

# Manganese contributions to the elastic constants of face centred cubic Fe–Cr–Ni stainless steel

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We determined experimentally the effect of manganese on the elastic constants of face centred cubic Fe–Cr–Ni alloys with chemical compositions near 304-type stainless steel. By a pulse-echo-overlap method, longitudinal and transverse sound-wave velocities were determined in ten alloys containing up to 6% manganese. All the elastic stiffnesses decrease linearly with increasing manganese. The bulk modulus decreases most strongly. Poisson's ratio changes least. We consider what the elastic constants reveal concerning changes in chemical bonding, caused by manganese additions.

## 1. Introduction

Manganese decreases the elastic stiffness of bcc iron [1]. Studies of alloys containing up to 10 at% manganese show a linear decrease in both Young's modulus,  $E$ , and the shear modulus,  $G$ . The decrease amounts to approximately 0.3% per at% manganese. Vegard's law predicts a 0.06% decrease for  $G$  and a 0.65% decrease for the bulk modulus,  $B$ .

Effects of manganese on the elastic stiffness of fcc iron remain unknown. Manganese's peculiar elemental properties — a 58 atom unit cell, a bulk modulus 0.35 that of iron, anti-ferromagnetic electronic interactions, negative low-temperature thermal expansivity — preclude any reliable predictions of such effects. Despite the proximity of manganese and iron in the first long row of the periodic table of elements, their properties differ dramatically; manganese dissolved in iron may behave very differently from manganese dissolved in manganese. Iron's fcc elastic constants remain unknown. Here, we assume that they do not differ significantly from those of fcc nickel; because the atomic volume of iron exceeds that of nickel by 8%, fcc iron may be slightly softer elastically. From available elastic constants of

fcc nickel and  $\alpha$ -manganese, Vegard's law predicts that manganese lowers all the elastic stiffnesses and Poisson's ratio,  $\nu$ :  $B$  by 0.33%,  $E$  by 0.18%,  $G$  by 0.18%, and  $\nu$  by 0.16%.

Face centred cubic Fe–Cr–Ni alloys provide the basis for commercial stainless steels. Manganese also occurs in such steels, mainly to improve fabricability and weldability.

Effects of manganese on the elastic properties of Fe–Cr–Ni alloys remain undetermined. Such knowledge of basic mechanical–physical properties underlies any modelling of macroscopic mechanical properties such as strength and toughness.

The present study sought to determine how manganese affects the polycrystalline elastic constants of Fe–Cr–Ni alloys containing up to 6% manganese. Such results would test the conjecture [2] that these alloys should “show large changes in their elastic moduli as functions of composition”. Complete sets of polycrystalline elastic constants were determined: Young's modulus, shear modulus, bulk modulus, and Poisson's ratio. The experimental approach consisted of measuring longitudinal and transverse sound velocities using a pulse-echo-overlap method.

One may ask also whether manganese affects chemical bonding in Fe–Cr–Ni alloys. As described above, manganese is truly a maverick metallic element. In considering chemical bonding in both nonmetals and metals, Pauling [3] referred to “the anomalous Mn radius” and to the “striking abnormality in behaviour” of manganese. We know that elastic stiffness depends relatively sensitively on atomic radius,  $r$ , varying as  $r^{-4}$ . Thus, the larger atomic volume of manganese arising from magnetic repulsions explains in part its lower elastic stiffness.

## 2. Experimental details

### 2.1. Materials

All alloys are manganese-modified type-304LN face centred cubic stainless steels. Custom-composition alloys were obtained from a commercial steel company in the form of plates approximately 2.5 cm by 14 cm by 41 cm.

Each plate was hot rolled at approximately 1175° C (2150°F), annealed for 0.5 h at 1065° C (1950°F), water quenched, and acid pickled. Table I shows chemical composition, hardness, mass density, and grain size. Grain size was measured in the plane perpendicular to the transverse plate direction.

