anisotropy factors $\alpha_1^{(3)}$, $\alpha_2^{(3)}$ and $\alpha_3^{(3)}$ are plotted versus $A^{(2)}$. It is apparent that the factors $\alpha_1^{(3)}$ and $(-\alpha_2^{(3)})$ have a pronounced tendency to be strongly positive for negative values of $A^{(2)}$, and to be weakly negative for positive values of $A^{(2)}$. On the other hand, the factor $\alpha_3^{(3)}$ tends to become more positive both with decreasing negative values and increasing positive values of $A^{(2)}$. The correlation between the anisotropy factors $\alpha_1^{(3)}$, $\alpha_2^{(3)}$ and $\alpha_3^{(3)}$, and $A^{(2)}$ can be approximately described by a functional dependence which is indicated by the dotted line in Fig. 2. Unfortunately, this functional relation between the anisotropy of the third- and second-order elastic constants is only of very limited usefulness. It is valuable for relating the relative spread between the Voigt and Reuss values of the TOE constants and thus the quality of the VRH approximation for the TOE constants to the anisotropy of the second-order elastic constants. It may not be taken, however, as a very indicative measure of the anisotropy of the TOE constants. The reason is that the anisotropy factors $\alpha_1^{(3)}$, $\alpha_2^{(3)}$, and $\alpha_3^{(3)}$ depend on the anisotropy factors $A_1^{(3)}$, $A_2^{(3)}$, $A_3^{(3)}$ of the TOE constants, and also on the anisotropy factor $A^{(2)}$ of the second-order elastic constants. It turns out that the dependence on $A^{(2)}$ is very strong and dominates the dependence on the other variables $A_1^{(3)}$, $A_2^{(3)}$ and $A_3^{(3)}$. In fact, for vanishing anisotropy of the second-order elastic constants the anisotropy factors $\alpha_1^{(3)}$, $\alpha_2^{(3)}$, and $\alpha_3^{(3)}$ vanish even if the single-crystal TOE constants are not isotropic. On the other hand the anisotropy factors, Eq. (33), are different from zero if $A^{(2)}\neq 0$, even if $A_1^{(3)}=A_2^{(3)}=A_3^{(3)}=0$. Thus the anisotropy factors $\alpha_1^{(3)}$, $\alpha_2^{(3)}$, $\alpha_3^{(3)}$ reflect the anisotropy of the crystal structure and of the interatomic forces in a manner which usually involves the second-order elastic constants more strongly than the TOE constants.

V. CONCLUSIONS

The approximations of Voigt, Reuss, and Hill for determining the elastic constants of polycrystals from the single-crystalline elastic constants have been extended to the third-order elastic constants. Numerical application to eleven cubic materials has been made, but due to lack of experimental data for these materials no experimental verification of the assumptions underlying the Voigt–Reuss–Hill approximation can be made. Still, the data presented are considered to be useful estimates of the polycrystalline TOE constants for these materials.

This will be especially useful for materials where the single-crystalline TOE constants can be measured more easily than the polycrystalline TOE constants, as for all materials that are difficult to be fabricated with high density sufficiently close to the value of the single crystal. In these cases ultrasonic attenuation due to voids and grain boundaries is generally too high to permit ultrasonic velocity measurements which are the basis for the most widely used technique to measure TOE constants.

Applications where polycrystalline TOE data are required range from geophysics through the nonlinear elasticity theory of crystalline defects to the theory of anharmonic physical properties. In geophysics the elastic and plastic behavior of polycrystalline matter under high hydrostatic and uniaxial compression is of relevance. In the nonlinear continuum theory of crystalline defects drastic simplifications are possible through assuming isotropy. In the theory of anharmonic properties directional averages over the third-order elastic constants or lattice theoretical coupling parameters are required. It seems well worth it to investigate the quality and usefulness of isotropic approximations which employ average values of the TOE elastic constants. The success of the approximate calculation of such harmonic properties as the Debye temperature from the VRH average of the second-order elastic constants[11] is very encouraging in this respect. Another interesting question is whether second harmonic generation in polycrystalline media can be accounted for in terms of the isotropic TOE constants.

