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Bounds and self-consistent estimates for elastic constants of polycrystals composed of orthorhombics or crystals with higher symmetries

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Methods for computing Hashin-Shtrikman bounds and related self-consistent estimates of elastic constants for polycrystals composed of crystals having orthorhombic symmetry have been known for about three decades. However, these methods are underutilized, perhaps because of some perceived difficulties with implementing the necessary computational procedures. Several simplifications of these techniques are introduced, thereby reducing the overall computational burden, as well as the complications inherent in mapping out the Hashin-Shtrikman bounding curves. The self-consistent estimates of the effective elastic constants are very robust, involving a quickly converging iteration procedure. Once these self-consistent values are known, they may then be used to speed up the computations of the Hashin-Shtrikman bounds themselves. It is shown furthermore that the resulting orthorhombic polycrystal code can be used as well to compute both bounds and self-consistent estimates for polycrystals of higher-symmetry tetragonal, hexagonal, and cubic (but not trigonal) materials. The self-consistent results found this way are shown to be the same as those obtained using the earlier methods, specifically those methods designed specially for each individual symmetry type. But the Hashin-Shtrikman bounds found using the orthorhombic code are either the same or (more typically) tighter than those found previously for these special cases (i.e., tetragonal, hexagonal, and cubic). The improvement in the Hashin-Shtrikman bounds is presumably due to the additional degrees of freedom introduced into the available search space.

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I. INTRODUCTION

Although it is well-known that isotropic elastic materials have compressional/extensional modes measured typically by a bulk modulus as well as distortional modes measured typically by a shear modulus, the majority of elastic materials have more complicated behavior than that observed in the isotropic case. In general there may be as many as five shear-like modes and just one bulk-like mode. But for anisotropic media the coupling among shear and bulk modes is nontrivial, and can lead to complexities in the analysis of elastic data, whether laboratory or field measurements, and whether the data are derived from quasistatic or dynamic measurements, as is often the case when acoustic or seismic waves are used to probe such media.

There are basically seven types of elastic crystal symmetries (see Nye [1]) usually considered: cubic, hexagonal, tetragonal, trigonal, orthorhombic, monoclinic, and triclinic. Of these seven, cubic symmetry is the only one that has a simply defined bulk modulus, since the bulk modulus in this case can be precisely determined and will give the same value whether the measurement is made in compression via uniformly applied external pressure, or in either extension or compression if the sample can be uniformly strained. In all other cases, the measured results can differ depending on whether they are obtained using applied strains, applied stresses, or combinations of these. Furthermore, the shear behavior of anisotropic media can be quite complex since there are three independent twisting shears that can be applied to any material sample, as well as three quite different shearing forces that result (for example) from applying a uniaxial compression in any of the three principal orthogonal directions. These cases do not exhaust all the possibilities for shearing motions, but the others can normally be found by considering linear combinations of the ones already mentioned.

It is because of these complexities that Voigt [2] and Reuss [3] studied elastic systems and determined that there were two sets of constants that seemed to capture much of the nature of a linear elastic material. These results were then called the Voigt and Reuss *averages* of shear and bulk behavior until Hill [4] showed that these same averages were actually *rigorous bounds* on the possible responses and behaviors of these complicated systems. Since Hill's work, the Voigt and Reuss estimates of elastic response have become known as the Voigt and Reuss (rigorous) bounds on elastic system behavior.

Subsequently, Hashin and Shtrikman [5] also studied the problem of finding bounds on elastic constants and determined that it was possible to do somewhat better than these early bounds of Voigt and Reuss. They established general procedures for computing such bounds and carried the work through themselves for some of the simpler cases, including cubic materials. Other workers continued to elaborate the theory, including first Peselnick and Meister, [6] Watt and Peselnick, [7] and also Watt [8] alone, who subsequently published a series of papers on methods for many of the crystal classes of common interest.

Another line of thinking on such problems arose around the same time as the work of Peselnick and Meister, [6] and was focused on effective-properties estimates, rather than rigorous bounding methods. This work was based in part on early scattering theory approaches by Soven [9] and Taylor [10] via the coherent potential approximation (CPA), and then carried further for elastic constants by Gubernatis and Krumhansl [11], and also by Willis [12], who based some of his ideas on earlier work in this area by Hill [13].

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The present study has grown out of a need to understand more clearly, while also quantifying more precisely, the relationships among the bounding and estimation methods, and to try to make these threads of the theory both easier to understand and to apply to the harder problems (such as orthorhombic, monoclinic, and triclinic) that continue to arise in current practice.

This work concentrates mainly on establishing some useful refinements of the work by Watt [8] and others, [14] and at the same time incorporating ideas related to CPA and/or self-consistent estimates of the same elastic properties of polycrystals. The work is restricted to orthorhombic systems and/or more symmetric systems including tetragonal, hexagonal, and cubic elastic polycrystals, which in fact will all be viewed here as special cases of orthorhombic symmetry. We also take advantage of this fact in the choices of examples to be considered.

II. ELASTIC PROPERTIES OF CRYSTALS AND POLYCRYSTALS

If the dimensionless second rank tensor of strain for an elastic body in three dimensions is ϵ_{ij}, with $i,j = 1,2,3$ being the three spatial dimensions in some convenient choice of coordinate system, and the second rank tensor of stress (having dimensions of pressure) of the same body is σ_{ij} in the same coordinate system, then the stress is related to the strain (see Landau and Lifshitz [15]) by the fourth rank tensor C_{ijkl} according to $\sigma_{ij} = C_{ijkl}\epsilon_{kl}$, assuming the Einstein convention of summation over repeated indices $k,l = 1,2,3$. It is often convenient to simplify the mathematics of these relationships by replacing tensor with matrix notation. In this case, the C_{ijkl}'s are replaced by the matrix c_{ij}, while the stress and strain tensors are replaced by vectors according to the well-known (see Ting [16] for extensive discussion) Voigt prescription:

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

The example shown in (1) is that for orthorhombic symmetry, which is the most general case that will be considered in the present work. 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 case) by $K = \lambda + 2\mu/3$ and $G = \mu$, respectively.

For orthorhombic media, there are three simple eigenvectors and eigenvalues, and these are the ones associated with the twisting shear modes and the stiffnesses, namely, c_{44}, c_{55}, and c_{66}. There will also be three eigenmodes associated with the 3×3 submatrix in the upper left-hand corner of the full elastic matrix. But these modes will not generally be simply related either to pure compression or extension or pure shear modes. Thus, information about effective moduli such as effective bulk and shear modulus of polycrystals has 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. It is this mixing of the modes that makes the problem of analyzing the effective modal behavior of (assumed) isotropic polycrystals difficult, and therefore necessitates the use of the methods to be discussed here. Analysis of these systems is 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 close to isotropic. The effective isotropic constants can therefore be taken to be effective bulk K and shear G moduli.

III. BOUNDS AND ESTIMATES OF ELASTIC CONSTANTS FOR POLYCRYSTALS

Results of Watt [8] for bounds on $K_{\rm HS}^{\pm}$ and those of Middya and Basu [14] for self-consistent estimates $K_{\rm SC}^{*}$ of bulk modulus can both be written in the same form:

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

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 corresponding results for shear modulus are presented in Appendix A. The denominator of expression (3) is the same as the denominator of the first term in (A12), and $D_{\pm}$ is defined in (A13). Other terms not defined here already are also found in Appendix A. The corresponding equation for the shear modulus is again given in Appendix A, Eq. (A2). In particular, $B_2^{\pm}$ is itself defined in (A12). [The significance of the various ± subscripts and superscripts—related to upper and lower bounds—is also clarified following Eq. (A20) in Appendix A.]