### 2.2. Methods

Sound velocities were determined by a method described in detail previously [4]. Briefly, 1.5 cm cubes were prepared by grinding so that opposite faces were flat and parallel within 5  $\mu$ m. Quartz piezoelectric crystals with fundamental resonances between 4 and 7 MHz were cemented with phenyl salicylate to the specimens. An  $x$ -cut transducer was used for longitudinal waves and an a.c.-cut for transverse waves. Ultrasonic

pulses 1 to 2 cycles long were launched into the specimen by electrically exciting the transducer. The pulses propagated through the specimen, reflected from the opposite face, and propagated back and forth. The pulse echoes were detected by the transducer and displayed on an oscilloscope equipped with a time delay and a micro-processor for time-interval measurements. The sound velocity was computed by

$$v = 2l/t \quad (1)$$

where  $l$  denotes specimen length, and  $t$  the round-trip transit time. On the oscilloscope,  $t$  was the time between adjacent echoes, the first and second echoes usually being measured, and within these the time between leading cycles. Elastic constants were computed from the general relationship

$$C = \rho v^2 \quad (2)$$

where  $\rho$  denotes mass density. The usual engineering elastic constants are related to the longitudinal and transverse sound velocities,  $v_l$  and  $v_t$ , by

$$\text{longitudinal modulus} = C_1 = \rho v_l^2 \quad (3)$$

$$\text{shear modulus} = G = \rho v_t^2 \quad (4)$$

$$\text{bulk modulus} = B = C_1 - (4/3)G \quad (5)$$

$$\text{Young's modulus} = E = 3GB/(C_1 - G) \quad (6)$$

$$\begin{aligned} \text{Poisson's ratio} = \nu &= (E/2G) - 1 \quad (7) \\ &= (1/2)(C_1 - 2G)/(C_1 - G) \end{aligned}$$

## 3. Results

For two alloys, Table II gives the variation of sound velocities and elastic constants with direction. In this table,  $n$  denotes propagation

TABLE I Chemical composition (wt%), hardness, grain size, and mass density

|    | Mn   | Cr    | Ni   | C     | N    | P     | S     | Si   | Mo   | Cu   | Hardness<br>(Rockwell B) | Grain<br>size<br>(ASTM No.) | Mass<br>density<br>(g cm <sup>-3</sup> ) |
|----|------|-------|------|-------|------|-------|-------|------|------|------|--------------------------|-----------------------------|--|
| 1  | 1.02 | 18.19 | 8.68 | 0.025 | 0.11 | 0.022 | 0.013 | 0.53 | 0.32 | 0.30 | 82                       | 5.4                         | 7.925                                    |
| 2  | 1.19 | 19.36 | 7.81 | 0.025 | 0.19 | 0.023 | 0.015 | 0.60 | 0.32 | 0.28 | 88                       | 5.5                         | 7.873                                    |
| 3  | 2.00 | 18.10 | 8.66 | 0.028 | 0.11 | 0.021 | 0.013 | 0.63 | 0.31 | 0.28 | 88                       | 5.5                         | 7.884                                    |
| 4  | 2.01 | 19.35 | 7.89 | 0.022 | 0.19 | 0.023 | 0.013 | 0.64 | 0.32 | 0.30 | 94                       | 5.5                         | 7.862                                    |
| 5  | 3.85 | 18.22 | 8.70 | 0.025 | 0.11 | 0.023 | 0.013 | 0.59 | 0.31 | 0.29 | 84                       | 5.8                         | 7.878                                    |
| 6  | 3.85 | 19.25 | 7.84 | 0.024 | 0.19 | 0.022 | 0.014 | 0.65 | 0.31 | 0.29 | 90                       | 5.6                         | 7.850                                    |
| 7  | 4.03 | 18.71 | 8.22 | 0.023 | 0.15 | 0.023 | 0.014 | 0.62 | 0.31 | 0.30 | 89                       | 5.6                         | 7.862                                    |
| 8  | 5.79 | 19.48 | 7.83 | 0.024 | 0.21 | 0.024 | 0.014 | 0.61 | 0.31 | 0.30 | 90                       | 5.6                         | 7.827                                    |
| 9  | 5.80 | 18.42 | 8.29 | 0.031 | 0.15 | 0.024 | 0.014 | 0.62 | 0.31 | 0.30 | 90                       | 5.6                         | 7.885                                    |
| 10 | 5.81 | 18.06 | 8.62 | 0.021 | 0.11 | 0.023 | 0.014 | 0.64 | 0.33 | 0.30 | 84                       | 5.4                         | 7.881                                    |