APPENDIX 1: THE THIRD-ORDER ELASTIC COMPLIANCES

The nth-order elastic constants and compliances are according to the definition of Brugger given by[18]

$$C_{i_1j_1\cdots i_nj_n}=(\partial^n\Phi/\partial\eta_{i_1j_1}\cdots\partial\eta_{i_nj_n})_{\tilde{\eta}=0}, \quad \text{(A1.1a)}$$

$$S_{i_1j_1\cdots i_nj_n}=-(\partial^n\psi/\partial t_{i_1j_1}\cdots\partial t_{i_nj_n})_{\tilde{t}=0}, \quad \text{(A1.1b)}$$

with

$$\psi=\Phi-\eta_{ij}t_{ij}. \quad \text{(A1.2)}$$

For adiabatic deformations $\Phi=\rho_0U(S,\tilde{\eta})$ and $\psi=\rho_0H(S,\tilde{t})$ are the internal energy and the enthalpy per unit undeformed volume, respectively, if U and H denote the internal energy and the enthalpy per unit mass, respectively, and ρ_0 is the initial density. In this case all differentiations in Eq. (A1.1) have to be performed for constant entropy S. For isothermal deformations the free energy, $F(T,\tilde{\eta})$, and the Gibbs free energy, $G(T,\tilde{t})$, occur instead of the internal energy and the enthalpy, respectively, and the differentiations are for constant temperature T.

The Lagrangian strains, $\eta_{ij}=\eta_{ji}$, and the thermodynamic tensions $t_{ij}=t_{ji}$ are conjugate variables. They are defined by[18]

$$t_{ij}=(\partial\Phi/\partial\eta_{ij}) \quad \text{(A1.3a)}$$

$$\eta_{ij}=-(\partial\psi/\partial t_{ij}) \quad \text{(A1.3b)}$$

Differentiating Eq. (A1.3a) with respect to t_{kl} gives because of $t_{ij}=t_{ji}$ and inserting Eq. (A1.3b)

$$-(\partial^2\Phi/\partial\eta_{ij}\partial\eta_{pq})(\partial^2\psi/\partial t_{pq}\partial t_{kl})=\tfrac{1}{2}(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}). \quad \text{(A1.4)}$$

This equation holds for arbitrary values of $\tilde{\eta}$ or $\tilde{t}$. Taking

$\tilde{\eta}=\tilde{t}=0$ and inserting Eqs. (A1.1a) and (A1.1b) gives the relation between the second-order elastic constants and the second-order elastic compliances as given in Eq. (3) (without the superscript R).

Differentiating Eq. (A1.4) with respect to t_{mn} and inserting Eq. (A1.3b) gives

$$\left(\frac{\partial^3\Phi}{\partial\eta_{ij}\partial\eta_{pq}\partial\eta_{rs}}\right)\left(\frac{\partial^2\psi}{\partial t_{rs}\partial t_{mn}}\right)\left(\frac{\partial^2\psi}{\partial t_{pq}\partial t_{kl}}\right)$$

$$-\left(\frac{\partial^2\Phi}{\partial\eta_{ij}\partial\eta_{pq}}\right)\left(\frac{\partial^3\psi}{\partial t_{pq}\partial t_{kl}\partial t_{mn}}\right)=0. \quad \text{(A1.5)}$$

For $\tilde{\eta}=\tilde{t}=0$ this becomes in view of Eqs. (A1.1a) and (A1.1b):

$$C_{uvpqrs}S_{rsmn}S_{pqkl}=-C_{uvpq}S_{pqklmn}. \quad \text{(A1.6)}$$

Multiplication with S_{ijuv} and summation over u, v gives then in view of Eq. (3) the desired relation, Eq. (10), for the third-order elastic compliances in terms of the TOE constants.

APPENDIX 2: VOIGT AVERAGE OF THE FIRST KIND FOR THE TOE CONSTANTS

In order to calculate the Voigt average of the first kind of the TOE constants the single-crystalline TOE constants must be averaged over all orientations of the individual grains according to Eq. (7). For complete random orientation such linear averages can easily be calculated from the condition that the linear invariants of the two tensors representing the single crystal and the polycrystal must be equal. This method was first used by Leibfried[33] to calculate the Voigt average of the second-order elastic constants for cubic symmetry, and by Bross[22] to calculate the Voigt average of the first kind of the TOE constants, again for cubic symmetry.

