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High-temperature elastic constants of gold single-crystals

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RICE UNIVERSITY

HIGH-TEMPERATURE ELASTIC CONSTANTS
OF GOLD SINGLE-CRYSTALS

by

STEPHEN MARTIN COLLARD

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE
DOCTOR OF PHILOSOPHY

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High-temperature Elastic Constants of Gold Single-crystals

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ABSTRACT

Non-linear deviations of Young's modulus (*modulus defects*) have been observed in many polycrystalline metals at elevated temperatures ($> 0.7 T_m$). As the quasi-harmonic theory of interatomic crystalline forces predicts a linear temperature dependence of elastic constants up to T_m , the observed modulus defect is thought to result from grain boundary effects. Comparison of polycrystalline modulus defects with single-crystal elastic constants at elevated temperatures should indicate if grain boundaries are involved in the modulus defect phenomenon.

Young's modulus measurements were made from $300 \leq T \leq 1275$ K on high purity polycrystalline gold wires using the thin-line ultrasonic pulse-echo method. The adiabatic elastic constants c_{ij}^S (c_{11} , c_{12} , c_{44}) were measured on two, high purity, gold single-crystals: (100) and (110) orientations. A modulus defect was observed for each of the c_{ij}^S at elevated temperatures. The c_{ij}^S were averaged according to Hill's arithmetic and geometric methods and the results compared to the measured polycrystalline Young's modulus. The modulus defect of the polycrystalline specimen was essentially identical to the averaged c_{ij}^S at elevated temperatures, indicating that the large modulus defect of gold is not due to grain boundary effects.

A modified quasi-harmonic model is proposed to account for the non-linear temperature dependence of the gold c_{ij}^S at elevated temperatures. The temperature dependence of the strictly harmonic terms due to thermal expansion are approximated using a Born-Mayer interatomic potential function and the temperature dependence of the atomic vibrational frequencies are included in the model by use of Grüneisen's approximation. The model suggested provides satisfactory agreement with measured c_{ij}^S at elevated temperatures.

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I. INTRODUCTION

A. ELASTICITY

The theory of elasticity is a broad science that involves many facets, including dynamics of continua, wave propagation, theory of structures, flow of viscous fluids, and energy principles. Elastic properties of solids are of great scientific and technological importance in fundamental theories of solid state physics, mechanics and thermodynamics, as well as (engineering) structural design. Love (1927/1944) presented the fundamentals of the modern theories of elasticity in his classic treatise *On the Mathematical Theory of Elasticity*. More modern references include Reismann and Pawlik's (1980) *Elasticity: Theory and Applications* and Weiner's (1983) *Statistical Mechanics of Elasticity*.

The elasticity of crystalline (anisotropic) structures, including metals, has been studied for many years. In 1940, Born described the stability of crystal lattices (Parts I and II). In 1946, Hearmon published the first part of a thorough two-part treatise on the elastic constants of anisotropic materials; the second part of which was not published until 1956. In 1948, Zener published a book entitled *Elasticity and Anelasticity of Metals*, a classic treatise with specific application to crystalline metals. In 1954, Born published *Dynamical Theory of Crystal Lattices*. In 1958, Huntington described the elastic constants of crystals in great detail. In 1961, Hearmon published *An Introduction to Applied Anisotropic Elasticity* which thoroughly covered the material of his earlier, two-part series. In 1961, Aleksandrov reviewed elastic properties of crystals, and in 1965, Zhdanov published a book entitled *Crystal Physics* which described most aspects of crystal elasticity. In 1969, Chung reviewed the elastic anisotropy of crystals, and in 1969, Hearmon published another book on elastic theory of solids *Physics of the Solid State*.

B. ELASTIC CONSTANTS

A description of the elastic properties of a material usually involves stating the values of *elastic constants*, which are proportionality constants in equations relating stress to strain under specified conditions. This was first described by Hooke (1678) as: $\sigma = c\epsilon$, where σ is the applied stress, ϵ is the resultant strain and c is the elastic *stiffness* constant. An alternate expression is: $\epsilon = s\sigma$, where $s \equiv 1/c$ is the elastic *compliance* constant. When the stress is removed, the atoms return to their original positions and the specimen assumes its original volume and shape.

Though Hooke's law states that stress is proportional to strain (for sufficiently small strains), it is frequently necessary to generalize the equation to take into account the known anisotropy in elastic behavior exhibited by three dimensional metal single-crystals and continua. In this case, the generalized form of Hooke's law becomes

$$\sigma_i = \sum_j c_{ij} \epsilon_j \quad \text{or} \quad \epsilon_i = \sum_j s_{ij} \sigma_j$$

where the units are in force/area. The first relation is usually stated more compactly using the notation $\sigma_i = c_{ij}\epsilon_j$, where the repeated ("dummy") index is summed. This form of Hooke's law is a fourth-order tensor with elastic constants as coefficients. When the tensor is written in the form "strain is proportional to stress", the coefficients are referred to as *compliances*. If written in the form "stress is proportional to strain", the coefficients are referred to as *stiffnesses*. Elastic stiffness is markedly different than elastic compliance: c_{ij} is not the simple reciprocal of s_{ij} , but rather the six-by-six matrix of elastic stiffnesses is reciprocal to the six-by-six elastic compliance matrix. There is no simple physical relation between compliance and stiffness. Though elastic compliances have been

experimentally measured, the elastic stiffness provides information that is of much greater use theoretically than elastic compliance.

The conditions for selecting elastic constants are such that the minimum number of constants necessary to describe the elastic behavior of the material are chosen, independent of the configuration or type of deformation (Armstrong, 1971). Application of symmetry conditions reduces the number of independent elastic constants from 21 (the most general case) to 2 for a perfectly elastic, isotropic, linear solid — one involving dilatational deformation and the other involving shear deformation (Love, 1927). Polycrystalline metals (aggregates) of randomly-oriented single-crystals (grains) are usually considered isotropic (Armstrong, 1971). The elastic resistance of isotropic materials is usually given in terms of Young's modulus (E_Y), shear modulus (or modulus of rigidity, G) and bulk modulus (B).

Three elastic constants are required for cubic crystals, five for hexagonal crystals, and six for tetragonal. It is customary to express the elastic properties of metal crystals having cubic symmetry in terms of the three independent coefficients of the appropriate tensor, i.e. c_{ij} (c_{11} , c_{12} and c_{44}). These elastic constants are *second-order*, and thus only applicable for very low strains. Higher (third or fourth) order terms may also be introduced into the stress-strain relations, resulting in third- or fourth-order elastic constants. Anelastic behavior complicates the stress-strain relationship at higher strains, where "strain is not a single-valued function of stress" (Zener, 1948). This becomes a concern when dynamic elastic constants/moduli vary with the frequency of the acoustic waves used for measurement.

The stress-strain relationships for metals are not perfectly linear, even for very low strains, and become progressively more non-linear as the strain increases. The macroscopic strain seldom exceeds a value greater than about 1.0% before

plastic deformation and fracture occur (Silvertsen, 1964).

C. RELATION BETWEEN ELASTIC CONSTANTS AND PROPERTIES

1. Investigations

It is difficult to describe a change in state or structure of metals that does not have an effect on the elastic constants. For this reason, measurement of elastic constants provides a mechanism for studying many physical and thermodynamic aspects of materials, and investigators have done so for many years.