TABLE II Directional variation of sound velocities and elastic constants

| Alloy | <i>n</i> | <i>p</i> | Velocity<br>(cm μsec <sup>-1</sup> ) | <i>C</i> <sub>1</sub><br>(10 <sup>11</sup> N m <sup>-2</sup> ) | <i>G</i><br>(10 <sup>11</sup> N m <sup>-2</sup> ) |
|-------|----------|----------|--------------------------------------|--|---|
| 1     | 100      | 100      | 0.576                                | 2.631  | 0.780   |
|       |          | 010      | 0.314                                |  |   |
|       |          | 001      | 0.315                                |  |   |
|       | 010      | 010      | 0.576                                | 2.628  | 0.780   |
|       |          | 100      | 0.314                                |  |   |
|       |          | 001      | 0.315                                |  |   |
|       | 001      | 001      | 0.576                                | 2.622  | 0.785   |
|       |          | 100      | 0.314                                |  |   |
|       |          | 010      | 0.314                                |  |   |
| 10    | 100      | 100      | 0.572                                | 2.579  | 0.778   |
|       |          | 010      | 0.314                                |  |   |
|       |          | 001      | 0.314                                |  |   |
|       | 010      | 010      | 0.572                                | 2.580  | 0.773   |
|       |          | 100      | 0.313                                |  |   |
|       |          | 001      | 0.313                                |  |   |
|       | 010      | 001      | 0.572                                | 2.576  | 0.771   |
|       |          | 100      | 0.314                                |  |   |
|       |          | 010      | 0.313                                |  |   |

direction and *p* denotes polarization direction. Table III contains the principal results of the study: for ten alloys the longitudinal and transverse sound velocities, *v*<sub>1</sub> and *v*<sub>t</sub>, and the various elastic constants *C*<sub>1</sub>, *G*, *B*, *E*, *v* are defined in Equations 3 to 7. Fig. 1 shows these constants as a function of manganese concentration. Estimated uncertainties of measured elastic constants are 1% or less. Thus, the scatter shown in Fig. 1 does not arise from experimental error. Some of the scatter must arise from chromium and nickel variations among the alloys. Table IV contains the results of linear least-squares fits to these compositional changes. In this table, *a* and *b* have units of the elastic constants. The dimensionless ratio *b/a* gives the quantity (1/*y*)(*dy/dx*) at *x* = 0, the fractional change in the elastic constant due to alloying. Also included in Table IV are predicted values of *b/a* based on Vegard's

law and handbook elastic constants for nickel and manganese. (Elastic constants of fcc iron are not available.)

#### 4. Discussion

First, we consider the possibility of texture. Results in Table II indicate the absence of texture in these alloys. For alloy 10, for example, in three orthogonal directions (corresponding to the rolling direction, transverse direction, and through-thickness direction) the longitudinal modulus varies less than 0.1% and the shear modulus less than 0.4%. These results agree with those reported previously for 304 stainless steel [4]. In these alloys the Zener anisotropy ratio *A* = 2*C*<sub>44</sub>/(*C*<sub>11</sub> - *C*<sub>12</sub>) is approximately 3.5 [5], that is, moderately high. Thus, significant texture would evidence itself in the elastic constants. Recent calculations by Ledbetter [6]

