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Bounds and self-consistent estimates for elastic constants of polycrystals of hcp solid He^4

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Abstract

Recent advances in methods for computing both Hashin-Shtrikman bounds and related self-consistent (or CPA) estimates of elastic constants for polycrystals composed of randomly oriented crystals can be applied successfully to hexagonal close packed solid He^4. In particular, since the shear modulus C_{44} of hexagonal close-packed solid He is known to undergo large temperature variations when 20 mK $\leq T \leq$ 200 mK, bounds and estimates computed with this class of effective medium methods, while using $C_{44} \rightarrow 0$ as a proxy for melting, are found to be both qualitatively and quantitatively very similar to prior results obtained using Monte Carlo methods. Hashin-Shtrikman bounds provide significantly tighter constraints on the polycrystal behavior than do the traditional Voigt and Reuss bounds.

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I. INTRODUCTION

Methods for computing Hashin-Shtrikman[1−4] bounds and related self-consistent (also coherent potential approximation, or CPA) estimates[5−8] of elastic constants for polycrystals composed of anisotropic crystals have been known for about five decades, and actively applied to a wide variety of real systems for about three decades. To reduce the overall computational effort required by these methods, some simplifications were introduced recently by the author.[9−10] In particular, difficulties inherent in tracking the Hashin-Shtrikman bounding curves have been minimized by noting that the self-consistent estimates of the effective elastic constants are themselves 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, especially for orthorhombic or less symmetric systems.

Although it is well-known that isotropic elastic materials have compressional/extensional modes measured typically by a hydrostatic 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 quasi-static or dynamic measurements, as is often the case whether ultrasonic, acoustic, or seismic waves[11] are used to probe such media.

There are basically seven types of elastic crystal symmetries (see Nye[12]) 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 K 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 – in orthorhombic symmetry systems (for example) – there are three independent twisting shears that can be applied to any material sample, as well as three quite different shearing forces that can result (for example) from applying a uniaxial compression (or extension) in any of the three principal orthogonal directions. These cases do not exhaust all the possibilities for shearing motions, but all others can normally be found by considering linear combinations of the ones already mentioned.

It is because of these complexities that Voigt[13] and Reuss[14] studied elastic systems and determined that there were two sets of constants that seemed to capture much of the nature of these linear elastic materials. These results were then called the Voigt and Reuss *averages* of shear and bulk behavior until Hill[15] 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 (really polycrystalline) behavior.

Subsequently, Hashin and Shtrikman[1] 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,[2] Watt and Peselnick,[3] and also Watt[4] alone, who subsequently published a long series of papers on methods covering essentially all 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[5] and Taylor[6] via the coherent potential approximation (CPA), and then carried further for elastic constants by Gubernatis and Krumhansl,[7] and also in related work by Willis,[8] who based some of his ideas on earlier work in this area by Hill.[16] Olson and Avellaneda[17] also contributed to the same stream of ideas.

The present study will make use of the same theoretical tools, but will apply them to the problem of determining what might be the predicted response of polycrystals composed of solid He^4, when it appears in the form of a polycrystal. In particular, the tools already at hand appear to be sufficiently rigorous and relatively easy to use for computing estimates and bounds on the elastic responses of such systems. The methods developed for orthotropic systems[10] are more general than what is required for polycrystals of hexagonal closed packed He^4. But those codes could also be used instead of the ones we develop here, based on the somewhat simpler earlier work.[9]

Recommended advanced textbooks on elasticity include Landau and Lifshitz[18] and Ting.[19]

The first application of this analysis will be to determine the isotropic polycrystal constants for an aggregate composed of hexagonal close-packed solid He^4. It is known that helium solidifies only in the presence of external pressure; so such prestress must also be the source of nonzero values of the shear constants C_{44} and C_{55} (to be defined in Section II) in particular. Therefore, a second application makes use of these results to study how the softening of these shear constants $C_{44} = C_{55}$ in such an isotropic polycrystal of hexagonal close-packed solid He^4 affects the overall behavior of such a system.

The physical issue to be addressed then concerns the observed large variation in elastic behavior observed in the temperature range 20 to 200 mK. Some similar work along these lines has been published previously by Maris and Balibar.[20] However, these authors used Monte Carlo computer simulations to obtain their estimates, whereas the present work shows how to get comparable results more quickly and easily using the established analytical and semi-analytical methods, including those published previously by the author.[9,10]

II. ELASTIC PROPERTIES OF POLYCRYSTALS COMPOSED OF HEXAGONAL CRYSTALS

There are both explicit and implicit assumptions in the polycrystal constants estimation procedures. In particular, one strong assumption is that a polycrystal is macroscopically isotropic, and (at least equally important) that there are no gaps (holes) within the polycrystal.