As is explained in more detail in Appendix A, these equations can sometimes be simplified by taking advantage of certain analytical structures that typically occur. [13] In particular, if we add the quantity $4G_{\pm}/3$ to both sides of (2), substitute the value of $\alpha_{\pm}$ from (A4), and then rearrange the resulting equation, we find that

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

which should be compared to the analogous shear formula in (A8), being analogous forms for the bulk and shear moduli, respectively.

As first stated, these equations are for the upper and lower bounds $K_{\rm HS}^{\pm}$ on the bulk modulus. These bounds are found when the constraints are optimal, meaning that [as the $\Omega^{\pm}$ are defined in Appendix A, Eq. (A19)] we must have $\Omega^{\pm} = \det(X^{\pm}) \equiv 0$; and where $X^{\pm}$ is a 3×3 positive- or negative-semidefinite matrix, as defined in (A18). This 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. [Clearly, nonoptimal bounds can also be found, but these are never our target values.]

As already shown by Middya and Basu [14], 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 for the self-consistency conditions to be satisfied. And so, it must also be true that $B_1 = 0$; but we never need to consider B_1 separately. The self-consistency conditions are therefore (obviously) given by

$$K_{\mathrm{SC}} = K^* \qquad \text{and} \qquad G_{\mathrm{SC}} = G^*, \tag{5}$$

where the conditions that determine the values of K^* and G^* are exactly the ones that cause B_1 and B_2 to vanish simultaneously. Although this simultaneity condition might sound hard to achieve, actually it is very easy to obtain by applying an iterative process wherein some initial K_0 and G_0 values are first chosen and substituted into (4) and (A2) for the $K_\pm$ and $G_\pm$ values. The results that are then obtained for the left-hand sides of both these equations next 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 the course of this work that made the process easier to complete, as will be elaborated in the following discussion. In particular, Sec. IVD provides an overview of a useful "shooting method of optimization" developed here.

IV. EFFECTIVE ELASTIC CONSTANTS FOR ORTHORHOMBIC MATERIALS

The results and methods described in the preceding sections and the Appendices were applied to 10 examples of orthorhombic materials. Tables I and III provide the input data used for these 10 materials. Tables II and IV contain the results found from the bounding and self-consistent estimation procedures. Sources of all the single-crystal data used in the paper are listed in Appendix C.

A. Materials considered

The first five cases include aragonite, an orthorhombic polymorph of calcite ($CaCO_3$), danburite ($CaB_2Si_2O_8$), enstatite ($MgSiO_3$), forsterite (Mg_2SiO_4), and topaz [$Al_2(F,OH)_2SiO_4$]. Some of these materials were purposely chosen because they had been studied by previous authors (in order to provide baseline comparisons), while others have apparently not been treated before.

The second set of five cases includes two examples of OsN_2 (having marcasite crystal structure), where these first two sets of values are taken from two different computations based, respectively, on the generalized gradient approximation (GGA) and the local-density approximation (LDA). The

TABLE I. Elastic stiffness constants and Voigt-Reuss-Hill averages of the bulk (K) and shear moduli (G) for the orthorhombic crystals: aragonite ($CaCO_3$), danburite ($CaB_2Si_2O_8$), enstatite ($MgSiO_3$), forsterite (Mg_2SiO_4), and topaz [$Al_2(F,OH)_2SiO_4$]. References for the data are found in Appendix C. All constants are in units of GPa.

	$CaCO_3$	$CaB_2Si_2O_8$	$MgSiO_3$	Mg_2SiO_4	$Al_2(F,OH)_2SiO_4$
c_{11}	160.0	131.0	224.7	328.0	281.0
c_{22}	87.2	198.0	177.9	200.0	349.0
c_{33}	84.8	211.0	213.6	235.0	294.0
c_{12}	37.3	50.0	72.4	69.0	108.0
c_{13}	1.7	64.0	54.1	69.0	132.0
c_{23}	15.7	34.0	52.7	73.0	131.0
c_{44}	41.3	64.0	77.6	66.7	125.0
c_{55}	25.6	59.8	75.9	81.3	84.0
c_{66}	42.7	74.9	81.6	80.9	88.0
K_{VRH}	46.9	91.7	107.8	129.5	167.4
G_{VRH}	38.5	64.2	75.7	81.1	114.8

TABLE II. Computed effective elastic constants for the orthorhombic crystals aragonite ($CaCO_3$), danburite ($CaB_2Si_2O_8$), enstatite ($MgSiO_3$), forsterite (Mg_2SiO_4), and topaz [$Al_2(F,OH)_2SiO_4$]. All constants are in units of GPa.

	$CaCO_3$	$CaB_2Si_2O_8$	$MgSiO_3$	Mg_2SiO_4	$Al_2(F,OH)_2SiO_4$
G_{HS}^-	37.56	63.50	75.52	80.352	114.73
G_{SC}	38.31	64.27	75.70	80.354	115.06
G_{HS}^+	38.35	65.06	75.71	80.888	115.09
K_{HS}^-	45.56	91.37	107.65	128.489	167.37
K_{SC}	46.36	91.89	107.83	128.493	167.46
K_{HS}^+	46.41	92.40	107.83	128.493	167.73
G_{eff}^r	40.11	58.23	70.95	86.18	102.21
G_{eff}^v	46.22	65.33	72.83	92.00	104.50
x_1	77.07	108.00	116.30	149.34	165.56
x_2	15.36	22.66	29.37	34.66	42.44

TABLE III. Elastic stiffness constants and Voigt-Reuss-Hill averages of the bulk (K) and shear moduli (G) for the orthorhombic crystals: OsN_2-GGA with marcasite crystal structure, OsN_2-LDA also with marcasite crystal structure, Rochelle salt (where RS = $KNaC_4H_4O_6 \cdot 4H_2O$), sulfur (S), and α-uranium (U). References for the data are found in Appendix C. For OsN_2, the constants were obtained by numerical methods: GGA = generalized gradient approximation; LDA = local-density approximation. All constants are in units of GPa.

	GGA OsN_2	LDA OsN_2	RS	S	α-U
c_{11}	744.0	835.0	25.5	24.0	215.0
c_{22}	913.0	1038.0	38.1	20.5	199.0
c_{33}	581.0	663.0	37.1	48.3	267.0
c_{12}	178.0	212.0	14.1	13.3	46.0
c_{13}	277.0	323.0	11.6	17.1	22.0
c_{23}	88.0	105.0	14.6	15.9	107.0
c_{44}	134.0	142.0	13.4	4.3	124.0
c_{55}	340.0	381.0	3.2	8.7	73.0
c_{66}	175.0	189.0	9.8	7.6	74.0
K_{VRH}	364.2	418.3	19.7	19.1	112.9
G_{VRH}	225.0	247.2	8.2	6.7	84.3

TABLE IV. Computed effective elastic constants for the orthorhombic crystals OsN_2-GGA and OsN_2, both having the marcasite crystal structure, Rochelle salt (RS = $KNaC_4H_4O_6 \cdot 4H_2O$), sulfur (S), and α-uranium (U). GGA = generalized-gradient approximation; LDA = local-density approximation. All constants are in units of GPa.