Zener (1949) described the relation between residual strain energy and elastic moduli. Lazarus (1949) reported the variation of adiabatic elastic constants of KCl, NaCl, CuZn, Cu and Al with pressure to 10,000 bars. Dienes (1952) proposed a theoretical estimate of the effect of radiation on elastic constants of simple metals. Rayne (1958 and 1959) studied the variation of α -brass elastic constants with solute concentration at and below room temperature. Schmunk (1959) reported the pressure derivatives of the elastic constants of aluminum and magnesium. Folweiler and Brotzen (1959) examined the effect of quenched-in vacancies on the elastic modulus of aluminum. Alers *et al.* (1960) reported the temperature dependent magnetic contributions to the high field elastic constants of Ni and Fe-Ni alloys. Lytton (1964) investigated the influence of ferromagnetic elastic modulus relaxation on determination of magnetic specific heats. Hinton and Green (1966) compiled the modes of elastic wave propagation and the orientation dependence of dislocation damping in aluminum. Golding *et al.* (1967) studied the composition and pressure dependence of the elastic constants of Au-Ni alloys. Henneke and Green (1968) compiled the modes of elastic wave propagation and the orientation dependence of dislocation damping in copper. Benedek and Nardelli (1968) studied bulk and local elastic constants of imperfect crystals. Johnson (1972) evaluated the relationship

between two-body interatomic potentials in a lattice model and elastic constants. Dederichs *et al.* (1975) studied the effect of interstitials on elastic constants. Arnoult and McLellan (1975) measured the variation in Young's modulus of austenite with carbon concentration. Soma *et al.* (1981) evaluated the elastic constants of noble metals under pressure. Jankowski and Tsakalakos (1985) reported the effects of strain on the elastic constants of noble metals. Ledbetter and Austin (1985) reported the effects of carbon and nitrogen on the elastic constants of stainless steel.

2. Interatomic Potentials and Elastic Constants

The elastic constants are closely related to *interatomic potentials*, which are functions of the interatomic energy versus interatomic distance relationship, evaluated at the equilibrium atom spacing of the solid. Interatomic potentials are typically calculated by computing the electronic energy as a function of small displacements of the atoms. The elastic and structural properties of ideal metal crystals at low temperatures depend on the energy of the ideal structure and the way the energy changes as the ideal crystal is subject to homogeneous strains. In defect calculations at constant volume, the structural dependent part of the total energy is described using pair-wise (atom-atom) interactions, with the hope that by suitably characterizing these potentials the volume dependent contribution can be accounted for by the pairwise interaction (de Hosson, 1981).

Metals consist of a lattice of positive ions in a background "continuum" of conductive electrons. Because the electrons tend to screen the positive ions, the charge density in the metal is not completely uniform. Ions influence their neighbors indirectly by the redistribution in electron charge they produce. The sum of these ion-electron-ion contributions results in a volume-dependent contribution to the lattice energy.

There are two types of interactions (forces) between atoms in a crystal: attraction and repulsion. Mie (1903) introduced an assumption that both forces are proportional to a power of reciprocal distance between ion cores:

$$\phi = -\frac{\alpha}{r^m} + \frac{\beta}{r^n}$$

where α and β are constants for the attractive and repulsive energy. At the equilibrium position, $n > m$. The total energy of a crystal $U(r)$ is obtained by summing over all two-body atom-atom interaction energies $\phi(r_{ij})$:

$$U(r) = \frac{1}{2} \sum_i \sum_{j \neq i} \phi(r_{ij})$$

where r_{ij} indicates the separation between atoms i and j (Ledbetter, 1989).

Grüneisen (1912, 1926) extended the Mie potential to solid-state physical properties and Fürth (1944) provided estimates of the two coefficients m and n . Combining the expressions for $\phi(r)$ and $U(r)$ results in

$$U(r) = -Ar^{-m} + Dr^{-n}$$

In general, elastic constants will be functions of the distribution of atoms in a crystal. Clustering of solute atoms, variations in short-range order and the onset of long-range order affect the elastic constants. Such changes in order and spontaneous magnetization can change the interatomic energy versus distance relations, and thus the interatomic potentials and lattice spacings (Silversten, 1964).

The elastic behavior of real crystals is also complicated by crystal imperfections such as vacancies, interstitials and dislocations. Interatomic spacings and the crystal relationships will no longer be that of a perfect crystal. Atoms no longer reside on the average crystal lattice sites defined by the Bragg reflections, partly because of atom size incongruities. There will be a heterogeneous distribution of lattice vectors joining pairs of neighboring atoms so the presence of vacancies, solute atoms, and other imperfections can cause measurably significant changes in the elastic constants (Silvertsen, 1964).

The coupling of the reversible elastic behavior with anelastic phenomena contributes nonelastic strains that result in observed values of the elastic constants that are less than the true values. Some of the well-known processes contributing to the anelasticity of metals are the stress-induced ordering of atoms in alloys, magnetostriction, reversible dislocation motion, and diffusion jumps. The observed elastic constants resulting from the combination of true elastic behavior with anelastic behavior is given by (Silvertsen, 1964)

$$M = \frac{\sigma}{\epsilon} \rightarrow M_{\text{obs}} = \frac{\sigma}{\sum_i \epsilon_i}$$

where $\sum_i \epsilon_i$ is the total strain due to all sources. Measurement of elastic constants provides a reliable method to study these phenomena.

In an excellent review, de Hosson (1981) described the significance of interatomic potentials in materials studies. He summarized the ideas and problems with the basic interatomic potential functions that have been proposed, with particular emphasis on metals. He reviewed the empirical, semi-empirical, pseudopotential approach, tight binding approximation, method of moments and *ab-initio* pair potentials calculated using the self-consistent augmented-spherical

wave method. His paper focused on the intrinsic merit of the various potential functions and the validity of the results obtained using pair-wise interaction functions. Portions of his review are included here with slight alteration.

3. Empirical Interatomic Potentials

These interatomic potentials are justified only by comparison with experimental data. The functional form of these potentials is free, which allows a reasonable function to be fitted to a greater number of parameters than the semi-empirical potentials. The most commonly used empirical potentials are the Johnson-I (Johnson, 1964), for *bcc* metals; and the Johnson-II (Johnson, 1966, 1972), for *fcc* metals.

The Johnson-I potential was developed for α -Fe and describes the short-range ionic interactions. The inclusion of only the nearest and next nearest neighbor interactions is in accord with dividing the elastic constants into long-range and short-range contributions. The short-range elastic constants, $(c_{ij})_{\text{SR}}$, for a *bcc* lattice can be related to the first and second derivatives of the spherically symmetric potentials $\phi(r)$ at the first (subscript 1) and second (subscript 2) neighbor equilibrium sites as:

$$(c_{11} - c_{12})_{\text{SR}} = \frac{2}{3r_2} \left[\left[\frac{6}{r_1} \phi_1' \right] + (3 \phi_2'') + \left[\frac{3}{r_2} \phi_2' \right] \right]$$

$$(c_{44})_{\text{SR}} = \frac{2}{3r_2} \left[(\phi_1'') + \left[\frac{2}{r_1} \phi_1' \right] + \left[\frac{3}{r_2} \phi_2' \right] \right]$$

$$(B)_{\text{SR}} = \frac{2}{3r_2} \left[(\phi_1'') - \left[\frac{2}{r_1} \phi_1' \right] + (\phi_2'') - \left[\frac{2}{r_2} \phi_2' \right] \right]$$

The right hand side of these equations was fitted to the short-range elastic constants. Johnson corrected the known elastic constants for the long-range electron contributions using analytical expressions derived by Fuchs (1936) from a theory based on the free electron model. The short-range elastic constants used in construction of the Johnson-I potential satisfy the Cauchy relations for a cubic crystal, $c_{12} = c_{44}$, and is therefore a central force equilibrium potential. Thus, the perfect Fe lattice is in equilibrium without external constraints at the correct lattice spacing.