TABLE III Sound velocities and elastic constants for ten manganese-alloyed stainless-steel-304-type alloys

| Alloy | Mn (%) | <i>v</i> <sub>1</sub><br>(cm μsec <sup>-1</sup> ) | <i>v</i> <sub>t</sub><br>(cm μsec <sup>-1</sup> ) | <i>C</i> <sub>1</sub><br>(10 <sup>11</sup> N m <sup>-2</sup> ) | <i>G</i><br>(10 <sup>11</sup> N m <sup>-2</sup> ) | <i>B</i><br>(10 <sup>11</sup> N m <sup>-2</sup> ) | <i>E</i><br>(10 <sup>11</sup> N m <sup>-2</sup> ) | <i>v</i> | <i>B/G</i> |
|-------|--------|---|---|--|---|---|---|----------|------------|
| 1     | 1.02   | 0.575   | 0.315   | 2.622  | 0.784   | 1.577   | 2.017   | 0.287    | 2.011      |
| 2     | 1.19   | 0.577   | 0.315   | 2.621  | 0.779   | 1.583   | 2.007   | 0.289    | 2.032      |
| 3     | 2.00   | 0.574   | 0.315   | 2.601  | 0.783   | 1.558   | 2.011   | 0.285    | 1.990      |
| 4     | 2.01   | 0.576   | 0.315   | 2.609  | 0.778   | 1.573   | 2.003   | 0.288    | 2.022      |
| 5     | 3.85   | 0.574   | 0.314   | 2.594  | 0.778   | 1.556   | 2.001   | 0.286    | 2.000      |
| 6     | 3.85   | 0.575   | 0.314   | 2.592  | 0.775   | 1.559   | 1.993   | 0.287    | 2.012      |
| 7     | 4.03   | 0.574   | 0.314   | 2.586  | 0.775   | 1.552   | 1.994   | 0.286    | 2.003      |
| 8     | 5.79   | 0.573   | 0.314   | 2.571  | 0.772   | 1.541   | 1.985   | 0.285    | 1.996      |
| 9     | 5.80   | 0.572   | 0.314   | 2.573  | 0.775   | 1.539   | 1.922   | 0.284    | 1.986      |
| 10    | 5.81   | 0.572   | 0.313   | 2.576  | 0.772   | 1.546   | 1.987   | 0.286    | 2.003      |

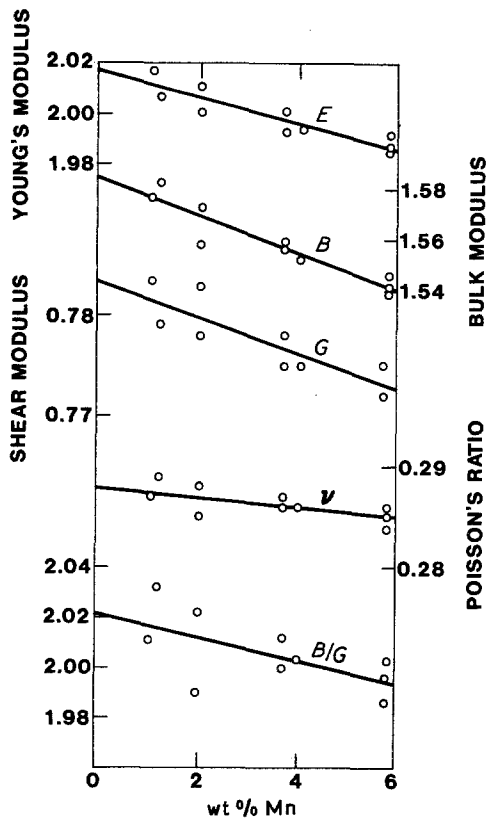


Figure 1 Compositional variation of elastic constants of Fe-Cr-Ni alloys containing manganese. Units on  $E$ ,  $B$ , and  $G$  are  $10^{11} \text{ N m}^{-2}$ ,  $\nu$  is dimensionless.

concerning the elastic constants of textured aggregates show that for 304 stainless steel along principal axes, fibre textures such as  $\langle 100 \rangle$ ,  $\langle 110 \rangle$ , and  $\langle 111 \rangle$  change  $C_1$  an average of 11% and  $G$  an average of 19%. These elastic constants can be measured readily within a fraction of a percent. We ascribe the lack of texture to the thermomechanical treatment: annealing after hot deformation, without recrystallization.