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[18]) 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[19] for extensive discussion) Voigt 6 × 6 matrix prescription relating the stiffnesses C_{ij} to stresses σ_{ij} and strains ϵ_{ij}:

$$\begin{pmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{33} \\ \sigma_{12} \\ \sigma_{13} \\ \sigma_{23} \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & & & \\ C_{12} & C_{22} & C_{23} & & & \\ C_{13} & C_{23} & C_{33} & & & \\ & & & C_{44} & & \\ & & & & C_{55} & \\ & & & & & C_{66} \end{pmatrix} \begin{pmatrix} \epsilon_{11} \\ \epsilon_{22} \\ \epsilon_{33} \\ \epsilon_{23} \\ \epsilon_{13} \\ \epsilon_{12} \end{pmatrix} . \qquad (1)$$

Equation (1) clearly implies the six equations: $\sigma_{11} = C_{11}\epsilon_{11} + C_{12}\epsilon_{22} + C_{13}\epsilon_{33}$, …, $\sigma_{23} = C_{66}\epsilon_{12}$. [Also note that we are using the lower-case c four-index notation for elastic tensor c_{ijkl} and the upper-case C two-index notation C_{ij} as shown in (1) commonly used in the Voigt matrix notation for elasticity. Both of these quantities as used here are for isothermal conditions, but may or may not (depending on the context) also incorporate prestress (see Barron and Klein[21] and Stixrude[22] for extended discussions of this point).]

The example shown in (1) is that for orthorhombic symmetry, which is the most general case that will be considered (although briefly) 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 a thorough discussion of the orthorhombic case, see Ref. 10.

For polycrystals composed of grains having hexagonal symmetry, the number of independent components of the elastic matrix for individual grains is reduced due to higher symmetry so that $C_{22} = C_{11}$, $C_{23} = C_{13}$, and $C_{55} = C_{44}$. One further restriction is the condition $C_{11} = C_{12} + 2C_{66}$, which is often used to eliminate either C_{12} or C_{66} from the list of measured constants.

For hexagonal symmetry elastic materials, there are four simple eigenvectors and eigenvalues. Three of these are associated with the twisting shear modes ϵ_{23}, ϵ_{13}, and ϵ_{12}, and their respective stiffnesses, namely C_{44}, $C_{55} = C_{44}$, and C_{66}. There will also be three eigenmodes associated with the 3 × 3 submatrix in the upper lefthand corner of the full elastic matrix. But typically (for hexagonal symmetry) only one of these modes will generally be simply related to a pure mode (since $C_{13} = C_{23}$ for hexagonal symmetry), and this is the shear mode corresponding to $\epsilon_{22} = -\epsilon_{11}$, having the eigenvalue $C_{11} - C_{12} = 2C_{66}$. Thus, there are four simple shear modes, and two other eigenmodes of the system that are of mixed character, being linear combinations of an effective bulk modulus and a fifth effective shear modulus. It is these last two modes that make it necessary to study these issues related to the Voigt, Reuss, and Hashin-Shitrikman bounding methods for overall bulk and shear moduli of hexagonal-symmetry-based polycrystals. Analysis of these systems is normally designed to quantify the behavior of random polycrystals, where the use of the word "random" implies that the polycrystals are composed of a large enough number of small (and tightly fitting) crystallites oriented randomly in space so that the overall polycrystalline behavior is close to isotropic, and there is no porosity present in the aggregate. The effective isotropic constants can therefore be taken to be effective bulk K^* and shear G^* moduli. The main goal of the polycrystal analysis is therefore to localize these values by providing rigorous upper and lower bounds on both quantities. The traditional bounds/estimates for these quantities are the Voigt (K_V, G_V) and Reuss (K_R, G_R) estimators. These were originally proposed as useful estimates, but later proven by Hill to be rigorous upper (Voigt) and lower (Reuss) bounds on the polycrystal constants K^* and G^*. The work of Hashin and Shtrikman then led to more refined upper and lower bounds that generally improve upon the Voigt and Reuss bounds.

III. BOUNDS AND ESTIMATES OF ELASTIC CONSTANTS FOR POLYCRYSTALS

Self-consistency conditions (which for elasticity are also the same as the CPA or coherent potential approximation) are given by:

$$K_{SC} = K^* \qquad \text{and} \qquad G_{SC} = G^*, \tag{2}$$

where in the formulas of Appendix A all the quantities having ± subscripts or superscripts are replaced with the corresponding expressions with either SC subscripts or $*$ superscripts [these being entirely equivalent in either case because of the identities in (2)]. The PM and and HS subscripts are also irrelevant for these self-consistency conditions. Self-consistency results have been easily achieved for all the hexagonal (and also cubic, trigonal and tetragonal) examples known to the author. Orthorhombic symmetry[10] (not specifically considered here) is however more difficult to treat than these other cases. We are studying only hexagonal symmetry in the present examples.