Johnson (1966) pointed out that since the cohesive energy was not fitted to his interaction function, formation energies calculated would be questionable because they are sensitive to the cut-off distance chosen. In fact, the Johnson-I potential yields very reasonable absolute vacancy- and interstitial-formation energies. Thus, the short-range potential based on elastic properties can give reasonable agreement with other properties. With such an empirical approach, it might be questionable whether the effects arising from electronic contributions should be subtracted. In view of this, the Johnson-II potential was constructed (for γ -Fe) by fitting the right-hand side of the Johnson-I potential equations to the **total elastic constants**. In contrast with potential I, potential II will not hold the Fe lattice at its equilibrium spacing. The total elastic moduli violate the Cauchy relations and an external constraint must be applied to maintain the lattice in equilibrium at the correct lattice spacing. This implicit external pressure now represents the volume-dependent part of the total lattice energy. In practice, there is very little difference between the two potentials for α -Fe.

The use of a central nearest-neighbor interaction in a *fcc* lattice leads to the following relations (Johnson-II)

$$\phi_1' = -\frac{r_1^2}{2\sqrt{2}}(c_{44} - c')$$

$$\phi_1'' = -\frac{r_1}{2\sqrt{2}}(7c_{44} - 3c')$$

$$3B = 9c_{44} - 5c'$$

where $c' = (c_{11} - c_{12})/2$. The α -Fe interatomic potential (Johnson-I) was used together with the lattice constant of γ -Fe to predict the elastic constants c_{ij} . The same was done for Ni. In both cases the agreement was good. Though the potentials were not fitted to the phonon dispersion data, the potentials yield the dispersion curves in good agreement with observation (de Hosson, 1981).

Johnson and Wilson (1972) suggested the use of *noncentral* interactions in the construction of *fcc* potentials for defect calculations, such as

$$\Psi(r) = \alpha(r) + \left(\beta(r) \times f(\theta, \phi) \right)$$

where $f(\theta, \phi)$ is the cubic harmonic, given by:

$$f(\theta, \phi) = \frac{x^4 + y^4 + z^4}{r^4} - \frac{3}{5}$$

One of the reasons a noncentral potential was suggested is that the elastic constants of many *fcc* metals cannot be fitted with a first neighbor central potential, independent of its form. Gold has a relatively large bulk modulus, but relatively

small shear constants. This situation is not easily approximated with short-ranged two-body central forces. When more neighbors are included in the interaction function, more parameters are introduced. Although the elastic constants can be matched, the potential requires some "rather severe wiggles" between the lattice distances. Equations similar to those from the central potential can be derived. The noncentral terms do not enter into the equation for the bulk modulus, but do affect the shear components $(c_{11} - c_{12})/2$ and c_{44} (de Hosson, 1981).

The potentials resulting from noncentral interactions are similar in form to central potentials in any given direction, but they vary in depth as a function of direction. For gold, the effect is to deepen the potential in the $\langle 111 \rangle$ directions and to make it more shallow in the $\langle 100 \rangle$ directions compared to the $\langle 110 \rangle$ directions. Baskes and Melius (1979) reported long-range pair potentials for the *fcc* metals Ni, Au, Ag, Pt, Pd, Cu and Al. Experimental data considered include the sublimation energies and stacking fault energies, as well as the elastic constants, the lattice parameters and vacancy-formation and migration energies. The major difference with the earlier proposed potentials is that they are consistent with experimental data (including stacking fault and sublimation energies), and also take into account the volume-dependent energy term, E_V . The specific volume-dependent term used is:

$$E_V = \Omega_0 \left[\frac{V}{V_0} \right] \left[p_0 + \frac{1}{2} p_2 \left[\frac{\Delta V}{V_0} \right]^2 \right]$$

where $\Delta V = V - V_0$ is the volume change due to deformation, Ω_0 is the undeformed atomic volume, and p_0 and p_2 are constants. This equation is actually based on the general form for the volume-dependent term proposed by Johnson (1972). The volume-dependent terms are added to Johnson-II and the potentials are calculated

by a variation of the parameters so that the various calculated quantities agree with the corresponding experimental data (de Hosson, 1981).

4. Semi-empirical Interatomic Potentials (Morse and Born-Mayer)

With semi-empirical potentials, the functional form of the potential is given and the appropriate coefficients are determined by matching various physical results. If $\phi(r)$ is the energy of interaction of two atoms a distance r apart, for $\phi(r)$ to represent the interatomic potential of two atoms in a stable crystal it must satisfy the conditions (Girifalco and Weizer, 1959): (1) the force $-\delta\phi/\delta r$ must be attractive at large r and repulsive at small r , so that $\phi(r)$ must have a minimum at some separation $r = r_e$, and (2) the magnitude of ϕ must decrease more rapidly with r than with r^{-3} . These two conditions arise from the existence of condensed phases and from the requirement that the cohesive energy is finite. Born (1940) formulated two additional requirements: (3) all elastic constants c_{ij} are positive and (4) $c_{11} - c_{12} > 0$ (de Hosson, 1981).

The Morse (1929) potential fulfills these conditions, and is given by

$$\phi(r_{ij}) = \phi_0 \left[\exp\left[-2\alpha(r_{ij} - r_e)\right] - 2\exp\left[-\alpha(r_{ij} - r_e)\right] \right]$$

where α and ϕ_0 are constants with dimensions of reciprocal distance and energy, respectively, and r_e is the equilibrium distance of approach for two atoms. Actually, ϕ_0 is equal to the dissociation energy. The energy of any atom in the crystal is then E_i , given by

$$E_i = \sum_{j=1}^N \phi(r_{ij})$$

where N is the number of atoms in the sphere of influence and is related by a geometrical factor to the distance over which the interaction extends. The values of the constants ϕ_0 and r_e depend on N . If N is taken to be equal to 12 in an *fcc* structure, r_e would be equal to the nearest neighbor distance. Girifalco and Weizer (1959) derived constants for the Morse potential for several metals. Cotterill and Doyama (1967) and Doyama and Cotterill (1967) used the Morse potential for the first calculations of atomic configurations of screw and edge dislocations in *fcc* metals. The advantage of semi-empirical potentials is that they are of the long-range type and as a consequence the lattice sum consists of a large number of terms. Some truncation is nonetheless required to avoid excessive computations (de Hosson, 1981).

The Born–Mayer (1932) repulsion is equivalent to the first term in the Morse potential and has been successfully used for calculating lattice energies of ionic crystals (de Hosson, 1981).

D. AVERAGING ELASTIC CONSTANTS

The elastic modulus may vary widely for a polycrystalline material, depending on the preferred orientation texture present. Most materials are strongly anisotropic, and single crystals have different elastic constants in different directions. Tungsten is one of the few elements that is crystallographically isotropic within about 1% over a large temperature range (Featherston and Neighbors, 1963; Armstrong and Brown, 1964). The difficulty of preparing completely random polycrystalline specimens has prompted investigators to develop methods of averaging single-crystal elastic constants to predict appropriate isotropic (polycrystalline) elastic constants. Additionally, averaging single-crystal elastic constants provides a better understanding of the polycrystalline aggregate

stress-strain states.

Methods of engineering mechanics have permitted the calculation of elastic constants of random polycrystalline aggregates from the single-crystal elastic constants. However, despite much effort on this seemingly simple problem, no final "best" solution exists. Hill (1952), Markham (1962), Kröner (1967), Hearmon (1969), Ledbetter (1974, 1980, 1981 and 1990), Watt *et al.* (1976) and Hashin (1983) have thoroughly reviewed this subject. Anderson (1965) reviewed the many applications of averaged single-crystal elastic constants. The review by Ledbetter (1990) is particularly thorough and current, and portions are included here with slight alteration.