We consider now what the elastic constants reveal concerning changes in the chemical bond when manganese is alloyed substitutionally into the fcc Fe-Cr-Ni matrix. Essentially, we look for changes in the degree of covalent bonding, which manifests itself as a resistance to bond

bending, a manifestation of many-body forces. Köster and Franz [7] concluded that "Poisson's ratio depends to a much greater extent on the conditions of bonding than do the other elastic coefficients". This assertion remains without theoretical basis, probably because theory does not predict directly the Poisson ratio, which is the negative ratio of two fourth-rank elastic compliances,  $-S'_{ijj}/S'_{iii}$ , where primes denote rotation of the coordinate system.

For quasi-isotropic solids, Poisson's ratio is a scalar that relates simply to the bulk and shear moduli:

$$\begin{aligned} \nu &= (1/2)(3B - 2G)/(3B + G) \\ &= (1/2)(3y - 2)/(3y + 1) \end{aligned} \quad (8)$$

where  $y$  is defined to be  $B/G$ . Thus, the dependence of  $\nu$  can be studied parametrically as the dependence of  $y$ . For cubic elements, Leibfried and Breuer [8] give a graph of  $B/C_{44}$  against elastic anisotropy,  $C_{44}$  being one of the usual two cubic-crystal elastic shear moduli. They point out that purely longitudinal first-neighbour spring interactions require that  $B/C_{44} = 4/3$ . For Voigt averaging, the equivalent ratio for polycrystals is  $B/G = 5/3$ ; for Reuss averaging it is  $28/15$ ; thus, the Hill arithmetic average is  $B/G = 280/159 = 1.76$ . Departure from this ratio indicates that many-body forces occur in the solid. In terms of a force-constant model, this means that bond-bending forces must occur along with more familiar bond-stretching (bond-compressing) forces. One should note that from Equation 8 it follows that  $B/G$  is a more sensitive parameter than  $\nu$  because for typical  $\nu$  values  $d\nu/\nu \cong (1/2) dy/y$ .

Examination of Table III shows that  $B/G = 2.005 \pm 0.014$  for all ten alloys. Thus, the marked departure from a value of 1.76 shows that many-body forces occur in these alloys. That many-body forces exist in transition-metal alloys is already well known [9]. The surprising result is that the ratio is nearly constant for all alloys, indicating no significant change in the

TABLE IV Compositional variation of elastic constants based on  $y = a + bx$  type relationship

| $y$   | $a$   | $b$                    | $b/a$                  | $b/a$ (Vegard)         |
|-------|-------|------------------------|------------------------|------------------------|
| $G$   | 0.783 | $-1.77 \times 10^{-3}$ | $-2.26 \times 10^{-3}$ | $-1.79 \times 10^{-3}$ |
| $B$   | 1.585 | $-7.43 \times 10^{-3}$ | $-4.69 \times 10^{-3}$ | $-3.31 \times 10^{-3}$ |
| $E$   | 2.017 | $-5.20 \times 10^{-3}$ | $-2.58 \times 10^{-3}$ | $-1.75 \times 10^{-3}$ |
| $\nu$ | 0.288 | $-0.47 \times 10^{-3}$ | $-1.62 \times 10^{-3}$ | $-1.59 \times 10^{-3}$ |

character of the chemical bonding. Table III shows that the Poisson's ratio is also nearly invariant with manganese content:  $\nu = 0.286 \pm 0.001$ , but also different from the  $\nu = 0.261$  predicted for longitudinal-force-constant-only bonding. As described above,  $B/G$  and  $\nu$  must behave similarly. (The Appendix explores more fully the force-constant viewpoint.)

In terms of the single-crystal cubic-symmetry elastic constants  $C_{11}$ ,  $C_{12}$ , and  $C_{44}$ , this means that  $C_{12}/C_{11}$  must be nearly constant. This follows because the usual crystal-axis Poisson's ratio is

$$\nu = -\frac{S_{12}}{S_{11}} = \frac{C_{12}}{C_{11} + C_{12}} = \frac{y}{1 + y} \quad (9)$$

where  $y = C_{12}/C_{11}$ .