	GGA OsN_2	LDA OsN_2	RS	S	α-U
K_R	359.0	412.6	19.3	17.56	111.3
K_{HS}^-	363.4	417.9	19.7	18.76	112.5
K_{SC}	364.5	418.6	19.7	18.85	112.7
K_{HS}^+	365.4	419.6	19.8	18.87	113.1
K_V	369.3	424.0	20.1	20.60	114.6
G_R	207.2	225.6	7.2	6.17	80.7
G_{HS}^-	221.8	243.6	8.4	6.61	83.6
G_{SC}	224.1	246.2	8.5	6.64	84.1
G_{HS}^+	227.3	250.1	8.6	6.66	84.9
G_V	242.8	268.8	9.3	7.22	87.9
G_{eff}^r	249.5	277.6	9.6	6.03	74.9
G_{eff}^v	282.5	316.0	10.1	7.75	84.3
x_1	468.4	524.9	16.2	13.32	139.6
x_2	96.6	107.1	3.9	2.18	29.1

remaining cases include Rochelle salt ($KNaC_4H_4O_6 \cdot 4H_2O$), sulfur (S), and α-uranium (U).

Of the final four materials considered (results summarized in Tables V–VIII), three were cases treated previously by the author—one each of tetragonal (urea), cubic (copper), and hexagonal (water ice). The remaining example (Table VIII) is cubic methane hydrate, which had not been treated previously.

B. Discussion of the bound optimization method

It should be clear from the detailed mathematical structure presented here that the self-consistent calculations are straightforward, while the bound evaluation methods require some careful choice of search procedure. For self-consistency, we require $B_2^\pm = 0 = B_1^\pm$, which might seem like a hard condition to achieve, but in practice it is quite easy to reach by establishing a straightforward iteration scheme. It only takes a very few iterations to find that the values of B_1 and B_2 approach numerical values on the order of 10^{-12} and below, having started at values comparable to the input stiffness values. On the other hand, the main requirement for the HS bounds themselves involves finding values such that the key constraint matrix [found in Eq. (A19)] $\Omega^\pm \equiv 0$. The difficulty with this is certainly not that zeros are hard to find,

TABLE V. Measured and computed effective elastic constants for the tetragonal crystals and polycrystals of urea [$CO(NH_2)_2$]. References for the data are found in Appendix C. All constants are in units of GPa.

Urea $CO(NH_2)_2$					
Elastic constants		Previous results		Present results	
c_{11}	21.7	K_R	11.6	K_R	11.6078
c_{12}	8.9	K_{HS}^-	12.6	K_{HS}^-	14.8104
c_{13}	24.0	K_{SC}	16.5	K_{SC}	16.4761
c_{33}	53.2	K_{HS}^+	18.7	K_{HS}^+	17.5505
c_{44}	6.26	K_V	23.4	K_V	23.3778
c_{66}	0.45	G_R	1.67	G_R	1.6707
K	16.5	G_{HS}^-	2.51	G_{HS}^-	3.4755
G	3.91	G_{SC}	3.91	G_{SC}	3.9137
		G_{HS}^+	4.33	G_{HS}^+	4.1640
		G_V	5.24	G_V	5.2406
μ_3	6.40	G_{eff}^v	6.83	G_{eff}^r	4.4348
				G_{eff}^v	6.6167
				x_1	11.7309
				x_2	1.5025

TABLE VI. Measured and computed effective elastic constants for the cubic crystals and polycrystals of copper (Cu). References for the data are found in Appendix C. All constants are in units of GPa.

Cu Copper					
Elastic constants		Previous work		Present results	
c_{11}	171.0	K_R	138.0	K_R	138.3
c_{12}	122.0	K_{HS}^-	138.0	K_{HS}^-	138.3
c_{44}	69.1	K_{SC}	138.0	K_{SC}	138.3
		K_{HS}^+	138.0	K_{HS}^+	138.3
K	138.0	K_V	138.0	K_V	138.3
G	45.6	G_R	40.0	G_R	39.98
		G_{HS}^-	44.8	G_{HS}^-	46.23
		G_{SC}	46.3	G_{SC}	46.30
		G_{HS}^+	47.2	G_{HS}^+	46.32
		G_V	51.3	G_V	51.26
μ_3	24.5	G_{eff}^v	24.5	G_{eff}^r	24.51
				G_{eff}^v	24.60
				x_1	38.87
				x_2	10.33

TABLE VII. Measured and computed effective elastic constants for the hexagonal crystals and polycrystals of H_2O ice. References for the data are found in Appendix C. All constants are in units of GPa.

H_2O Ice					
Elastic constants		Previous work		Present results	
c_{11}	13.85	K_R	8.89	K_R	8.8966
c_{12}	7.07	K_{HS}^-	8.89	K_{HS}^-	8.8966
c_{13}	5.81	K_{SC}	8.89	K_{SC}	8.8966
c_{33}	14.99	K_{HS}^+	8.89	K_{HS}^+	8.8966
c_{44}	3.19	K_V	8.89	K_V	8.8967
c_{66}	3.39	G_R	3.48	G_R	3.4871
K	8.89	G_{HS}^-	3.52	G_{HS}^-	3.5180
G	3.52	G_{SC}	3.52	G_{SC}	3.5194
		G_{HS}^+	3.52	G_{HS}^+	3.5231
		G_V	3.55	G_V	3.5540
		G_{eff}^v	4.61	G_{eff}^r	4.6099
				G_{eff}^v	4.6100
				x_1	9.2200
				x_2	2.4705

TABLE VIII. Measured and computed effective elastic constants for the cubic crystals and polycrystals of methane hydrate (ideally $CH_4 \cdot 5.75H_2O$) at $P = 1$ atm and $T = 270$ K. References for the data are found in Appendix C. All constants are in units of GPa.

		Methane hydrate			
Elastic constants		Previous method		Present method	
c_{11}	12.8	K_R	8.41	K_R	8.41
c_{12}	6.215	K_{HS}^-	8.41	K_{HS}^-	8.41
c_{44}	3.6	K_{SC}	8.41	K_{SC}	8.41
		K_{HS}^+	8.41	K_{HS}^+	8.41
K	8.41	K_V	8.41	K_V	8.41
G	3.54	G_R	3.470	G_R	3.470
		G_{HS}^-	3.474	G_{HS}^-	3.474
		G_{SC}	3.474	G_{SC}	3.474
		G_{HS}^+	3.474	G_{HS}^+	3.474
		G_V	3.477	G_V	3.477
μ_3	3.293	G_{eff}^v	3.293	G_{eff}^r	3.293
				G_{eff}^v	3.293
				x_1	5.19
				x_2	1.39

but rather that there are multiple zeros. This fact does not mean that *the optimal solution* is nonunique, but rather that it is important to choose the right zeros corresponding to the best choices of upper and lower bounds, which are unique. This process goes smoothly if we have the proper information at hand: in particular, we need to know what the signs are of the various quantities previously defined that need to be positive or negative semidefinite. These quantities are the six principal minors [see (A21)] of the appropriate 3×3 matrices $X^{\pm}$. If we find a region in which these minors are all (say) positive and then some of them become negative as we pass a certain boundary, then we have found a candidate for one of the HS bounds (and it is necessary that this transition occurs simultaneously for both $K_{\mathrm{HS}}^{\pm}$ and $G_{\mathrm{HS}}^{\pm}$). Similarly, if the values of these principal minors are all negative and some become positive at some boundary, then we have found another pair of candidates for values for the bounds. As we scan through these sign changes, it becomes clear that the best choices for the bounds are the ones that happen closest to the well-defined self-consistent values K_{SC}^* and G_{SC}^*. It can and does happen that there are several of these sign changes near the vicinity of the self-consistent values; and then the algorithm for choosing the best bounds is also clear: the ones that occur closest to K_{SC}^* and G_{SC}^* without violating the constraints are the values we want.