All the averaging methods share common assumptions: (1) small grain-to-specimen sizes, (2) absence of voids and inhomogeneities, (3) cohesion of crystallites occurs through very thin grain-boundary regions that are deformed relative to the crystal interiors, (4) randomly oriented grains and (5) grains large enough so that interfaces remain unimportant. These assumptions apply fairly well to most polycrystalline aggregates (Ledbetter, 1990).

Voigt (1898, 1928) proposed a method that assumes a uniform strain during elastic deformation of a polycrystalline aggregate. Continuity of displacement at the grain-boundary would exist under such an assumption, whereas the stress would vary from grain to grain and additional forces are necessary at grain-boundaries to maintain equilibrium. Voigt's predicted result is higher than the experimental value. Voigt's averaging method remained unquestioned until Reuss (1929) proposed a method that assumes a uniform stress during elastic deformation of a polycrystalline aggregate. In this case, the strain will vary from grain to grain, with the result that the condition for continuity of displacement at the grain boundaries is not fulfilled (Sherby, 1967). Reuss' method predicts a lower modulus than that predicted by

Voigt and is generally lower than the experimentally observed modulus.

The *Huber–Schmid–Boas* method was developed in the mid–1930's by Huber and Schmid (1934), Boas and Schmid (1934) and Boas (1934 and 1935). In 1947, Boas briefly described the method in English. This method makes two additional assumptions: (1) individual crystallites behave completely independently of neighboring crystallites (i.e. crystallites respond only to external macroscopic forces) and (2) the averaging problem proceeds independently of macroscopic specimen geometry. Like Reuss' method, the Huber–Schmid–Boas method assumes constant stress.

Hill (1952) pointed out that the Huber–Schmid–Boas method amounts to assuming that within each crystallite, the stress is pure tension or pure torsion acting along a direction fixed with respect to the specimen axis. One defines a general modulus for that direction and averages that modulus over all possible crystal orientations. Hill's thermodynamic strain–energy study (1952) established that the Voigt (G_V) and Reuss (G_R) methods are first–order bounds on the shear modulus (zeroth–order bounds are c_{44} and $(c_{11} - c_{12})/2$), so that $G_R \leq G \leq G_V$. Hill recommended using either the arithmetic (G_{VRH-a}) or geometric (G_{VRH-g}) mean of the Voigt and Reuss averages.

In 1958, Kröner combined the ideas developed by Eshelby (1957) and the concept of elastic polarizability to consider the averaging of single–crystal elastic constants from the viewpoint of a "self–consistent elastic–inclusion model." He obtained a quartic–cubic equation which was later rewritten by Gairola and Kröner (1981) in a form that is solved iteratively. Because of the equivalence of Kröner's result with one obtained by Hershey (1954), this averaging method is referred to as *Hershey–Kröner–Eshelby*.

Hashin and Shtrikman (1962) proposed methods of predicting upper and lower

bounds for the effective elastic moduli of multiphase materials of arbitrary phase geometry, based on variational principles in the linear theory of elasticity. Their method improved the upper and lower bounds of Voigt and Reuss. In 1976, Kröner and Koch derived improved third-order bounds using variational principles. Cubic symmetry bounds of arbitrarily high order can be calculated using the Gairola–Kröner method (1981), though higher order bounds are unnecessary for most materials for practical purposes.

In 1953, Leibfried noted that one of the two linear invariants $(3(c_{11} + 2c_{44}))$, which leads to the sum of the three ρv^2 values (explained later) produces different results for G : $(c_{11} + 2c_{44})$ gives the Voigt result while $(s_{11} + 2s_{44})$ gives the Reuss result, where the c 's are elastic stiffness constants and the s 's are elastic compliance constants. In 1966, Aleksandrov obtained an unambiguous averaging result by considering a sixth-order invariant. The Voigt result averages c_{44} and $(c_{11} - c_{12})/2$ arithmetically with the weights $3/5$ and $2/5$, while Aleksandrov's result represents a geometric average with the same weight.

Ledbetter and Naimon (1974) proposed an averaging method utilizing the Debye characteristic temperature (θ_D), where it was assumed that $\theta_D(\text{polycrystal}) = \theta_D(\text{single crystal})$ so that grain boundaries contribute nothing to elastic stiffness or specific heat. The method involves determining a mean sound velocity from three specific sound velocities in single crystals, and iteratively solving for G (Ledbetter, 1990).

E. TEMPERATURE DEPENDENCE OF ELASTIC CONSTANTS

According to the quasi-harmonic model (described below), it is generally believed that true elastic behavior with temperature should reveal no temperature dependence of the modulus below about one-third the Debye temperature

(Armstrong and Brown, 1964) and a linear dependence above the Debye temperature (Huntington, 1958; Leibfried and Ludwig, 1961; Varshni 1970). However, the temperature dependence seen experimentally is actually curvilinear above the Debye temperature (very high temperatures). Many (particularly noble) metals show very steep elastic modulus temperature dependencies; and the slopes of the curves decrease with increasing temperature (i.e. large *modulus defects*). This elevated-temperature, non-linear temperature-dependence of the elastic constants of the elements has not been fully explained.

1. Investigations

There have been numerous measurements of single-crystal and polycrystalline elastic constants at room temperature, low temperatures (some down to the liquid helium region) and high temperatures. Köster (1948) demonstrated for many polycrystalline metals that increasing temperature will generally decrease the elastic modulus. Frederick (1948) measured the elastic moduli of several polycrystalline metals at high and low temperatures. Levitt and Martin (1960) measured the elastic moduli of polycrystalline "super alloys", steels, and titanium alloys to very high temperatures (1200–2000° F). Only the elastic moduli of the steels demonstrated the curvi-linear behavior in the high temperature region; the others were linear with temperature.

Featherston and Neighbours (1963) measured the single-crystal elastic constants of Ta, W, and Mo between 4.2 and 300 K. In each case, the elastic constants approached zero slope as $T \rightarrow 0\text{K}$. Brown and Armstrong (1963) measured the elastic modulus of polycrystalline W up to 2400° C and Ni up to 1000° C. Armstrong and Brown (1964) measured the elastic modulus of polycrystalline Mo, Ta, V, W, Cr, Ni up to 1000° C. Most had curvi-linear modulus defects at higher

temperatures. They observed that the general pattern for an elastic modulus of a metal seems to be a linear decrease with increasing temperature over the range between $0.1 - 0.4 T_m$, then a progressively decreasing value up to the melting point. Single-crystal elastic constants of W were also measured and demonstrated the same behavior, though less pronounced than the polycrystalline W.

Dunegan (1964) measured the elastic moduli of polycrystalline hafnium, 4340 steel, and Hastelloy "C" up to 870°C and reported curvilinear modulus defects at high temperatures for all but the hafnium. Carnevale *et al.* (1964) measured the elastic moduli of polycrystalline Al up to 600°C and 4340 steel up to 1100°C , and reported curvilinear modulus defects at elevated temperatures. Lowrie and Gonas (1965 and 1967) measured single-crystal and polycrystalline elastic constants of W up to 1800°C . All elastic constants and moduli showed marked curvilinear behavior in the high-temperature region (above 1200°C). Chang and Himmel (1966) measured the single-crystal elastic constants of Cu and Ag up to 527°C (800 K) and Au up to 277°C (550 K). For the temperature ranges evaluated, they reported only linear temperature dependence for these elastic constants.