## 5. Conclusions

1. Alloying manganese into a stainless-steel-304-type Fe-Cr-Ni alloy decreases all the elastic stiffness constants.

2. The bulk modulus decreases most, reflecting the high compressibility of manganese atoms.

3. Poisson's ratio and the  $B/G$  ratio both vary slowly with manganese concentration. This indicates that manganese does not change the nature of the chemical bonding. The unusual bonding characteristics and magnetic properties of manganese lead one to expect possible changes.

4. By factoring into force constants, the relationship of many-body forces to elastic constants and bonding becomes more clear.

## Acknowledgements

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## Appendix: force-constant approach

One always profits from considering elastic constants in terms of force constants, which relate more directly to forces between pairs of atoms in solids. Many force-constant models exist [10]. For fcc lattices, Leibfried and Breuer ([8] p. 42) consider a three-force-constant model summarized in Fig. 2. The three parameters consist of a longitudinal spring,  $f_1$ , and two different transverse springs,  $f_2$  and  $f_3$ , corresponding to bending along  $[001]$  and  $[110]$ , respectively.

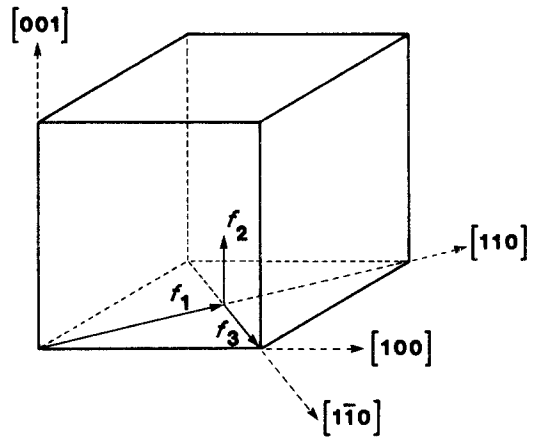


Figure 2 Face centred cubic unit cell showing eigenvectors and eigenvalues of the coupling matrices to the nearest-neighbour atoms at  $[\frac{1}{2}\frac{1}{2}0]$ -type positions.

The coupling matrix for this model is

$$-\phi_{ij}^{[100]} = \begin{bmatrix} \alpha & \beta & 0 \\ \beta & \alpha & 0 \\ 0 & 0 & \gamma \end{bmatrix} \quad (A1)$$

Physically,  $\phi_{ij}^{[d]}$  denotes the force in the  $i$  direction on the atom at the origin when the atom at  $d$  is displaced a unit length in direction  $j$ . If the displacement vector corresponds to an eigenvector, then  $-\phi_{ij}^{[d]}$  corresponds to a spring constant. By symmetry,  $\phi_{ij}^{[100]} = \phi_{ji}^{[100]}$  and  $\phi_{11}^{[100]} = \phi_{22}^{[100]}$ . Components such as  $\phi_{13}^{[100]}$  vanish because force and displacement are perpendicular, thus no coupling. Diagonalization of  $\phi_{ij}$  gives three eigenvalues:

$$f_1 = \alpha + \beta \quad (A2)$$

$$f_2 = \gamma \quad (A3)$$

$$f_3 = \alpha - \beta \quad (A4)$$

Leibfried and Breuer relate the  $f$ s to the six eigenvalues of the  $6 \times 6$  Voigt  $C_{ij}$  matrix:

$$f_1 = \frac{a}{24}(4C^1 + 2C^2 + 3C^4) \quad (A5)$$

$$f_2 = \frac{a}{12}(-C^1 - 2C^2 + 3C^4) \quad (A6)$$

$$f_3 = \frac{a}{8}(2C^2 - C^4) \quad (A7)$$

where  $a$  denotes cubic unit-cell size.