C. Discussion of results

Two examples considered in Tables I and II were also considered by Watt, [8] although the data sources were not the same as the data used here. For comparison, Watt's Voigt-Reuss-Hill values (in GPa) for danburite were $K_{\mathrm{VRH}} = 91.7$ and $G_{\mathrm{VRH}} = 64.1$, whereas the corresponding values presented here in Table I are $K_{\mathrm{VRH}} = 91.7$ and $G_{\mathrm{VRH}} = 64.2$. Similarly, for forsterite, Watt's Voigt-Reuss-Hill values (in GPa) were $K_{\mathrm{VRH}} = 129.1$ and $G_{\mathrm{VRH}} = 81.6$, whereas the corresponding values presented here in Table I are $K_{\mathrm{VRH}} = 129.5$ and $G_{\mathrm{VRH}} = 81.1$. So Watt's values and ours agree quite well, despite the use of somewhat different values for the input constants. Middya and Basu [14] also considered forsterite, and found the self-consistent estimates (in GPa) to be $K_{\mathrm{SC}} = 128.8$ and $G_{\mathrm{SC}} = 81.5$. Our results for forsterite are also comparable, being $K_{\mathrm{SC}} = 128.5$ and $G_{\mathrm{SC}} = 80.4$ GPa. The only differences anticipated between these calculations of the *self-consistent estimates* in the previous work and the present work are those due to differences in input values of the elastic constants themselves. However, there are anticipated to be some more significant differences in results for the *HS bounds* between Watt's approach and our approach, due to the introduction here of the additional comparison moduli x_1 and x_2 (Appendix B) that were not considered by Watt.

Although the two OsN_2 (osmium nitride with marcasite crystal structure) examples (GGA and LDA) in Tables III and IV are nominally for the same material, the results differ substantially. We can quantify these differences by considering first the percentage discrepancies between input values for the c_{ij}'s: LDA results are higher than GGA results in all cases. The differences for c_{11}, c_{22}, c_{33} ranged from 12%–14%; differences for c_{12}, c_{13}, c_{23} ranged from 17%–19%; while differences for c_{44}, c_{55}, c_{66} ranged from 6%–12%. Computed polycrystal values for bulk moduli differed by about 15%; for the shear moduli by 9–11%; for the auxiliary constants (i.e., G_{eff}^r, G_{eff}^v, x_1, x_2), the range was about 11%–12%. Thus, the range of the input (data) differences was about 6%–19%, while the range for the output (averaged) constants was narrower, being about 9%–15%. So the averaging process does tend to narrow the range of these differences by about a factor of 2 for this particular set of input elastic constants. It would obviously be of some practical concern if the averaging process made these differences larger, rather than smaller.

D. A restatement and evaluation of the methods developed

Voigt and Reuss bounds are determined by simple formulas depending only on the stiffness (c_{ij}) or compliance (S_{ij}) matrix elements of the anisotropic rock crystals. These easy-to-compute Voigt (A14)–(A15) and Reuss (A16)–(A17) bounds on both bulk (K) and shear (G) moduli can be viewed as establishing a rectangle in the two-dimensional space (G,K), since—if the point (G_R,K_R) falls at the lower left-hand corner of a rectangle—then the point (G_V,K_V) lies at (and defines) the upper right-hand corner of this rectangle. All the modulus values of interest in this paper must always fall inside this rectangle. In particular, the self-consistent estimator (G^*,K^*) falls somewhere in the middle, but seldom (if ever) lies exactly at the center of this rectangle. In fact, the center point of the rectangle is exactly the Hill estimator (G_H,K_H) based on the arithmetic means of the shear and bulk moduli. But this point is only a very crude estimate of the points of most interest—both of the Hill averages G_H and K_H, both typically being somewhat too high in value.

The next easiest point to compute is actually the self-consistent estimator (G^*,K^*). This point will also always fall within the Voigt-Reuss rectangle, but again not necessarily exactly in the middle. Virtually the same equations that determine these self-consistent estimators also determine the

Hashin-Shtrikman bounds on G and K. However, these equations for the Hashin-Shtrikman bounds actually may be used to determine many effective constant estimates, depending on exactly what algorithm is used to explore the values within the Voigt-Reuss rectangle already defined. So one method (which is NOT the one used here) would be to evaluate all points on some fine grid within this rectangle, and then choose the values that produce the best results for the Hashin-Shtrikman bounds. Although this is clearly another viable searching approach, it was not the one pursued in the present work.

Other researchers have used more complicated search routines, instead of the simplified method proposed and employed here, which we will term (for presumably obvious reasons) a "shooting method." The method in outline first finds the self-consistent values G^* and K^*, which are themselves easily and uniquely determined. The self-consistent values must also by their nature also fall within the smaller HS rectangle determined by the points $(G_{\mathrm{HS}}^-, K_{\mathrm{HS}}^-)$ and $(G_{\mathrm{HS}}^+, K_{\mathrm{HS}}^+)$.

The entire Hashin-Shtrikman rectangle itself must also necessarily lie within the Voigt-Reuss rectangle. So, if we shoot toward the self-consistent point (G^*, K^*) from anywhere on the boundary of the Voigt-Reuss rectangle, we must cross the Hashin-Shtrikman rectangle boundary somewhere along the way. When we cross such a boundary, sign changes occur in the factors that we monitor, indicating that the values of the functionals of interest are passing through zero. Hence, we can map out this boundary defined by Hashin-Shtrikman bounds while taking a relatively small number of "shots" toward the self-consistent point near the middle of the Voigt-Reuss rectangle.

We need to make several of these shots to be sure that we have located the four HS boundaries—i.e., G_{HS}^-, G_{HS}^+, K_{HS}^-, K_{HS}^+—in this two-dimensional space, and not some spurious solution of these equations. (This reasonable concern did not ever appear to become a problem in actual practice.) Other researchers who have attempted to find the Hashin-Shtrikman boundaries have typically used global searching techniques, and these methods—while certain to locate the boundaries eventually—are not usually as efficient as the shooting method proposed and used here. Furthermore, if these searching methods are terminated too soon, they may in fact miss the optimal bounds. So it is the existence of the uniquely defined and quite easily determined point (G^*, K^*) that makes the present shooting method both viable and attractive.