Sather (1968) measured the elastic moduli of polycrystalline Al and 304 stainless steel from $0 - 675^\circ\text{C}$ and $0 - 1300^\circ\text{C}$, respectively. The elastic moduli for both metals were curvilinear for the entire temperature range, but were particularly curved at elevated temperatures. Gerlich and Fisher (1969) measured the single-crystal elastic constants of Al between 300 and 900 K. All of the elastic constants were curved (decreasing) over the entire temperature range; the curvature was exaggerated in the higher temperature region (above 700 K). Papadakis *et al.* (1974) measured the elastic modulus of polycrystalline Re, W, Ir, Pt, Ru and Mo wires up to 2250, 2250, 2050, 1400, 2000 and 2000°C , respectively. The Pt wire was alloyed with 6% Rh. All of the metals tested showed large curvilinear modulus

defects in the high temperature region; Mo and Rh showed particularly large modulus defects.

Talmor and Walker (1977) measured the single-crystal elastic constants of Nb between 1300 and 2600 K. The elastic constant $(c_{11} + c_{12})/2$ decreased rapidly (curvilinearly) in the elevated temperature region (above 1500 K), but c_{44} displayed anomalous behavior and increased for all temperatures above 500 K. Drapkin *et al.* (1980) measured the elastic moduli of polycrystalline Sn, Bi, Cd, and Pb up to the melting point. All metals except Pb demonstrated large curvilinear moduli defects at $0.5 - 0.8 T_m$. McLellan and Ishikawa (1987) measured the high-temperature elastic moduli of polycrystalline Al from room temperature to 575°C and found marked curvilinear behavior above 400°C. Yoshihara *et al.* (1987) measured the polycrystalline elastic moduli and single-crystal elastic constants of Pd from room temperature to 1200 K. Marked modulus defects were reported for both polycrystalline and single-crystal specimens above approximately 800 K. Collard and McLellan (1990) reported curvilinear moduli defects in polycrystalline Au up to 1000°C and polycrystalline Pt up to 1200°C. In work yet to be published, Pt single-crystals demonstrated the same behavior, though less pronounced.

2. Harmonic Theory

According to current theory, thermal variations of elastic constants have two characteristics: (1) an approach to zero slope as $T \rightarrow 0K$, and (2) a negative (linear) slope at higher temperatures. At room temperature, the thermal variation is very small, in the parts per million per °C. Usually the modulus has rather high values right up to the melting point, often one-half to two-thirds of the room temperature values. This should be expected, since metals are known to retain their crystallinity right up to the melting point and the forces between the atoms should not vary

appreciably throughout the solid-state range of temperature (Sherby, 1967).

Temperature and pressure variations of elastic constants are thought to be due to the anharmonic nature of the crystalline potential. Theoretical justification for the temperature dependence of elastic constants was first attempted by Born and Huang (1954), who suggested that the temperature dependence is due to variation in the lattice interatomic potential energy due to anharmonicity. In an excellent treatise on the theory of anharmonic effects in crystals, Leibfried and Ludwig (1961) examined the inadequacy of the harmonic model for providing a quantitative description of the properties of a crystal. Portions of their description of the harmonic and quasi-harmonic theories are presented here with slight alterations.

The basis of the harmonic model is the adiabatic approximation of Born and Oppenheimer (1927), according to which there exists a potential energy $\phi(\mathbf{R}^n)$ for the nuclei. If ϕ is known as a function of the positions of the nuclei $\mathbf{R}^n$, then all properties of the crystal can be calculated in principle. Since the displacements of the atoms from their mean positions are small (at sufficiently low temperatures), one can expand the potential energy in powers of these displacements. All terms of higher than second order are dropped. The free energy F is the sum of a purely mechanical and a temperature-dependent contribution, the latter containing the oscillations. It is uniquely determined by the second-order coefficients in the expansion of the potential energy (*CP, coupling parameters*). All thermal quantities can be obtained solely from the mechanical part, which does not contain the temperature. The equilibrium positions of the atoms are determined by the minimum of the potential energy. There is no thermal expansion; adiabatic and isothermal elastic constants are equal and are independent of pressure and temperature. There is a simple relationship between the velocity of sound and the elastic constants. The caloric data (derivatives of the free energy with respect to

temperature) are obtained correspondingly only from the vibrational part. The specific heat becomes constant at higher temperatures (higher than the Debye temperature). For low temperatures it is proportional to T^3 . The characteristic quantity for lower temperatures, the Debye θ , can be calculated from the elastic constants.

However, as pointed out by Leibfried and Ludwig: (1) thermal expansion does occur, (2) the adiabatic and isothermal elastic constants are different from each other and depend on temperature and pressure and (3) the specific heat is temperature dependent at high temperatures. Thus the harmonic model, though qualitatively and in order of magnitude confirmed by experiments, is quantitatively inadequate to describe the properties of a crystal. The harmonic model should not be correct at very low temperatures because, due to zero-point vibrations, the influence of anharmonicity does not disappear even at 0K. Thus, the equilibrium positions do not coincide with the minimum of the potential energy. In elastic theory, which for the harmonic case is purely classical-mechanical, quantum effects and thermodynamics must be taken into account (Leibfried and Ludwig, 1961).

3. Quasi-harmonic Theory

The first allowance for anharmonicity was made by Mie (1903) and Grüneisen (1908) in developing their equation of state. Assuming a temperature-dependent interatomic distance (i.e. lattice parameter) r , the lattice structure of cubic crystals is uniquely described as a function of temperature by $r(T)$. In the harmonic model, the oscillator frequencies (ν) of the lattice are independent of r . However, if one starts with the correct potential energy, then the second order CP 's (and therefore also the ν) are functions of r . If expanded terms of order higher than quadratic are omitted, then part of the anharmonic effect is already described by the dependence

$\nu(a)$. This approximation is called the *quasi-harmonic approximation*. Using these assumptions, the free energy can be calculated as a function of r and T : $F(r, T)$. By minimizing F with respect to r at constant T , the thermal expansion is obtained

$$\left(\frac{\partial F}{\partial r} \right)_T = 0 \rightarrow r(T)$$

The compressibility can be easily calculated, being proportional to $(\partial^2 F / \partial r^2)_T$ at $r(T)$. Grüneisen and Mie also made simplifying assumptions about the spectrum of lattice vibrations.

Born (1939, 1943), Bradburn (1943) and Gow (1944) used the quasi-harmonic approximation in studying the temperature dependence of simple cubic elastic constants at high temperatures. Born suggested that the frequencies $\nu(r)$ depend on the structure of the unit cell, so all elastic data can be calculated. He also made allowance for the influence of the lattice spectrum. His expression can easily be extended to low temperatures and nonprimitive lattices (Leibfried, 1955 and Leibfried and Hahn, 1958). Stern (1957 and 1958) proposed a method for direct calculation of the adiabatic constants.

The influence of anharmonicity on the caloric equation of state for high temperatures was first investigated by Born and Brody (1921). Extension to lower temperatures, considering quantum effects, is more difficult than for the thermal equation of state. In this regard, the quasi-harmonic approximation is no longer sufficient. In calculating the free energy, allowance must be made for terms that depend (in a complicated manner) on the eigenfrequencies, the temperature and the higher order CP 's, in addition to the vibrational energy terms. Ludwig (1958) developed an appropriate expression for the free energy which contains thermal and caloric equations of state treating the anharmonic effects with perturbation theory

(Leibfried, 1955; Nakajima, 1955). Expressions showing the essential features can be derived for all the physical quantities, though mathematical difficulties are often encountered with specific practical examples (Leibfried and Ludwig, 1961).

Anharmonic terms cause a coupling between the different modes of oscillations, so the dynamic theory of elasticity (velocity of sound in crystals) must be reanalyzed in terms of this approximation. Mechanically and thermally excited (sound wave) vibrations must be superposed. Anharmonicity causes an exchange of energy between thermal and mechanical vibrations: mechanical waves lose energy to the thermal vibrations. Macroscopically this is seen as damping, which cannot be calculated from the free energy. Leibfried and Ludwig (1961) concluded that the velocity of sound is determined by the adiabatic elastic data.