Table 1 lists the elastic constant values used for the first example. Experimental data are from Crepeau *et al.*,[21] Greywall and Munarin,[22] and Greywall.[23] Table 2 displays the corresponding results found for the Reuss bound (R), Hashin-Shtrikman lower bound (HS$^-$), self-consistent estimate (SC), Voigt-Reuss-Hill estimate (VRH), geometric mean estimate (GM), Hashin-Strikman upper bound (HS$^+$), and Voigt upper bound (V). The geometric mean (GM) estimate for bulk and shear moduli is given by

$$K_{GM} \equiv (K_R K_V)^{1/2} \qquad \text{and} \qquad G_{GM} \equiv (G_R G_V).^{1/2} \tag{3}$$

A graphical representation of these same results is presented in Figure 1.

Table 3 lists the elastic constant values used for the second example. These simulation results are from Pessoa *et al.*[24] and Ardila *et al.*[25] Table 4 displays the corresponding results again, as in Table 2. A graphical representation of the same results is also presented in Figure 2.

When considering the graphical results in Figures 1 and 2, note that the VRH arithmetic mean always lies exactly at the center of Voigt-Reuss (VR) bounding box. Although it appears to be true that the self-consistent results lie at the center of the Hashin-Shitrikman bounding box for hexagonal systems, we know (from other work) that this is not always true for arbitrary anisotropic symmetry. Also note that the HS bounding box is NOT centered within the VR bounding box. The geometric mean (GM) estimate is expected to lie close to, but somewhat lower than and to the left of, the VRH estimate in such diagrams, since $K_{VRH}^2 - K_{GM}^2 = (K_V - K_R)^2/4$ and, similarly, for the corresponding averages of shear modulus G.

While some bound optimization effort is generally required for orthorhombic-based polycrystals[10], the formulas for hexagonal-based polycrystals are quite straightforward[9] to apply, and no additional effort is normally required to obtain valid and useful results.

All the formulas used in these examples are summarized in Appendix A.

IV. EFFECTS DUE TO RISING TEMPERATURE OR DECREASING CONFINING PRESSURE

To understand how the mechanical behavior of hcp solid He^4 changes when the system temperature increses and/or when confining pressure declines, we can treat certain elastic constants as variable and thereby use them as proxies for the changing thermodynamic conditions. Shear modulus is expected to serve as a good proxy for these purposes, since significant reduction of shear modulus results in an effective liquefaction of the medium. As discussed in the Appendices A and B, there are effectively four (possibly) distinct elastic constants associated with shear modes of the hexagonal system: $C_{44} = C_{55}$, C_{66}, G^v_{eff}, and G^r_{eff}. The formulas for G^v_{eff} and G^r_{eff} are (15) and (18), which show that they are *not* likely to be strong functions of changing thermodynamic conditions. However. changes in both C_{44} and C_{66} have similarly strong effects on the values of G_V and G_R in (14) and (17). Since the value of $C_{66} = (C_{11} - C_{12})/2$ is clearly tightly coupled to two other elastic constants, we will use only C_{44} as our proxy for changing thermodynamic conditions.

Examples of the results for effective C^*_{11} and G^* are displayed in the following two examples.

A. Examples based on measured elastic constant data for solid He^4

The first set of examples (Figures 3 and 4) makes use of data from experimental results of Crepeau *et al.*[23], Greywall and Munarin[24], and Greywall.[25] Figure 3 shows polycrystal results for effective value $C^*_{11} = K^* + 4G^*/3$. Figure 4 shows polycrystal results for effective overall shear modulus value G^*.

B. Examples based on elastic constant values for solid He^4 obtained using the SWF (shadow wave function) formalism

The second set of examples (Figures 5 and 6) makes use of simulated data obtained by Pessoa *et al.*[26] and Ardilla *et al.*[27] using the shadow wave function (SWF) formalism.[28,29] Figure 5 shows polycrystal results for effective value $C^*_{11} = K^* + 4G^*/3$. Figure 6 shows polycrystal results for effective overall shear modulus value $G.^*$

