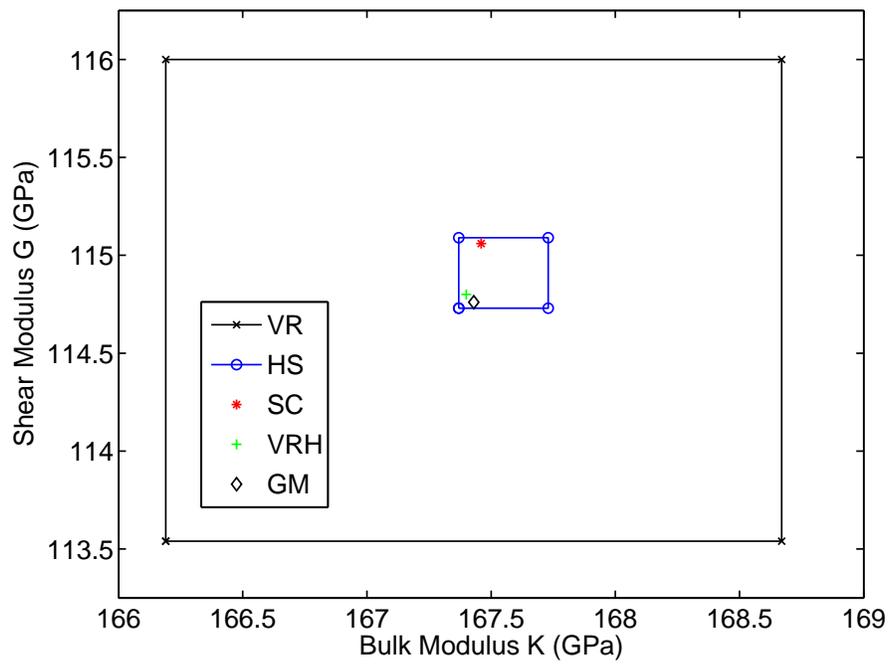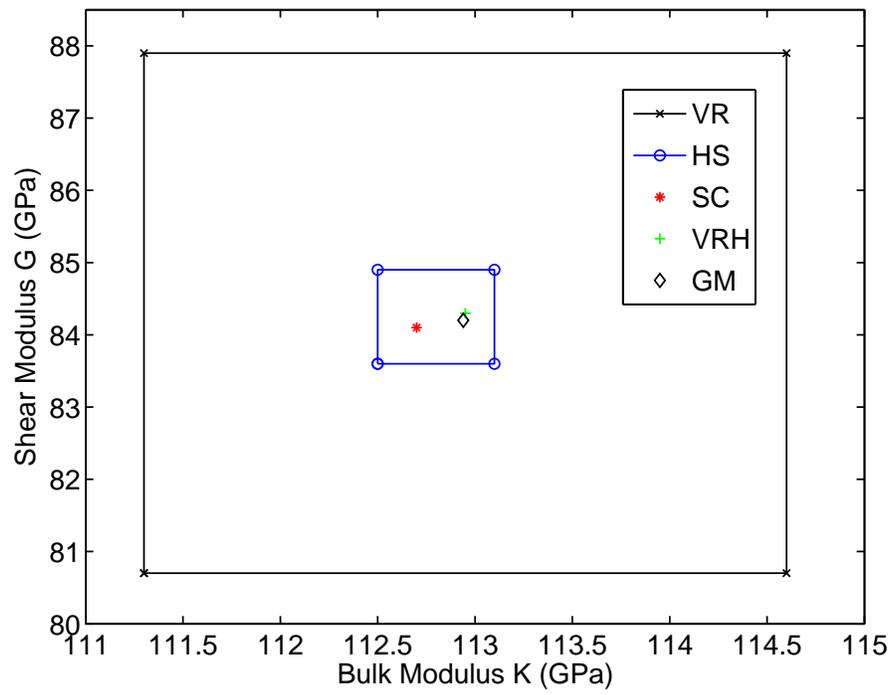FIG. 5: Same as Fig. 1 for polycrystalline OsN$_2$ (LDA).

FIG. 6: Same as Fig. 1 for polycrystalline Sulfur.

FIG. 7: Same as Fig. 1 for polycrystalline Topaz.

FIG. 8: Same as Fig. 1 for polycrystalline α-U.

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