Overall, the quasi-harmonic theory improves understanding of the properties of crystals over the harmonic theory. In summary, the temperature-dependence of the elastic constants is due to the variation of the lattice potential energy due to anharmonicity. In the limiting cases, the theory predicts that the lattice contribution to $c_{ij}(T) - c_{ij}(0)$ should vary as T^4 at very low temperatures and as T at high temperatures. The theory is relatively simple, but problems remain due to the inadequate knowledge of interatomic potential energy. Huntington (1958) summarized the temperature-dependence of elastic constants as arising only in part from the direct effect of thermal vibrations. A considerable part is due to changes in ϕ with V (volume) as the solid expands thermally. The theory predicts a linear dependence of the elastic constants at high temperatures.

In 1970, Varshni reported that experimental measurements of elastic constants at elevated temperatures conforms to the quasi-harmonic theory, i.e. linear dependence of c_{ij} on T . However, he found that elastic constants at low temperatures do not vary as T^4 , as predicted. The elastic constants of some metals

have been found to vary as T^2 (Alers and Waldorf, 1961; Graham and Chang, 1964; Chang and Graham, 1966). Bernstein (1963) demonstrated that this could be from the temperature dependence of the electron energy due to the Fermi–Dirac distribution of electrons.

Several investigators have attempted to represent the temperature dependence of elastic constants by empirical equations. Sutton (1953) represented the variation of c_{44} of aluminum for $63 \leq T \leq 773$ K using: $c_{44} = A \exp(-B\beta T) R^{-2}$, where β is the volume expansion coefficient and R is the ratio of volume at temperature T to that at some fixed temperature. Overton and Gaffney (1955) found a similar relation for c_{44} of copper, and Wachtman *et al.* (1961) suggested the equation:

$$E_Y = E_0 - BT \exp\left[\frac{-T_0}{T}\right]$$

for Al_2O_3 , MgO and ThO_2 for $77 \leq T \leq 850$ K, which was later found to hold very well for ThO_2 up to 1300 K (Spinner *et al.*, 1963). Anderson (1966) attempted a theoretical explanation for Wachtman's equation. Varshni (1970) suggested two equations for the variation of elastic stiffness constants with temperature and examined their applicability, along with Wachtman's, for 22 substances. The two equations proposed were

$$c_{ij} = c_{ij}^0 - \frac{s}{e^{t/T} - 1}$$

and

$$c_{ij} = a - \frac{bT^2}{T + c}$$

where s , t , b , and c are constants. c_{ij}^0 and a represent the values of the elastic

constants at 0K according to the two equations. A theoretical justification of the first equation was offered by Varshni. According to Leibfried and Ludwig (1961), the lattice contribution to the temperature dependence of adiabatic elastic constants can be represented by

$$c_{ij} = c_{ij}^0 (1 - D \bar{\epsilon})$$

where D is a parameter which depends on the crystal type or model. $\bar{\epsilon}$ is the mean energy per oscillator, given by

$$\bar{\epsilon} = \frac{h\nu}{2} + \frac{h\nu}{e^{h\nu/kT} - 1}$$

if an Einstein model is assumed for the solid. Each of the equations proposed by Varshni showed good agreement with experimentally measured elastic constants.

4. Internal Friction

Zener (1941) calculated that the effect of shear stress relaxation at grain boundaries can reduce the measured value of Young's modulus by up to 38%. Armstrong and Brown (1964) suggested that the deviation from linearity in the temperature dependence of elastic moduli at elevated temperatures can be explained as the effect of various damping processes (*internal friction*, or dissipation of vibrational energy) active in the materials. They observed that increasing the frequency at which (resonance) dynamic modulus measurements are made increases the temperature at which a particular damping mechanism becomes active. Drapkin *et al.* (1980) measured Young's modulus and internal friction of Sn, Bi, Cd and Pb from 20° C to the melting temperature.

Entwistle (1962) reviewed the major internal friction mechanisms: (1) stress

induced ordering of solute atoms, (2) relaxation associated with crystal boundaries, (3) dislocations and (4) ferromagnetic materials. Some of the mechanisms do not involve grain boundaries and hence would produce an effect even in single-crystal specimens. Portions of Entwistle's thorough review are included here with slight alteration.

Internal friction peaks in polycrystalline pure metals were originally presumed to be due to limited grain-boundary sliding. More recently, the energy-loss mechanism is considered to be due to grain-boundary migration rather than slip (Entwistle, 1962). Dislocations have been demonstrated to be sources of internal friction in single-crystals (Read, 1940). One method is due to generation of relaxation peaks, such as Bordoni peaks, which were first reported at low temperatures in cold-worked *fcc* metals (Bordoni, 1954) and peaks seen at megacycle frequencies ascribed to scattering of the thermal waves of the lattice by oscillating dislocation loops. Dislocations may also contribute hysteresis damping, which is independent of frequency but markedly dependent on vibration strain, through dislocations being torn from points at which they are pinned either by solute atoms or vacancies (Entwistle, 1962).

Very high anelastic internal-friction peaks were reported by Kê (1947) in polycrystalline Al for $250 \leq T \leq 300^\circ\text{C}$. Because these peaks were absent in Al single-crystals, Kê suggested that the relaxation was associated with crystal boundaries. He proposed that the anelastic strain is caused by relative sliding of adjacent crystals along crystal boundaries. This relaxes the shear stress across the boundary, which behaves mechanically like a film of viscous fluid. The internal friction will pass through a maximum only if the magnitude of the relaxation of strain is limited — which it will be in this model by geometrical interlocking of the grain corners (Entwistle, 1962).

Leak (1961) demonstrated that this grain-boundary damping occurs in polycrystalline Fe, Cu, Mg, Ag, Au, Sn, Zr, Ti and Mo. According to Kê, the activation energy derived from the displacement of the temperature of the grain-boundary peak with frequency is the same as that for volume self-diffusion. However, better agreement has been found with grain-boundary self-diffusion (Miles and Leak, 1961), implying that Kê reached an erroneous conclusion due to the extreme sensitivity of the boundary relaxation to impurities. Miles and Leak (1961) demonstrated that 0.02% carbon in iron raises the activation energy for grain-boundary damping from 46 kcal/mole to 80 kcal/mole. Kê's reported value of 85 kcal/mole may have reflected the presence of impurities (C or Ni) in his specimens, so that the agreement between his value and the activation energy for volume self-diffusion (78 kcal/mole) was coincidental. The value of 46 kcal/mole for high purity iron reported by Miles and Leak agrees very well with the activation energy for grain-boundary self-diffusion (Entwistle, 1962).

Kê developed a model for grain-boundary sliding which predicted that the relaxation time should be proportional to

$$\frac{D\eta_0 \exp \left[\frac{Q_b}{kT} \right]}{dG}$$

where D is the crystal size, d the boundary thickness, and G is an average elastic modulus for the crystals. The coefficient of viscosity of the grain-boundary materials is given by $\eta = \eta_0 \exp(Q_b/kT)$. If all boundaries are assumed to be identical, then an internal friction with a single value of τ would be expected. Thus all the normalized internal-friction curves would be a function of $\nu\tau$ only, i.e. of

$$\frac{\nu D \eta_0}{dG} \exp \left(\frac{Q_b}{kT} \right)$$

where ν is the vibration frequency. The results of Leak's (1961) measurements on Fe, Cu and Al over a wide range of grain sizes fit better into a relation in which grain size appears as D^2 , in disagreement with Kê's predictions (Entwistle, 1962).