V. SUMMARY AND CONCLUSIONS

A modification of earlier methods has been developed for determining effective elastic constants in polycrystals composed of crystalline grains each of which has orthorhombic symmetry or higher. The methods employed are in fact fairly well-known, since the main ideas used are based on the early work of Hashin and Shtrikman, [5] Hill [13], Peselnick and Meister [6], Gubernatis and Krumhansl [11], Watt and Peselnick [7], Willis, [12] Watt [8], Middya and Basu [14], and Berryman [17]. There were, however, two innovations added to the known approaches to be found in these references. The first innovation was to introduce the concept of two effective shear moduli for the comparison materials needed by the Hashin-Shtrikman approach (see Appendix B) in orthorhombic polycrystals. These two effective shear moduli are neither eigenvalues, nor normal shear moduli in any usual sense, but they nevertheless supply reasonable comparison numbers for use in the search routines that are necessary to determine (i.e., piece together) the complicated boundaries of the Hashin-Shtrikman bounding construction for orthorhombic materials.

In particular the smaller of these two comparison shear moduli is typically much smaller than all the other pertinent shear moduli present, and thus widens the search region for the Hashin-Shtrikman lower bounds. Similarly, the other comparison shear modulus is sometimes larger than all the other shear moduli in the system, which then widens the search region for the Hashin-Shtrikman upper bounds.

The second innovation revolves around the fact that some of the more symmetric elastic materials, including hexagonal, tetragonal, and cubic symmetries (but not trigonal), can be considered special cases of orthorhombic symmetry. Therefore, just one (for the orthorhombic case) routine can be used to determine constants for all these four types (including orthorhombic itself of course) of elastic polycrystalline media. It has then been shown explicitly in these case studies that this approach never leads to worse Hashin-Shtrikman bounds, and can actually lead to somewhat tighter bounds for some of the materials considered. All the other constants found, including the self-consistent estimates and the Voigt and Reuss averages, are not altered by using the orthorhombic code for these purposes. In three cases studied, direct comparisons were made to previously published results of the present author on tetragonal, cubic, and hexagonal media. Results were found always to be consistent, and often identical (to a precision consistent with the available experimental input data on the elastic constants themselves).

One overall conclusion reached is that the self-consistent results always lie within the bounds, as would normally be expected. This result, together with the fact that the self-consistent iteration process for these estimates is itself always very robust and quickly converging, has suggested that these same self-consistent values can be used to simplify the search routines used for locating the HS bounding values and/or curves. This approach was the one used here and was found to be a very effective tool for speeding up the search processes for the HS bounding curves and limiting modulus values.

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APPENDIX A: SIMPLIFIED RESULTS NEEDED FOR SPECIAL CASES, INCLUDING TETRAGONAL, HEXAGONAL, AND CUBIC ELASTIC MATERIALS

In earlier work the author has discussed the Peselnick and Meister [6] and the Watt and Peselnick [7] bounds for hexagonal, trigonal, tetragonal, and cubic symmetries. It seems worthwhile to make note of some simplifications in these bounding methods that can be understood now, especially since similar simplifications apply to the main case being studied, which is the orthorhombic class of elastic symmetry.

Parameters needed to optimize Hashin-Shtrikman bounds can be taken to be $K_\pm$ and $G_\pm$, where the $\pm$ symbols designate the best comparison material values for the upper bounds $+$ and lower bounds $-$, with the $K_\pm$ being bulk moduli and $G_\pm$ being shear moduli of the comparison materials needed in the Hashin-Shtrikman approach. Normally K_+ and G_+ are used together, and K_- and G_- are used together, without mixing of the subscripts in the same formulas. An exception is the limit of the self-consistent estimates, in which case only one set of constants applies, and we typically label the starting values as K_0 and G_0, and the final results as K^* and G^*, although K_{SC} and G_{SC} or some variant thereof may also be used by some authors. The Hashin-Shtrikman bounds themselves will be labeled $K_{\text{HS}}^\pm$ and $G_{\text{HS}}^\pm$, although other labels are sometimes also used to give credit to the workers who obtained bounding results for specific crystal symmetries.

Formulas for the Hashin-Shtrikman bounds in the notation of Peselnick and Meister [6] take the form

$$K_{\text{PM}}^\pm = K_\pm + \frac{K_V - K_\pm}{1 + 2\beta_\pm\left(G_\pm - G_{\text{eff}}^v\right)} \tag{A1}$$

and

$$G_{\text{PM}}^\pm = G_\pm + \frac{B_2^\pm}{1 + 2\beta_\pm B_2^\pm}. \tag{A2}$$

The Hashin-Shtrikman bounds themselves are then given exactly by $K_{\text{HS}}^\pm \equiv K_{\text{PM}}^\pm$ and $G_{\text{HS}}^\pm \equiv G_{\text{PM}}^\pm$. Here K_V is the Voigt average of bulk modulus, and the remaining constants are defined carefully in Appendix B. Definitions of G_{eff}^v depend specifically on the crystal symmetry, and examples will be provided later in this Appendix.

It is worthwhile noting that two additional quantities that essentially always play a role in the Hashin-Shtrikman bounds and also in the self-consistency conditions are the quantities $4G_\pm/3$ and the combinations:

$$\zeta_\pm \equiv \frac{G_\pm(9K_\pm + 8G_\pm)}{6(K_\pm + 2G_\pm)}. \tag{A3}$$

These quantities have been shown by Hill [13], Willis [12], and others (including Olson and Avellaneda [18]) to be important factors specifically for comparison materials having spherical shapes. Such spherical shapes are the ones typically assumed, whether explicitly or implicitly, in such work on polycrystals. The source of these contributions can probably be most easily understood by considering Eshelby's work [19] on elasticity of composites containing ellipsoids. In such cases, it is again exactly such factors that play the same type of role in the formulas for effective elastic constants [17]. If the comparison materials have other shapes, then other combinations [20] of constants can come into play, but the spherical shapes have been the only ones usually considered for polycrystal studies to date.

Parameters $\alpha_\pm$ and $\beta_\pm$ that appear repeatedly in the PMW (Peselnick-Meister-Watt) works [6,7] can be related to the Eshelby results by rewriting them in the form

$$-\frac{1}{\alpha_\pm} = K_\pm + 4G_\pm/3 \tag{A4}$$

and

$$-\frac{1}{2\beta_\pm} = G_\pm + \zeta_\pm. \tag{A5}$$

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

$$\gamma_\pm = \frac{\alpha_\pm - 3\beta_\pm}{9}. \tag{A6}$$

The reason for pointing out this similarity across the different applications is that the resulting rather complicated formulas often collapse in unexpectedly simple ways if we look for formulas of the right type. For example, the Hashin-Shtrikman bounds for bulk modulus found by PMW can be rewritten as

$$K_{\text{PM}}^\pm = \frac{K_V\left(G_{\text{eff}}^r + \zeta_\pm\right)}{G_{\text{eff}}^v + \zeta_\pm}, \tag{A7}$$

which is valid for hexagonal, tetragonal, and also trigonal (not otherwise considered here) crystal structures. The quantities G_{eff}^v (G_{eff}^r) are the uniaxial shear energies per unit volume for a unit applied shear strain (shear stress), whose main compressive strain (stress) is applied to the grains along their axes of symmetry (also see Berryman [17] for more discussion). (Note that cubic symmetry is special in this regard, since it has a well-defined bulk modulus—so neither bounds nor estimates are required for bulk modulus in this case.) Similarly, if we add $\zeta_\pm$ to both sides of (A2), then we find that this result can be simplified to read

$$\frac{1}{G_{\text{PM}}^\pm + \zeta_\pm} = \frac{1 - B_2^\pm/(G_\pm + \zeta_\pm)}{G_\pm + \zeta_\pm}, \tag{A8}$$