From the cubic-symmetry invariants,

$$C^1 = C_{11} + 2C_{12} \quad (A8)$$

$$\overset{2}{C} = \overset{3}{C} = C_{11} - C_{12} \quad (\text{A9})$$

$$\overset{4}{C} = \overset{5}{C} = \overset{6}{C} = 2C_{44} \quad (\text{A10})$$

the  $f$ s relate to the Voigt  $C_{ij}$ s:

$$f_1 = \frac{a}{4}(C_{11} + C_{12} + C_{44}) \quad (\text{A11})$$

$$f_2 = \frac{a}{4}(-C_{11} + 2C_{44}) \quad (\text{A12})$$

$$f_3 = \frac{a}{4}(C_{11} - C_{12} - C_{44}) \quad (\text{A13})$$

and vice versa:

$$C_{11} = \frac{1}{a}(2f_1 + 2f_3) \quad (\text{A14})$$

$$C_{12} = \frac{1}{a}(f_1 - 2f_2 - 3f_3) \quad (\text{A15})$$

$$C_{44} = \frac{1}{a}(f_1 + 2f_2 + f_3) \quad (\text{A16})$$

More interesting physical  $C_{ij}$  combinations are:

$$(C_{11} - C_{12}) = \frac{1}{a}(f_1 + 2f_2 + 5f_3) \quad (\text{A17})$$

$$(C_{11} + 2C_{12}) = \frac{1}{a}(4f_1 - 4f_2 - 4f_3) \quad (\text{A18})$$

$$(C_{12} - C_{44}) = \frac{1}{a}(-4f_2 - 4f_3) \quad (\text{A19})$$

$$A = 2C_{44}/(C_{11} - C_{12}) \\ = (2f_1 + 4f_2 + 2f_3)/(f_1 + 2f_2 + 5f_3) \quad (\text{A20})$$

$$(C_{11} - C_{12} - 2C_{44}) \\ = \frac{1}{a}(-f_1 - 2f_2 + 3f_3) \quad (\text{A21})$$

$C_{11} - C_{12}$  is the resistance to shear on a  $[110]$ -type plane in a  $[\bar{1}10]$ -type direction. Since this deformation involves both bond stretching (and shortening) and bond bending, not surprisingly it includes  $f_1, f_2$  and  $f_3$ .  $C_{11} + 2C_{12}$  is three times the bulk modulus (reciprocal compressibility). Since uniform dilatation changes bond lengths but not bond angles, it may seem surprising that  $B$  depends on  $f_2$  and  $f_3$  in addition to  $f_1$ . This occurs because the spring constants  $f_2$  and  $f_3$  relate also to many-body forces. (Recall that the third-order perturbation theory calculation of Axilrod and Teller [11] for interactions between triplets of atoms contained three interatomic distances -  $r_{12}, r_{23}, r_{13}$  - and three included

angles -  $\gamma_1, \gamma_2, \gamma_3$  - with  $\gamma_i$  being the angle between  $r_{ij}$  and  $r_{ik}$ .)  $C_{12} - C_{44}$  is the Cauchy (noncentral-force) discrepancy for cubic crystals. Thus, if accidentally  $f_2 = -f_3$ , then the material will appear to have central forces by the familiar Cauchy criterion  $C_{12} = C_{44}$ . Thus, this criterion is necessary but not sufficient. The Zener anisotropy ratio,  $A$ , depends on all three force constants. For vanishing many-body forces,  $A = 2$ . Thus, departures of  $A$  from this value also indicate the contribution of many-body forces. In summary, vanishing many-body forces imply that  $C_{11} = 2C_{12} = 2C_{44} = 4C'$ , where  $C' = \frac{1}{2}(C_{11} - C_{12})$ . Finally, elastic isotropy demands that  $C' = C_{44}$  or that  $C_{11} - C_{12} - 2C_{44} = 0$ . In terms of force constants, isotropy demands that  $f_1 = 3f_3 - 2f_2$ , a condition that arises only accidentally.

We now consider the polycrystalline case, which has two independent elastic constants. Following Stokes [12], we choose to consider  $B$  and  $G$ , the elastic constants that represent the two extreme types of deformation - pure dilatation (volume change without shape change) and pure shear (shape change without volume change). For aggregates of cubic crystallites, because the bulk modulus is a rotational invariant, it is

$$B = (C_{11} + 2C_{12})/3 \quad (\text{A22})$$

For the shear modulus, no unique averaging method exists. Many methods using different physical principles have been proposed [13]. A method due to Hershey [14], Kröner [15], and Eshelby [16] is used increasingly. For copper, Ledbetter [17] verified that this method agrees best with observation.