V. DISCUSSION OF RESULTS

A. 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 (13)-(14) and Reuss (16)-(17) bounds on both bulk (K) and shear (G) moduli can be viewed as establishing a rectangle in the two-dimensional space (K, G) (see Figures 1 and 2), since — if the point (K_R, G_R) falls at the lower left-hand corner of a rectangle — then the point (K_V, G_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 $(K_{SC}, G_{SC}) = (K^*, G^*)$ falls somewhere in the middle. But in general (*i.e.*, for arbitrary crystal symmetries) it seldom lies exactly at the center of this rectangle. However, we find for these hexagonal-symmetry-based polycrystals that the SC estimates do in fact tend to lie at the center of the rectangle formed by the Hashin-Shtrikman bounds. This rectangle is itself offset slightly from the center of the of Voigt-Reuss bounding rectangle. So the self-consistent values are not identical to the Voigt-Reuss-Hill arithmetic average, or to the comparable Voigt-Reuss geometric mean (GM) as shown in these same Figures. But at least for the cases considered here, the SC estimates fall essentially precisely in the middle of the Hashin-Shtrikman bounding box, which is a convenient simplification – and one known not to hold in general (specifically, it is definitely NOT true for general polycrystals formed from crystals having orthorhombic symmetry).

Furthermore, the center point of the VR rectangle is exactly the Hill estimator (G_{VRH}, K_{VRH}) based on the arithmetic means of the shear and bulk moduli, in all cases for any symmetry. But this point is only a rather crude estimate of the points of most interest – both of these Hill averages G_{VRH} and K_{VRH}, being typically too high in value (especially for the bulk modulus as seen in the present examples).

The next easiest point to compute is actually the self-consistent estimator (K^*, G^*). This point will also always fall within the Hashin-Shtrikman rectangle, which itself always falls within the Voigt-Reuss rectangle. But again, the HS rectangle does not necessarily fall exactly in the middle of the VR rectangle, and probably only does so when the crystals involved are nearly isotropic (for example, cubic symmetry is a case where such behavior might be observed). Virtually the same equations that determine these self-consistent estimators, also determine the Hashin-Shtrikman bounds on K and G. However, these equations for the HS-bounds actually may also be used to determine many effective constant estimates, depending on exactly what algorithm is used to explore the values within the Voigt-Reuss rectangle as already defined.

VI. SUMMARY AND CONCLUSIONS

Hexagonal symmetry for crystals forming solid He polycrystals lead to formulas that are particularly simple to compute. This fact makes the current results quite straightforward to analyze compared to the effort that might be required for systems (such as orthorhombic ones) having lower symmetry.

The analysis methods employed are also fairly well-known, since the main ideas used are based on the early work of Hashin and Shtrikman,[1] Peselnick and Meister,[2] Hill,[15] Gubernatis and Krumhansl,[7] Willis,[8] Watt and Peselnick,[3] Watt,[4] and others including Berryman,[9,10] and additional references in these last two papers.

Figures 3 and 4 for the first data set, and Figures 5 and 6 for the second data set illustrate the use of the methods presented here for hcp solid He^4 polycrystals as the shear constant $C_{44} = C_{55} \rightarrow 0$. This exercise provides a different and convenient means of estimating overall behavior of these systems as they soften due to changes in temperature (*i.e.*, increases) or pressure (*i.e.*, decreases).

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Appendix A: Simplified results needed for elastic materials having hexagonal symmetry

In earlier work the author has discussed the Peselnick and Meister[2] and the Watt and Peselnick[3] bounds for hexagonal, trigonal, tetragonal, and cubic symmetries. Note that some of these simplifications are important to apply to the hexagonal class of elastic symmetry under consideration here.

Parameters needed to optimize Hashin-Shtrikman bounds can be taken to be $K_\pm$ and $G_\pm$, where the ± symbols designate the best comparison material values respectively 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 HS bounds themselves will be labelled $K_{HS}^\pm$ and $G_{HS}^\pm$, 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[2] take the form:

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

and

$$G_{PM}^\pm = G_\pm + \frac{B_2^\pm}{1 + 2\beta_\pm B_2^\pm}. \tag{5}$$

The Hashin-Shtrikman bounds themselves are then given exactly by $K_{HS}^\pm \equiv K_{PM}^\pm$ and $G_{HS}^\pm \equiv G_{PM}^\pm$. 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 HS bounds and also in the self-consistency conditions are the quantities $4G_\pm/3$ and the combinations:

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

These quantities have been shown by Hill,[16] Willis,[8] and others (including Olson and Avellaneda[17]) to be important factors specifically for comparison materials having spherical shapes. Such spherical shapes are the ones typically assumed, whether explicited or implicitly, in such work on polycrystals. The source of these contributions can probably be most easily understood by considering Eshelby's work[30] 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.[8,16] If the comparison materials have other shapes, then other combinations[30,31] of constants can come into play, but the spherical shapes have been the only ones usually considered for studies to date involving polycrystals of *randomly oriented* anisotropic components.