which is valid for the same three crystal symmetries. After determination of the $B_2^\pm$ factors, these results imply for hexagonal crystals that

$$\frac{1}{G_{\text{hex}}^\pm + \zeta_\pm} = \frac{1}{5}\left[\frac{1 - \alpha_\pm(K_V - K_\pm)}{G_{\text{eff}}^v + \zeta_\pm + \frac{\alpha_\pm}{2\beta_\pm}(K_V - K_\pm)} + \frac{2}{c_{44} + \zeta_\pm} + \frac{2}{c_{66} + \zeta_\pm}\right], \tag{A9}$$

where $G_{\text{eff}}^{v} = (c_{11} + c_{33} - 2c_{13} - c_{66})/3$. For tetragonal crystals, we have

$$\frac{1}{G_{\text{tetr}}^{\pm} + \zeta_{\pm}} = \frac{1}{5}\left[\frac{1 - \alpha_{\pm}(K_V - K_{\pm})}{G_{\text{eff}}^{v} + \zeta_{\pm} + \frac{\alpha_{\pm}}{2\beta_{\pm}}(K_V - K_{\pm})} + \frac{1}{\mu_3 + \zeta_{\pm}} + \frac{2}{c_{44} + \zeta_{\pm}} + \frac{1}{c_{66} + \zeta_{\pm}}\right], \tag{A10}$$

where $\mu_3 \equiv (c_{11} - c_{12})/2$, and $G_{\text{eff}}^{v} = (c_{11} + 2c_{33} + c_{12} - 4c_{13})/6$. And similarly, for polycrystals of cubics, we have that

$$\frac{1}{G_{\text{cub}}^{\pm} + \zeta_{\pm}} = \frac{1}{5}\left[\frac{2}{G_{\text{eff}}^{v} + \zeta_{\pm}} + \frac{3}{c_{44} + \zeta_{\pm}}\right], \tag{A11}$$

where $G_{\text{eff}}^{v} = \mu_3 = (c_{11} - c_{12})/2$.

For the main results of the present paper, we also need the formulas for the shear modulus of orthorhombic media. The general forms shown in (A2) and especially (A8) hold without change for orthorhombic media, but the formula for the main factor $B_2^{\pm}$ for shear modulus bounds and estimates is now given by

$$\begin{aligned} 15B_2^{\pm} = {} & \frac{a^{\pm} - b^{\pm} + \beta_{\pm}(2d^{\pm} - 2c^{\pm} - e^{\pm}) + 3\gamma_{\pm}(d^{\pm} - c^{\pm} + e^{\pm}) + \alpha_{\pm}\beta_{\pm}\Omega^{\pm}}{1 - a^{\pm}\beta_{\pm} - 9\gamma_{\pm}(K_V - K_{\pm}) + D_{\pm}} \\ & + 3(G_{\pm} + \zeta_{\pm})^2\left(\frac{3}{G_{\pm} + \zeta_{\pm}} - \frac{1}{c_{44} + \zeta_{\pm}} - \frac{1}{c_{55} + \zeta_{\pm}} - \frac{1}{c_{66} + \zeta_{\pm}}\right). \end{aligned} \tag{A12}$$

The constants $\alpha_{\pm}$, $\beta_{\pm}$, and $\gamma_{\pm}$, appearing here, were defined earlier in (A4), (A5), and (A6). The term $D_{\pm}$ is given by

$$D_{\pm} = \beta_{\pm}(\beta_{\pm} + 2\gamma_{\pm}(c^{\pm} - d^{\pm}) - 2e^{\pm}\beta_{\pm}\gamma_{\pm} - \frac{\alpha_{\pm}\beta_{\pm}^2\Omega_{\pm}}{3}. \tag{A13}$$

The Voigt average of the bulk modulus is

$$K_V = \tfrac{1}{9}[c_{11} + c_{22} + c_{33} + 2(c_{12} + c_{23} + c_{13})]. \tag{A14}$$

Similarly, the Voigt average of the shear modulus is

$$\begin{aligned} G_V = {} & \tfrac{1}{15}[c_{11} + c_{22} + c_{33} - c_{12} - c_{23} - c_{13} \\ & + 3(c_{44} + c_{55} + c_{66})]. \end{aligned} \tag{A15}$$

For completeness, we also note that the corresponding Reuss averages [21] for orthorhombic crystals are determined by

$$\frac{1}{K_R} = (S_{11} + S_{22} + S_{33}) + 2(S_{23} + S_{31} + S_{12}) \tag{A16}$$

and

$$\begin{aligned} \frac{15}{G_R} = {} & 4\,(S_{11} + S_{22} + S_{33}) - 4\,(S_{23} + S_{31} + S_{12}) \\ & + 3\,(S_{44} + S_{55} + S_{66})\,, \end{aligned} \tag{A17}$$

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

Some of these constants are defined in terms of the comparison matrices $\mathbf{X}^{\pm}$ having matrix elements:

$$\begin{aligned} X_{11}^{\pm} &= c_{11} - K_{\pm} - \tfrac{4}{3}G_{\pm}, & X_{12}^{\pm} &= c_{12} - K_{\pm} + \tfrac{2}{3}G_{\pm}, \\ X_{22}^{\pm} &= c_{22} - K_{\pm} - \tfrac{4}{3}G_{\pm}, & X_{13}^{\pm} &= c_{13} - K_{\pm} + \tfrac{2}{3}G_{\pm}, \\ X_{33}^{\pm} &= c_{33} - K_{\pm} - \tfrac{4}{3}G_{\pm}, & X_{23}^{\pm} &= c_{23} - K_{\pm} + \tfrac{2}{3}G_{\pm}. \end{aligned} \tag{A18}$$

Then the determinant of this matrix is given by

$$\begin{aligned} \Omega^{\pm} \equiv \det(X^{\pm}) = {} & X_{11}^{\pm}X_{22}^{\pm}X_{33}^{\pm} + 2X_{12}^{\pm}X_{23}^{\pm}X_{13}^{\pm} - X_{11}^{\pm}(X_{23}^{\pm})^2 \\ & - X_{22}^{\pm}(X_{13}^{\pm})^2 - X_{33}^{\pm}(X_{12}^{\pm})^2. \end{aligned} \tag{A19}$$

The remaining constants appearing in (A12) are given by

$$\begin{aligned} a^{\pm} = X_{11}^{\pm} + X_{22}^{\pm} + X_{33}^{\pm}, \quad & b^{\pm} = X_{12}^{\pm} + X_{23}^{\pm} + X_{13}^{\pm}, \\ c^{\pm} &= X_{11}^{\pm}X_{22}^{\pm} + X_{22}^{\pm}X_{33}^{\pm} + X_{33}^{\pm}X_{11}^{\pm}, \\ d^{\pm} &= (X_{12}^{\pm})^2 + (X_{23}^{\pm})^2 + (X_{13}^{\pm})^2, \end{aligned} \tag{A20}$$

$$\begin{aligned} e^{\pm} = {} & X_{12}^{\pm}X_{13}^{\pm} + X_{13}^{\pm}X_{23}^{\pm} + X_{23}^{\pm}X_{13}^{\pm} \\ & - X_{11}^{\pm}X_{23}^{\pm} - X_{22}^{\pm}X_{13}^{\pm} - X_{33}^{\pm}X_{12}^{\pm}. \end{aligned}$$

[Notational clarification: The symbol ± always appears here 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 ± 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.]