The width of the damping vs. temperature peaks is consistently found to be greater than would be expected from a single relaxation process with an activation energy equal to that deduced from the displacement of the peak temperature by a change of frequency. Thus the total damping is due to a distribution of relaxations. Marsh and Hall (1953) found that 99.9998% pure Au wire, cold-worked 36% and annealed between 320 and 550°C, had a single internal-friction peak at 260°C (1 Hz). On annealing above 550°C, where secondary recrystallization occurred, they found that the single peak was replaced by two peaks, one at 240°C and one at 410°C. Similar tests on 99.98% pure Au never resulted in double peaks. The suggestion is that two peaks occur in very high purity Au because of the presence of two types of crystal boundaries — one formed during primary recrystallization and the other (giving the higher-temperature peak) by secondary recrystallization. If the orientation change across the boundaries differs, then the two types of boundary will not have identical structure and may have different mechanical relaxation times. Alternatively, the spread of orientation changes across the boundaries in any polycrystalline metal will give rise to a distribution of relaxation times, which would explain the broad internal-friction peaks. Kê's theory falls short because it assumes a uniform boundary structure throughout the polycrystal, which does not agree with measurements of grain-boundary energies.

In the temperature range where grain-boundary relaxation peaks occur, the

measured damping includes a significant contribution generally referred to as "background damping", which rises monotonically with temperature, is relatively insensitive to changes of vibration frequency and is usually much smaller in single-crystal specimens than in polycrystals. The damping is not anelastic. Friedel *et al.* (1955) reported that an increase in background damping can be correlated with the development of sub-boundaries by polygonization. The suggestion is that the damping results from the stress-induced migration of the polygonized boundaries. Friedel (1961) proposed a mechanism for this: the effect of stress on orthogonal sets of edge dislocation walls will be to cause vacancies to be emitted selectively from one group and absorbed on the other — giving rise to dislocation climb and a hysteretic strain. An alternating vacancy flux will be generated by alternating strain and the decrement resulting from this will depend on

$$\frac{\exp \left[-\frac{U}{k T} \right]}{l^2 T f}$$

where l is the sub-grain size, T the temperature, U is the activation energy for self-diffusion, and f is the frequency of vibration. The term $1/f$ appears because the hysteresis strain is proportional to the number of vacancies transported, which is proportional to the time available for transport, in turn proportional to $1/f$. An important condition is that vacancy emission from dislocations should be the rate-determining factor, which means that the time for transport of vacancies across a sub-grain should be short compared with the periodic time of the vibration. If $l = 30 \mu\text{m}$ and f is 1 Hz, this condition demands $T > 300^\circ\text{C}$ for Al. This analysis agrees with observations by Friedel *et al.* (1955) that successive heating of polygonized Al reduced the measured background damping, caused by progressive

coarsening of the sub-structure. This reduces the decrement predicted by Friedel, since it varies as $1/l^2$.

F. RESEARCH OBJECTIVE

Wagner (1971) observed that statistical models for solid solutions which assume a constant specific volume are not compatible with constant-pressure thermodynamic data unless "volume corrections" are made. Such corrections have been calculated from the elastic behavior of the solid using linear isotropic elastic theory (Lupis, 1977 and 1978; Tallon, 1980; McLellan, 1982). The resulting volume corrections may be expressed in terms of the temperature and pressure derivatives of the bulk modulus (McLellan, 1982). As most of the thermodynamic data for solid solutions have been obtained for temperatures greater than half the melting temperature ($T > 0.5 T_m$), it is also necessary to obtain elastic data for high temperatures.

For cubic metals, the bulk modulus (B) is readily determined from the single-crystal elastic stiffness constants (c_{ij}), using the relation $B = (c_{11} + 2c_{12})/3$, but the c_{ij} have not been measured for most metals at $T > 0.5 T_m$. The Young's modulus (E_Y) and shear modulus (G) have been measured for many polycrystalline metals at elevated temperatures, though some (particularly noble) metals exhibit large departures from linearity (modulus defects) at elevated temperatures. Whether the modulus defects are due to anelastic grain boundary relaxation or intrinsic elastic behavior of the lattice has not been resolved.

Measurements of the c_{ij} of Al up to 930 K reveal small modulus defects (Gerlich and Fisher, 1969). However, the large modulus defect observed in polycrystalline Al at high temperatures is due principally to Zener relaxation of the grain boundaries (Yoshihara *et al.*, 1987). Grain boundary diffusion energies (Q_b)

calculated from Al polycrystalline (Collard and McLellan, 1991) and single-crystal elastic data agree reasonably well with independent estimates of Q_b (Kaur and Gust, 1988). If it is assumed that the large modulus defect observed in Au, Ag and Cu is due exclusively to Zener relaxation of the grain boundaries (as with Al), the calculated values of Q_b are approximately half the values obtained experimentally (Kaur and Gust, 1988; Collard and McLellan, 1990). Thus, for Au, Ag and Cu, either the analysis of the relaxation phenomenon is incorrect (Yoshihara *et al.*, 1987), or lattice elasticity is not accurately predicted by the quasi-harmonic theory at elevated temperatures (Weiner, 1983). To resolve this question, it is necessary to measure the high-temperature c_{ij} of metals exhibiting a large polycrystalline modulus defect and such was the goal of this work.

The elastic data utilized in volume correction calculations do not refer to pure metals, but to solid solutions. The solution lattice may exhibit relaxation effects due to the presence of defects, as well as intrinsic departures from simple elastic behavior. Although the formal thermodynamic relationships between B and the volume corrections have been determined, a more direct approach is to use constant-pressure models (grand canonical ensembles) where volume-dependent interaction energies are utilized.

II. EXPERIMENTAL METHODS

A. OVERVIEW OF EXPERIMENTAL TECHNIQUE

The elastic moduli (E_V and G) of polycrystalline Au and the elastic stiffness constants (c_{11} , c_{12} and c_{44}) of Au single-crystals were determined using the pulse-echo technique. The round trip transit time of extensional and torsional (transverse) acoustic waves through the specimens was measured as a function of temperature. From these measurements, the velocity of the acoustic waves through the specimens was determined. The elastic moduli and elastic constants were calculated from the acoustic velocity and the density of the specimens.

B. HISTORICAL BACKGROUND

1. Theoretical Literature

The use of ultrasonic techniques to determine dynamic elastic moduli of polycrystalline aggregates and elastic constants of single crystals has been reported by many investigators. Musgrave (1954) published a brief survey of the general theory of elastic wave propagation in single crystals up to 1904. In 1973, Green published an excellent treatise on *Ultrasonic Investigation of Mechanical Properties*, in which he summarized the theory and techniques of measuring linear and nonlinear elastic wave propagation in crystals, as well as energy loss (attenuation) mechanisms. He presented an extensive survey of the theoretical literature published up to 1973, portions of which are included here with slight alteration. Pohlman (1967, 1969, 1971, 1972) published a four-volume bibliography of the literature entitled *Documentation in Ultrasonics*, which involved all aspects of ultrasonic investigations between 1957 and 1972.

In his treatise on the mathematical theory of elasticity, Love (1927) included sections on elastic wave propagation. Sakadi (1941) calculated the directions in

which pure mode elastic waves could propagate in single crystals. Hearmon (1946) presented a summary of elastic constants of anisotropic materials. Gold (1950) computed wave speeds as a function of crystallographic orientation for some cubic and hexagonal metals. Musgrave (1954) continued to describe elastic wave propagation in hexagonal and cubic crystals (de Klerk and Musgrave, 1955; Miller and Musgrave, 1956). Borgnis (1955) presented relations that permitted determination of the directions of pure-mode elastic wave propagation in anisotropic media. Hearmon (1956) published another review of elastic constants of anisotropic media. Aleksandrov (1956) described the propagation of elastic waves along pure-mode axes in various crystals and suggested analogies between ultrasonic wave and light propagation in crystals. The next year (1957) he suggested further analogies.