Parameters $\alpha_\pm$ and $\beta_\pm$ that appear repeatedly in the PMW (Peselnick-Meister-Watt) works[2–4] can be related to the Eshelby[30] results by rewriting them in the form:

$$-\frac{1}{\alpha_\pm} = K_\pm + 4G_\pm/3 \tag{7}$$

and

$$-\frac{1}{2\beta_\pm} = G_\pm + \zeta_\pm. \tag{8}$$

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

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

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:

$$K_{PM}^\pm = \frac{K_V(G_{eff}^r + \zeta_\pm)}{G_{eff}^v + \zeta_\pm}, \tag{10}$$

which is valid for hexagonal (as well as tetragonal and 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[9] 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 (5), then we find that this result can be simplified to read:

$$\frac{1}{G^\pm_{PM}+\zeta_\pm} = \frac{1-B_2^\pm/(G_\pm+\zeta_\pm)}{G_\pm+\zeta_\pm}, \tag{11}$$

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

$$\frac{1}{G^\pm_{hex}+\zeta_\pm} = \frac{1}{5}\left[\frac{1-\alpha_\pm(K_V-K_\pm)}{G^v_{eff}+\zeta_\pm+\frac{\alpha_\pm}{2\beta_\pm}(K_V-K_\pm)} + \frac{2}{C_{44}+\zeta_\pm} + \frac{2}{C_{66}+\zeta_\pm}\right], \tag{12}$$

where $G^v_{eff} = (C_{11}+C_{33}-2C_{13}-C_{66})/3$.

APPENDIX B: Voigt and Reuss bounds and a product formula for elastic systems having 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 the effective bulk modulus of polycrystal systems composed of hexagonal crystals is well-known to be

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

Similarly, for the effective shear modulus we have

$$G_V = \frac{1}{5}\left(G^v_{\rm eff}+2C_{44}+2C_{66}\right), \tag{14}$$

where the new term appearing here is essentially defined by (14) [in terms of the traditional Voigt formula] and given explicitly by

$$G^v_{eff} = (C_{11}+C_{33}-2C_{13}-C_{66})/3. \tag{15}$$

The quantity $G^v_{\rm eff}$ is the energy per unit volume in a grain when a pure uniaxial shear *strain* of unit magnitude [*i.e.*, $(e_{11},e_{22},e_{33}) = (1,1,-2)/\sqrt{6}$], whose main compressive strain is applied to the grain along its axis of symmetry.[9]

The Reuss average for bulk modulus is determined by $1/K_R = 2(S_{11}+S_{12})+4S_{13}+S_{33}$, where the S_{ij}'s are compliances determined by taking the inverse of the stiffness matrix C_{ij}. The Reuss average can also be written as

$$\frac{1}{K_R-C_{13}} = \frac{1}{C_{11}-C_{66}-C_{13}} + \frac{1}{C_{33}-C_{13}} \tag{16}$$

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

$$G_R = \left[\frac{1}{5}\left(\frac{1}{G^r_{eff}} + \frac{2}{C_{44}} + \frac{2}{C_{66}}\right)\right]^{-1}, \tag{17}$$

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 [*i.e.*, $(\sigma_{11}, \sigma_{22}, \sigma_{33}) = (1, 1, -2)/\sqrt{6}$], whose main compressive pressure is applied to a grain along its axis of symmetry.

We use the following product formula as the formal definition of G^r_{eff}. For each grain having hexagonal symmetry, two product formulas hold (see Ref. 9):

$$3K_R G^v_{\text{eff}} = 3K_V G^r_{\text{eff}} = \omega_+\omega_-/2 = C_{33}(C_{11} - C_{66}) - C^2_{13}. \tag{18}$$

The symbols $\omega_\pm$ stand for the quasi-compressional and quasi-uniaxial-shear eigenvalues for the crystalline grains. Thus, $G^r_{eff} = K_R G^v_{eff}/K_V$ – which is a general formula that holds not only for hexagonal systems, but also for trigonal and tetragonal symmetries. We can therefore treat (14) and (17) [or their equivalents for other symmetries] as the fundamental defining equations for effective shear moduli G^v_{eff} and G^r_{eff}

APPENDIX C: Peselnick-Meister-Watt Bounds for Hexagonal Symmetry

Hashin-Shtrikman-style bounds[1] on the bulk and shear moduli of isotropic random polycrystals composed of hexagonal grains have been derived by Peselnick and Meister,[2] with later corrections by Watt and Peselnick.[3] Notation used is very similar to that in the original Hashin-Shtrikman paper on random polycrystals of grains having cubic symmetry.[1] We will use a slightly modified notation here, taking into account the product formulas (see Eq. (18) in Appendix B) in order to simplify the statement of the results. Derivations are found in the references, and therefore not repeated here.