The pertinent conditions on the matrix elements of $X^{\pm}$ come from the requirement of either positive semidefiniteness or negative semidefiniteness. (Positive or negative definiteness implies that zero is never attained; positive or negative semidefiniteness means that zero limiting values are permitted.) These requirements mean that all the principal minors of the determinant $\Omega^{\pm}$ must be either simultaneously positive semidefinite, or simultaneously negative semidefinite. Thus, the requirements are for positive semidefiniteness are

$$\begin{aligned} X_{11}^{+} &\geqslant 0, & X_{11}^{+}X_{22}^{+} - (X_{12}^{+})^2 &\geqslant 0, \\ X_{22}^{+} &\geqslant 0, & X_{22}^{+}X_{33}^{+} - (X_{23}^{+})^2 &\geqslant 0, \\ X_{33}^{+} &\geqslant 0, & X_{33}^{+}X_{11}^{+} - (X_{13}^{+})^2 &\geqslant 0, \end{aligned} \tag{A21}$$

and $\Omega^{+} \geqslant 0$. For negative semidefiniteness, all the superscript pluses are replaced by superscript minuses, and the $\geqslant$ symbols are replaced by $\leqslant$'s.

APPENDIX B: TWO EFFECTIVE SHEAR MODULI FOR COMPARISON MATERIALS IN GRANULAR POLYCRYSTALS OF ORTHORHOMBIC ELASTIC MATERIALS

Elastic materials generally have six modes (which we treat as eigenvalues in this discussion), one of which may be viewed approximately as a bulk mode (i.e., an eigenvector whose elastic response is dominated by pure compression or extension, but may still have a small component of shear), while the other five modes are mostly dominated by shearing responses of the elastic system. The Voigt and Reuss averages for overall shear response for orthorhombic media may be defined by

$$G_V = \tfrac{1}{5}\left[2G^v_{\rm eff} + c_{44} + c_{55} + c_{66}\right] \tag{B1}$$

and

$$\frac{1}{G_R} = \frac{1}{5}\left[\frac{2}{G^r_{\rm eff}} + \frac{1}{c_{44}} + \frac{1}{c_{55}} + \frac{1}{c_{66}}\right]. \tag{B2}$$

We are using these forms as the first step in a process of defining two effective composite shear constants for polycrystals of orthorhombics:

$$G^v_{\rm eff} \equiv \tfrac{1}{6}[c_{11} + c_{22} + c_{33} - c_{12} - c_{13} - c_{23}] \tag{B3}$$

and

$$\frac{3}{G^r_{\rm eff}} \equiv \frac{2}{\Delta}[c_{11}(c_{22}+c_{33}) + c_{22}(c_{33}+c_{13}) + c_{33}(c_{11}+c_{12}) - c_{13}(c_{13}+c_{12}) - c_{12}(c_{12}+c_{23}) - c_{23}(c_{23}+c_{13})], \tag{B4}$$

where the factor Δ is given by

$$\Delta = c_{11}c_{22}c_{33} + 2c_{12}c_{23}c_{13} - c_{11}c_{23}^2 - c_{22}c_{13}^2 - c_{33}c_{12}^2, \tag{B5}$$

which is the pertinent determinant of the upper left 3×3 segment of the elastic constant matrix. Equations (B1) and (B2) are exactly the usual definitions of the Voigt [2] and Reuss [3] averages for shear if we substitute the expressions (B3) and (B4) into these formulas. Formula (B4) could also be written more simply in terms of compliances, but to do so requires inversion of the stiffness matrix, and this has already been accomplished explicitly by using the expressions in the present equation. We will follow Watt [7,8] in this regard, while trying to simplify the notation somewhat as we go by introducing these two useful combinations of shear stiffness constants: $G^v_{\rm eff}$ and $G^r_{\rm eff}$.

The two constants are *not,* however, our ultimate goal in this process. Instead they provide an intermediate step in the task of finding useful comparison values for the Hashin-Shtrikman bounding process. From the structure of Eqs. (B1) and (B2), we see that these two constants each play the role of a different type of average of two other shear moduli. We will call these two moduli x_1 and x_2. They are not intended to represent typical shear moduli, and should not be interpreted as such. Instead, they are helpful constructs that can be used in the process of determining Hashin-Shtrikman bounds on shear modulus for the polycrystal systems of interest. We need them, because without them we are not able to explore the full region that should be spanned by comparison materials. These two quantities are defined by the following statements:

$$2G^v_{\rm eff} \equiv x_1 + x_2, \tag{B6}$$

while

$$\frac{2}{G^r_{\rm eff}} \equiv \frac{1}{x_1} + \frac{1}{x_2}. \tag{B7}$$

Thus, we are treating $G^v_{\rm eff}$ and $G^r_{\rm eff}$, respectively, as the Voigt and Reuss averages of the two unknown shear-like quantities x_1 and x_2. We will call these two constants “effective comparison shear moduli.” We find that their values are significantly different from each other and also from the two quantities from which they are derived in all cases considered here (see the examples in Tables II, IV–VIII). Thus, they provide usefully different measures of the possible range of shear modulus to be explored in the process of locating the boundaries needed ultimately to determine the Hashin-Shtrikman bounds themselves. This feature helps to expand the search region for the optimal Hashin-Shtrikman bounds.

To determine the values of x_1 and x_2, we also need to solve the quadratic equation found by multiplying (B6) and (B7) together, giving

$$4\frac{G^v_{\rm eff}}{G^r_{\rm eff}} = 2 + \frac{x_1}{x_2} + \frac{x_2}{x_1}. \tag{B8}$$

Then, with the definitions $R \equiv G^v_{\rm eff}/G^r_{\rm eff}$ and $r_{12} \equiv x_1/x_2$, while also defining the quantity $C \equiv 2(2R-1)$, we have

$$r_{12} = C \pm \sqrt{C^2 - 1}. \tag{B9}$$

It is easy to see that $R \geqslant 1$ always holds and also that $C \geqslant 2$, so the argument of the radical is always non-negative, and $r_{12} \geqslant 0$ for either choice of the sign in front of the radical (since $C \geqslant \sqrt{C^2-1}$). Thus, we have

$$x_2 \equiv 2G^v_{\rm eff}/(1 + r_{12}) \tag{B10}$$

and

$$x_1 \equiv r_{12}x_2. \tag{B11}$$

The roles of x_1 and x_2 are reversed by making different sign choices in (B9), but we are interested in both these quantities, so this freedom actually makes no difference to us. Examples of the values determined this way are shown in all the tables of examples (i.e., Tables II, IV–VIII).

As is discussed more fully in the main text, the values of x_1 and x_2 have been found to differ substantially from the values of both $G^r_{\rm eff}$ and $G^v_{\rm eff}$, thus providing more insight into the total range of behaviors being experienced by the orthorhombic system in the presence of applied shear stress.

APPENDIX C: SOURCES OF SINGLE-CRYSTAL ELASTIC DATA

The elastic data for orthorhombic materials considered in Tables I and II for aragonite, danburite, enstatite, forsterite, and topaz were all taken from Bass [22]. The data for Rochelle salt, sulfur, and α-uranium in Tables III and IV were also taken from Bass [22]. The same values can also be found in Musgrave [23] and Huntington [24]. The two examples of OsN_2 having marcasite crystal structure considered in Tables III and IV were the results of first-principles physics calculations using the GGA (the generalized gradient) and LDA (the local-density) approximations in work by Wang et al [25].