For triclinic symmetry the three linear invariants of the TOE constant tensor are

$$J_1=C_{iikkmm}=A_1+3A_2+6c_{123}, \quad \text{(A2.1a)}$$

$$J_2=C_{iiklkl}=A_1+A_2+2A_3+2A_4, \quad \text{(A2.1b)}$$

$$J_3=C_{ijjlli}=A_1+3A_4+6c_{456}. \quad \text{(A2.1c)}$$

The constants A_1, A_2, A_3, A_4 are linear combinations of the TOE constants as shown in Eqs. (15a) to (15d). The invariants of the polycrystalline TOE constants corresponding to the Voigt average can be obtained from Eq. (19) for $n=3$ and isotropy ($M_3=3$) in connection with Eq. (21) and Eq. (23). The result is

$$J_1^V=3(9c_{123}^V+18c_{144}^V+8c_{456}^V), \quad \text{(A2.2a)}$$

$$J_2^V=3(3c_{123}^V+16c_{144}^V+16c_{456}^V), \quad \text{(A2.2b)}$$

$$J_3^V=3(c_{123}^V+12c_{144}^V+22c_{456}^V). \quad \text{(A2.2c)}$$

Equating the invariants, Eqs. (A2.1) and (A2.2), and solving for c_{123}^V, c_{144}^V, and c_{456}^V yields Eqs. (14a) to (14c).

[33] G. Leibfried, Z. Phys. **135**, 23 (1953).

APPENDIX 3: VOIGT AVERAGE OF THE SECOND KIND FOR THE TOE CONSTANTS

In order to evaluate the Voigt average of the second kind the constants occurring in the relation between the Cauchy stress tensor, σ_{ij}, and the deformation gradient tensor, $x_{i,j}$, must be averaged over all orientations. This relation is given by[17]

$$\sigma_{ij}=(\rho/\rho_0)x_{i,k}x_{j,l}t_{kl}, \quad \text{(A3.1)}$$

ρ and ρ_0 are the density in the deformed and in the undeformed state, respectively. Their ratio is given by[17]

$$\rho/\rho_0=F(\tilde{\eta})=(1+2I_1+4I_2+8I_3)^{-1/2}, \quad \text{(A3.2)}$$

where I_1, I_2, I_3 are the three invariants of the Lagrangian strain tensor[17]:

$$I_1=\eta_{ii}, \quad \text{(A3.3a)}$$

$$I_2=\tfrac{1}{2}(\eta_{ii}\eta_{jj}-\eta_{ij}\eta_{ij}), \quad \text{(A3.3b)}$$

$$I_3=\tfrac{1}{6}(\eta_{ii}\eta_{jj}\eta_{kk}-3\eta_{ij}\eta_{ij}\eta_{kk}+2\eta_{ij}\eta_{jk}\eta_{ki}). \quad \text{(A3.3c)}$$

The Lagrangian strain tensor is related to the deformation gradient tensor according to Eq. (6).

t_{kl} denotes the second Piola–Kirchhoff tensor which is identical with the thermodynamic tensions as defined in Eq. (A1.3a).

For deformations which do not contain rotations the deformation gradient tensor becomes symmetric, $x_{i,k}=x_{k,i}$. In this special case Eq. (6) may be inverted in the form of a Taylor series:

$$x_{i,j}=\delta_{i,j}+\eta_{ij}-\tfrac{1}{2}\eta_{ik}\eta_{kj}+\cdots \quad \text{(A3.4)}$$

In general the six components of the Cauchy stress tensor depend, according to Eq. (A3.1), on the nine components of the deformation gradient tensor. For the special case of pure deformations without rotations, however, the stress tensor can be expressed in terms of the Lagrangian strain tensor. This relation is obtained by inserting Eqs. (A3.4) and (A1.3a) into (A3.1) and using Eq. (5). The result is

$$\sigma_{ij}=F(\tilde{\eta})[C_{ijkl}\eta_{kl}+D_{ijklmn}\eta_{kl}\eta_{mn}+\cdots]. \quad \text{(A3.5)}$$

$F(\tilde{\eta})$ is according to Eq. (A3.2) a scalar function of the strain tensor. By using for the second-order elastic constants the representation, Eq. (19), the second-order expansion coefficients can be written as

$$D_{ijklmn}=c_{12}(E_{ijmn}{}^{(2)}\delta_{kl}+E_{ijkl}{}^{(2)}\delta_{mn})+2c_{44}E_{ijklmn}{}^{(3)}$$
$$+a[E_{imkl}{}^{(3)}\delta_{jn}+E_{mjkl}{}^{(3)}\delta_{im}+E_{ikmn}{}^{(3)}\delta_{jl}+E_{ilmn}{}^{(3)}\delta_{jn}$$
$$+E_{inkl}{}^{(3)}\delta_{jm}+E_{mjkl}{}^{(3)}\delta_{in}+E_{jkmn}{}^{(3)}\delta_{il}+E_{jlmn}{}^{(3)}\delta_{ik}]$$
$$+\tfrac{1}{2}C_{ijklmn}. \quad \text{(A3.6)}$$

Here $a=a_3{}^{(2)}=c_{11}-c_{12}-2c_{44}$ is the anisotropy factor of the second-order elastic constants. The coefficients