Parameters needed 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 (±) 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:

$$K^\pm_{PM} = K_\pm + \frac{K_V - K_\pm}{1 + 2\beta_\pm(G_\pm - G^v_{\text{eff}})}, \tag{19}$$

and

$$G_{PM}^{\pm} = G_{\pm} + \frac{B_2^{\pm}}{1 + 2\beta_{\pm} B_2^{\pm}}, \tag{20}$$

where

$$\alpha_{\pm} = \frac{-1}{K_{\pm} + 4G_{\pm}/3}, \qquad \beta_{\pm} = \frac{2\alpha_{\pm}}{15} - \frac{1}{5G_{\pm}}, \qquad \gamma_{\pm} = \frac{1}{9}(\alpha_{\pm} - 3\beta_{\pm}). \tag{21}$$

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

For the case of hexagonal symmetry under consideration, we have

$$B_2^{\pm} = \frac{1}{5}\Big[\frac{G_{\text{eff}}^{v} - G_{\pm}}{\mathcal{D}_{\pm}} + \frac{2(C_{44} - G_{\pm})}{1 - 2\beta_{\pm}(C_{44} - G_{\pm})} + \frac{2(C_{66} - G_{\pm})}{1 - 2\beta_{\pm}(C_{66} - G_{\pm})}\Big], \tag{22}$$

with

$$\mathcal{D}_{\pm} = 1 - \beta_{\pm}(C_{11} + C_{12} + C_{33} - 3K_{\pm} - 2G_{\pm}) - 9\gamma_{\pm}(K_V - K_{\pm}). \tag{23}$$

Using the product formulas, (23) can be simplified to

$$\mathcal{D}_{\pm} = 1 - 2\beta_{\pm}(G_{\text{eff}}^{v} - G_{\pm}) - \alpha_{\pm}(K_V - K_{\pm}). \tag{24}$$

The comparison materials have definite values assigned to both $K_{\pm}$ and $G_{\pm}$. We have the general form:

$$K_{\pm} = \frac{K_V(G_{eff}^{r} - G_{\pm})}{(G_{eff}^{v} - G_{\pm})}. \tag{25}$$

The range of values of $G_{\pm}$ for hexagonal symmetry is given by

$$0 \leq G_{-} \leq \min(C_{44}, G_{eff}^{r}, C_{66}) \tag{26}$$

for the K_{-} formula. And, similarly, the K_{+} formula for hexagonal symmetry is determined by

$$\max(C_{44}, G_{eff}^{v}, C_{66}) \leq G_{+} \leq \infty. \tag{27}$$

When the values of C_{44}, G_{eff}^{r}, G_{eff}^{v}, and C_{66} are known, as they always are if all the crystal elastic constants are known, it is then straightforward to determine the $K_{\pm}$ values.

For example, note that, when $G_{-} = 0$, $K_{-} = K_R$, because $K_R = K_V G_{\text{eff}}^{r}/G_{\text{eff}}^{v}$ from the product formulas[9]. When $G_{+} \to \infty$, $K_{+} \to K_V$. Watt and Peselnick[3] performed searches in the appropriate parameter ranges as determined by (26) and (27). They found consistently that the optimum choices of the parameters were very close to the upper limits for the case of G_{-}, and also close to the lower limits for the case of G_{+}. The overall algorithm for determining the bounds can be greatly simplified if we are willing to accept slightly suboptimal values of the bounds (the results are still bounds, but not quite as tight as they could be). This approach is easily implemented in code by choosing to use the upper limits for G_- and the lower limits for G_+ themselves as our practical estimates of these bounding values. This approach is the one taken previously by the author.[9] For data with normal ranges of measurement uncertainty, this method is both appropriate, very practical, and the one used in all our examples here.

Peselnick and Meister[2] had originally obtained all the results for hexagonal symmetry, except for one additional condition that permits C_{44} to be replaced in some circumstances by G^r_{eff}. This new condition was the one added later by Watt and Peselnick.[3]

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TABLE 1. Elastic stiffness constants C_{ij} for hcp solid He^4. Crystal data from Crepeau *et al.*[23], Greywall and Munarin[24] and Greywall[25]. [Note that $C_{11} = C_{12} + 2C_{66}$ for hexagonal symmetry.] All constants are in units of MPa.