In three cases (Tables V, VI, and VII), the examples were purposely chosen from among the cases studied previously by the author [17]. These cases include tetragonal urea, for which the data came from Fischer and Zarembowitch [26], cubic copper, for which the data were taken from the original paper by Hashin and Shtrikman [5], and hexagonal H_2O ice, for which the data were obtained from Simmons and Wang [27].

The data for methane hydrate (Table VIII) were taken from Shimizu *et al.* [28].

APPENDIX D: SIGNIFICANCE OF SELF-CONSISTENT ESTIMATES

There are two main issues concerning the worth of self-consistent estimates of the overall elastic constants. The first issue is whether or not any special significance should be accorded such estimates, and in particular should we presume that the self-consistent estimates are actually the best possible estimates of the overall bulk and shear moduli of the polycrystals studied here. The answer to this question may not be universal, but the more general answer in our present context is surely that the self-consistent estimates, while good and definite estimators, should *not* be viewed as the "true values" of the effective bulk and shear moduli of such polycrystals. They are very reasonable estimates (lying always between the known rigorous bounds—as will be shown next), but should not be given any more special interpretation than this. Indeed, if the self-consistent estimates were always the true values, there would clearly be no practical reason to study the bounding methods. However, by combining the information contained in the self-consistent estimates and the bounds, we have not only these estimates themselves, but we can also put rigorous error bars around these estimates using the bounds. In general, we expect that different polycrystalline realizations of the same material may have a range (though perhaps not a very wide range) of behavior due to differences in the random microstructural arrangements that have not been explicitly accounted for in these models. There can be significant consequences of local ordering that affect the overall response even through the resulting polycrystal behavior nevertheless remains macroscopically isotropic.

A second question concerning the significance of the self-consistent estimators is whether or not they are actually unique, and also the related question of whether or not they are in fact guaranteed to lie between the rigorous bounds. The answers to both these questions are yes they are unique, and yes they always lie between the bounds [14,17].

To demonstrate these facts in a case that is simple enough to analyze (but also easily generalized to the other cases studied in this paper), we will now consider only simple cubic materials. This choice is most convenient from the point of view of simplifying the math, because polycrystals of grains of the same cubic elastic materials all have uniquely defined average bulk moduli, which are determined by the identity $3K = c_{11} + 2c_{12}$. So all the bulk modulus bounds collapse to this constant K value for polycrystals having well-bonded simple cubic grains of the same type, and therefore need not be analyzed further. To see how this works out in the equations, note again that

$$K_{\mathrm{PM}}^{\pm} = \frac{K_V\left(G_{\mathrm{eff}}^{r} + \zeta_\pm\right)}{G_{\mathrm{eff}}^{v} + \zeta_\pm}. \tag{D1}$$

But since we always have $K_{\mathrm{PM}} \to K_R$ as $\zeta \to 0$ and $K_{\mathrm{PM}} \to K_V$ as $\zeta \to \infty$, while $K_R = K_V = K$, we must also have (which is easy to verify) that $G_{\mathrm{eff}}^{r} = G_{\mathrm{eff}}^{v} = (c_{11} - c_{12})/2$. So the bulk modulus bounds and estimates all collapse to the same constant K, while at the same time we have the shear modulus bounds:

$$\frac{1}{G_{\mathrm{PM}}^{\pm} + \zeta_\pm} = \frac{1}{5}\left[\frac{2}{G_{\mathrm{eff}}^{v} + \zeta_\pm} + \frac{3}{c_{44} + \zeta_\pm}\right], \tag{D2}$$

where $0 \leqslant \frac{3}{2}G_- \leqslant \zeta_\pm \equiv G_\pm(9K + 8G_\pm)/6(K + 2G_\pm) \leqslant \frac{2}{3}G_+ \leqslant \infty$. The next-to-final inequality follows in the limit when $G_+ \to$ some large, but still finite value.

Now it is also known [12,17,19] that the self-consistent shear modulus G^* for simple cubic materials satisfies the cubic equation:

$$8(G^*)^3 + (9K + 4G_{\mathrm{eff}}^{v})(G^*)^2 - 3c_{44}(K + 4G_{\mathrm{eff}}^{v})G^* - 6c_{44}KG_{\mathrm{eff}}^{v} = 0. \tag{D3}$$

In fact, it is straightforward to show that this result follows from (D2) by replacing $G_\pm$ everywhere (including within the definition of $\zeta_\pm$) by G^*. This cubic equation has three real roots. Because the coefficient of $(G^*)^2$ is positive while the final constant term (independent of G^*) is negative, it follows that these three eigenvalues cannot all have the same sign. The final term also shows then that only one of the eigenvalues is positive, while the other two are necessarily negative. Thus, it is important to recognize that the only positive root is also the only physically pertinent root of (D3), as well as being the one consistent with (D2) for $0 \leqslant \zeta_\pm \leqslant \infty$.

In particular, we can rearrange (D2) into the form

$$G_{\mathrm{PM}}^{\pm} = \Gamma(\zeta_\pm), \tag{D4}$$

where

$$\Gamma(\zeta_\pm) \equiv \left[\frac{1}{5}\left(\frac{2}{G_{\mathrm{eff}}^{v} + \zeta_\pm} + \frac{3}{c_{44} + \zeta_\pm}\right)\right]^{-1} - \zeta_\pm. \tag{D5}$$

This rearrangement is useful to us because

$$\frac{d}{d\zeta}\Gamma(\zeta) = \frac{6}{25}\,[\Gamma(\zeta) + \zeta]^2\left(\frac{1}{G_{\mathrm{eff}}^{v} + \zeta} - \frac{1}{c_{44} + \zeta}\right)^2 \geqslant 0, \tag{D6}$$

and also because, as the argument $\zeta_\pm$ goes to 0 or ∞, the results are, respectively,

$$\Gamma(\zeta_-) \to \left[\frac{1}{5}\left(\frac{2}{G_{\mathrm{eff}}^{v}} + \frac{3}{c_{44}}\right)\right]^{-1} \equiv G_R, \quad \text{as} \quad \zeta_- \to 0, \tag{D7}$$

and

$$\Gamma(\zeta_+) \to \frac{1}{5}\left(2G_{\mathrm{eff}}^{v} + 3c_{44}\right) = G_V, \quad \text{as} \quad \zeta_+ \to \infty, \tag{D8}$$

according to the definitions given in (B2) and (B1), since here $c_{66} = c_{55} = c_{44}$.

Thus, for cubic symmetry, we find that the only pertinent functional $\Gamma(\zeta)$ is a monotonic function of its argument, and ranges from the Reuss average G_R for small arguments to the Voigt average G_V for large arguments. We can infer from these facts that there exists one unique ζ corresponding to each value of shear modulus G in the range $G_R \leqslant G \leqslant G_V$. The equations already quoted therefore guarantee that there exists a value of $G = G^*$ at which $\zeta(G^*) = \zeta^*$. Proving this kind of result in more general cases [12,29] is considerably more difficult than for the cubic example because the resulting polynomial can be of much higher order than 3. But nevertheless it is straightforward to check these facts numerically, as has been done repeatedly in the examples presented in this paper.

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