For simplicity, we use Voigt's averaging method here. Voigt [18] showed that when the aggregate has uniform elastic strain the shear modulus of cubic aggregates is

$$G_V = (C_{11} - C_{12} + 3C_{44})/5 \quad (\text{A23})$$

In terms of force constants:

$$G_V = \frac{4}{5a}(f_1 + 2f_2 + 2f_3) \quad (\text{A24})$$

The Reuss [19] shear modulus, based on constant stress in the aggregate, is

$$G_R = \frac{5}{2}C_{44}(C_{11} - C_{12})/[\frac{3}{2}(C_{11} - C_{12}) + 2C_{44}] \quad (\text{A25})$$

TABLE A1 For a typical metal, copper, and for stainless steel, relative contributions of three force constants to various constants

|                             | Copper |        |        | Stainless steel |        |
|-----------------------------|--------|--------|--------|-----------------|--------|
|                             | $f_1$  | $f_2$  | $f_3$  | $f_2$           | $f_3$  |
| $C_{11}$                    | 1.00   | 0.00   | -0.08  | 0.00            | -0.12  |
| $C_{12}$                    | 1.00   | 0.10   | 0.23   | -0.17           | 0.36   |
| $C_{44}$                    | 1.00   | -0.10  | -0.08  | 0.17            | -0.12  |
| $C'$                        | 1.00   | -0.10  | -0.38  | 0.17            | -0.59  |
| $B$                         | 1.00   | 0.05   | 0.08   | -0.09           | 0.12   |
| $C_{12} - C_{44}$           | 0.00   | -1.00  | -1.00  | -1.00           | -1.00  |
| $C_{11} - C_{12} - 2C_{44}$ | -1.00  | -0.10  | 0.23   | 0.17            | 0.36   |
| $A$                         | 1.00   | (0.0)* | (0.31) | (0.00)          | (0.47) |
| $C_{12}/C_{11}$             | 1.00   | (0.10) | (0.31) | (-0.17)         | (0.47) |

\*Parentheses indicate the approximation that both  $f_2/f_1$  and  $f_3/f_1$  are small relative to unity.

and must also depend on all three force constants.

Consider now a typical metal – copper, where  $C_{11} = 1.696$ ,  $C_{12} = 1.224$ , and  $C_{44} = 0.754 \times 10^{11} \text{ N m}^{-2}$ . Thus,  $f_1/a = 0.9185$ ,  $f_2/a = -0.0470$ , and  $f_3/a = -0.0705$  in the same units. Table A1 shows how the three force constants contribute to various elastic constants and to the elastic anisotropy,  $A$ . For both  $A$  and  $C_{12}/C_{11}$ , we made the very rough approximation that both  $f_2$  and  $f_3$  are small compared with  $f_1$ . Except for the Cauchy discrepancy,  $C_{12} - C_{44}$ ,  $f_1$  dominates every elastic constant. As expected, many-body effects show most strongly in  $C_{12} - C_{44}$ , but also strongly in  $C'$ ,  $A$ , and  $C_{12}/C_{11}$ . The bulk modulus is least sensitive to many-body terms. In all cases except  $C_{44}$  the  $f_2$  force constant contributes less than the  $f_3$  force constant; bending out of the (100) plane contributes less than bending in the plane. Negative  $f_2$  and  $f_3$  values apparently imply instabilities with respect to bending. But one must remember that the bending springs represent many-body, not two-body, interactions. Thus, they do not represent simple local effects but, rather, complicated “environmental”, long-range effects. Even if all springs are longitudinal and positive, a negative transverse spring can arise quite naturally.

Table A1 contains results also for fcc stainless steel. Principal differences are that  $f_2$  and  $f_3$  are approximately double those of copper with the sign on  $f_2$  being reversed. This means that the stainless steel elastic anisotropy is higher (higher negative  $f_3$ ). Except for thorium, and plutonium, all fcc elements exhibit a negative  $f_2$ . Implications of a positive  $f_2$  remain unclear. Because

both thorium and plutonium are relatively unstable in the fcc structure, a positive  $f_2$  may indicate a tendency toward structural instability.

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