Solid He^4					
C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}
40.5	21.3	10.5	55.4	12.4	9.6

TABLE 2. Various estimates of the effective elastic stiffness constants of bulk modulus K and shear modulus G for polycrystalline hcp solid He^4. as computed using crystal data from Crepeau *et al.*[23], Greywall and Munarin[24], and Greywall[25]. Labels indicate Reuss average (R), Hashin-Shtrikman lower bound (HS$^-$), self-consistent estimate (SC), Hashin-Shtrikman upper bound (HS$^+$), Voigt-Reuss-Hill arithmetic average (VRH), geometric mean (GM), and Voigt average (V). All constants are in units of MPa.

Solid He^4			
K_R	24.527	G_R	12.59
K^-_{HS}	24.537	G^-_{HS}	13.08
K_{SC}	24.540	G_{SC}	13.21
K_{VRH}	24.541	G_{VRH}	13.19
K_{GM}	24.541	G_{GM}	13.18
K^+_{HS}	24.543	G^+_{HS}	13.34
K_V	24.556	G_V	13.79

TABLE 3. Elastic stiffness constants C_{ij} for hcp solid He^4, as computed using the shadow wave function (SWF) formalism as quoted by Pessoa *et al.*[26] and Ardilla *et al.*[27] [Note that $C_{11} = C_{12} + 2C_{66}$ for hexagonal symmetry.] All constants are in units of MPa. Quoted errors are ±0.8 MPa.

Solid He^4					
C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}
60.8	34.4	14.4	77.9	17.1	13.2

Table 4. Various estimates of the effective elastic stiffness constants of bulk mludlus K and shear modulus G for polycrystalline hcp solid He^4. as computed using the shadow wave function (SWF) formalism as quoted by Pessoa *et al.*[26] and Ardilla *et al.*[27] Labels indicate Reuss average (R), Hashin-Shtrikman lower bound (HS$^-$) self-consistent estimate (SC), Hashin-Shtrikman upper bound (HS$^+$), Voigt-Reuss-Hill arithmetic average (VRH), geometric mean (GM), and Voigt average (V). All constants are in units of MPa.

Solid He^4			
K_R	36.201	G_R	17.03
K_{HS}^-	36.205	G_{HS}^-	17.45
K_{SC}	36.206	G_{SC}	17.94
K_{VRH}	36.206	G_{VRH}	17.98
K_{GM}	36.206	G_{GM}	17.95
K_{HS}^+	36.207	G_{HS}^+	18.14
K_V	36.211	G_V	18.93

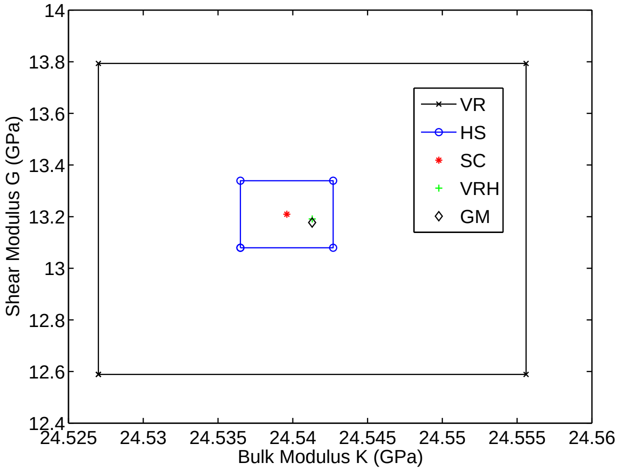

FIG. 1: Bulk and shear modulus bounds and estimates using solid He^4 crystal data from Crepeau *et al.*,[23] Greywall and Munarin,[24] and Greywall.[25]

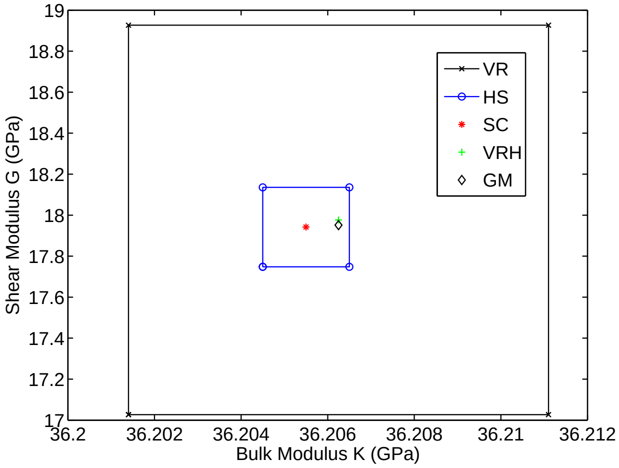

FIG. 2: Bulk and shear modulus bounds and estimates using solid He^4 simulation data from Pessoa *et al.*[26] and Ardila *et al.*[27]

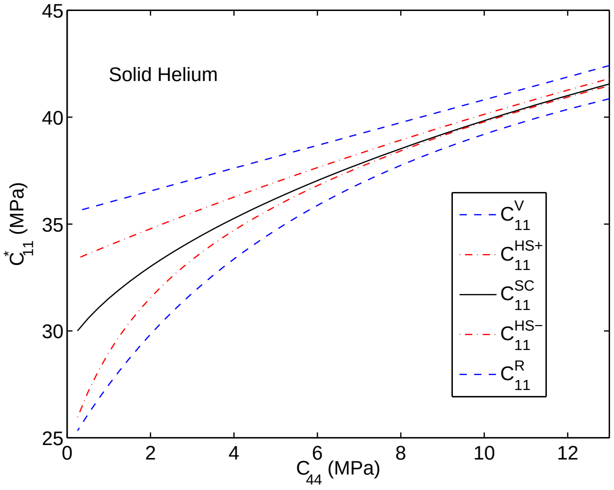

FIG. 3: Polycrystal effective $C^*_{11} = K^* + 4G^*/3$ for crystal data from Crepeau *et al.*,[23] Greywall and Munarin,[24] and Greywall.[25]

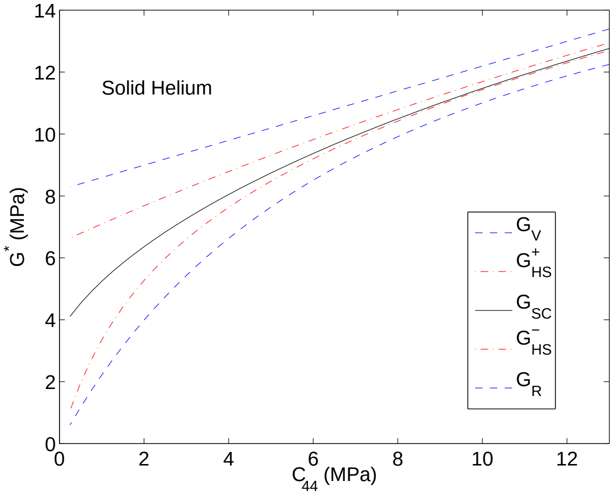

FIG. 4: Polycrystal effective shear modulus G^* for crystal data from Crepeau *et al.*,[23] Greywall and Munarin,[24] and Greywall.[25]

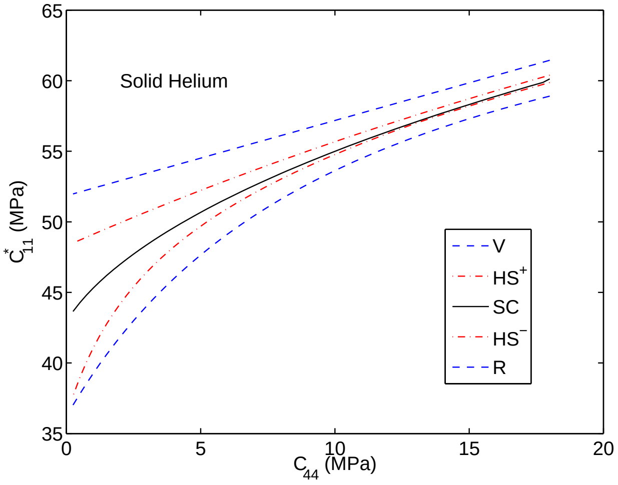

FIG. 5: Polycrystal effective $C^*_{11} = K^* + 4G^*/3$ for simulation data from Pessoa *et al.*[24] and Ardila *et al.*[25]

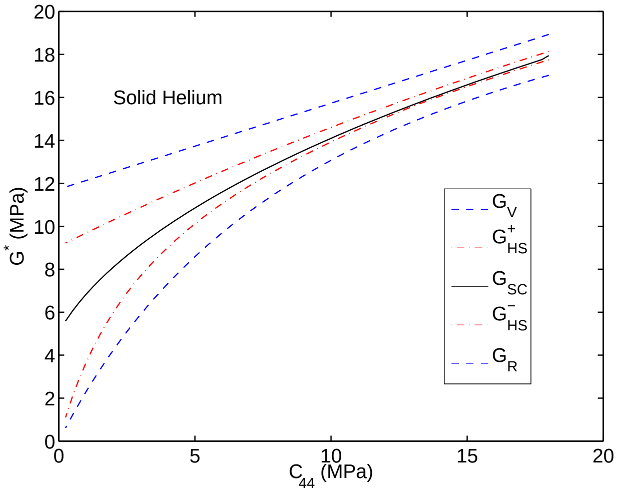

FIG. 6: Polycrystal effective shear modulus G^* for simulation data from Pessoa *et al.*[24] and Ardila *et al.*[25]