In 1957, Markham derived equations for elastic wave propagation in anisotropic media and presented methods for determination of second-order elastic constants from these equations and ultrasonic wave propagation. He pointed out that energy-flux deviations from the wave normal have no direct influence on elastic constant measurements since the energy-flux deviation has an associated phase velocity which corresponds to the wave normal defined by the parallel faces of the test specimen — and this phase velocity is used to determine the elastic constants. However, Green (1973) pointed out that this is restricted to linear elastic wave propagation in *unbounded* media. Energy-flux deviations in actual test specimens with limited lateral dimensions may cause the ultrasonic beam to impinge on side walls — causing mode conversion and deterioration of the wave. In thin rods, guided wave propagation exists and diffraction effects may arise from the finite size of the wave source (transducer). In general, the physical size of the test specimen, the parallelism of opposite faces, the size of the transducer relative to the

ultrasonic wavelength, the curvature of the wave beam and other geometrical factors exert a significant effect on the propagational characteristics of elastic waves and on the apparent energy loss from such waves (Truell *et al.*, 1969). In 1956, Synge presented a general mathematical analysis of elastic wave propagation in anisotropic media and in 1957, presented an analysis of the energy flux associated with these waves.

In *Physical Acoustics and the Properties of Solids*, which has become the classic work on elastic wave propagation in solids, Mason (1958) presented the physical principles associated with all types of elastic wave propagation in solids. He discussed various experimental techniques and provided an excellent review of energy loss mechanisms. Also in 1958, Huntington presented a review of the elastic constants of crystals.

In 1959, Musgrave published a general treatment of the propagation of elastic waves in crystals and other anisotropic media. He described the conditions under which surface waves can be propagated and wave propagation in anisotropic aggregates. Waterman (1959) presented a general treatment of the propagation of elastic waves in crystals. Considering individual rotational symmetries associated with different crystal classes, he presented a unified approach to properties of pure modes.

In 1961, Farnell described elastic wave propagation in trigonal crystals (sapphire and quartz). Aleksandrov and Ryzhova (1961) published a review of all known single-crystal elastic constants. Sullivan and Papadakis (1961) utilized the theory of ultrasonic wave propagation to determine the extent of preferred orientation in polycrystalline metals. Hearmon (1961) published *An Introduction to Applied Anisotropic Elasticity*, which provides an excellent review of single-crystal elastic constants, polycrystalline aggregate elastic moduli and elastic wave

the interactions of elastic waves propagating through solids and the properties of the solids. In 1963, Khatkevich described acoustic axes (along which both transverse waves propagate at the same velocity) for all crystal classes except triclinic. The same year, Kolsky (1963) published *Stress Waves in Solids*, a concise account of the classical theory of stress wave propagation in solids. In 1964, Smith and Stephens described the effects of anisotropy on ultrasonic wave propagation in solids. The same year, Thurston (1964) published a paper on wave propagation in fluids and solids and McSkimin (1964) published a paper on ultrasonic methods for measuring mechanical properties of liquids and solids.

In 1965, Brugger presented expressions for the wave speeds and particle displacement vectors for pure mode directions in all crystal point groups for selected crystal classes, including cubic. In 1966, Hinton and Green described the modes of linear elastic wave propagation in aluminum crystals. In 1967, Portigal published a description of acoustical activity in crystals. The same year, Neighbours and Schacher (1967) presented a method for determining single-crystal elastic constants from sound velocity measurements in crystals with any type of symmetry. In 1968, Henneke and Green compiled the modes of linear elastic wave propagation in copper crystals. The same year, an English translation of Fedorov's *Theory of Elastic Waves in Crystals* (1968) was published, which was the first textbook exclusively devoted to the theory of linear elastic wave propagation in crystals. In 1969, Truell, Elbaum and Chick published *Ultrasonic Methods in Solid State Physics*, which contains a section on the theory of ultrasonic wave propagation in solids. In 1970, Musgrave published *Crystal Acoustics*, which summarized his previous work and treated the subject from both a continuum and discrete particle perspective.

2. Ultrasonic Measurement of Elastic Constants at Elevated Temperatures

Ultrasonic measurement of dynamic polycrystalline elastic moduli and single-crystal elastic constants is particularly well-suited for elevated temperature investigations and has been used for many years. Köster (1948) pioneered measurement of elastic moduli for many polycrystalline metals from room temperature to near T_m using the ultrasonic resonance technique. Frederick (1948) measured elastic properties of polycrystalline materials at low and high temperatures. McSkimmin described ultrasonic techniques applicable to small specimens (1950) and evaluated elastic constants of germanium and silica single crystals (1953). McSkimmin (1959) measured ultrasonic wave velocities and elastic moduli of small specimens at high temperatures (1959). Levitt and Martin (1960) described ultrasonic determination of elastic constants of metals at elevated temperatures. Kalugin and Mikhailov reported techniques for measuring elastic properties of solids at elevated temperatures (1961) and metals (1966) up to 3000 K. Armstrong and Brown (1964) used the ultrasonic resonance technique to measure dynamic Young's modulus on some polycrystalline and single-crystal tungsten at very high temperatures. Carnevale *et al.* (1964) reported ultrasonic measurement of elastic moduli at elevated temperatures using momentary contacts. Dunegan (1964) described the use of ultrasonics for high temperature dynamic modulus measurements. Sather (1968) described the use of buffer-rods attached to short specimens for ultrasonic measurement of elastic moduli at high temperatures. Lynnworth (1973) reported the measurement of elastic moduli in slender specimens using extensional and torsional wave pulses. Papadakis *et al.* (1974) reported ultrasonic measurements of Young's modulus and extensional wave attenuation in refractory metal wires at elevated temperatures with application to ultrasonic

thermometry. Arnoult and McLellan (1975) used ultrasonics to study the variation in Young's modulus of austenite with carbon concentration.

Overton and Gaffney (1955) used ultrasonic methods to study the variation of copper elastic constants at low temperatures. Neighbours and Alers (1958) studied the elastic constants of silver and gold at low-temperatures. Rayne used ultrasonic methods to evaluate the effect of solute concentrations on elastic constants of α -brasses at room temperature (1958) and between 4.2 and 300 K (1958). Rayne later used similar methods to evaluate the elastic constants of palladium (1958) and iron (1961) between 4.2 and 300 K. Armstrong and Brown (1964) reported dynamic Young's modulus measurements of commercial graphites and some polycrystalline metals at temperatures above 1000° C. Lynnworth (1973) also described the ultrasonic measurement of elastic properties of graphite rods. Lowrie and Gonas reported ultrasonic measurement of the dynamic elastic modulus of polycrystalline tungsten (1965) and single-crystal tungsten (1967) between 24 and 1800° C. Chang and Himmel (1966) reported the temperature dependence of copper, silver and gold elastic constants above room temperature. Gerlich and Fisher (1969) reported the high temperature elastic moduli of aluminum. Farraro and McLellan described the temperature dependence of Young's modulus and shear modulus of nickel, platinum and molybdenum (1977) and polycrystalline niobium, tantalum and vanadium (1979) using ultrasonic methods. Talmor and Walker (1977) also reported the elastic constants of niobium up to the melting point. Ledbetter (1985) reported the effects of carbon and nitrogen on the elastic constants of stainless steel.

Recently, ultrasonic methods have been used to evaluate the high temperature elastic properties of polycrystalline aluminum (McLellan and Ishikawa, 1987), palladium single crystals (Yoshihara and McLellan, 1987), polycrystalline gold and platinum (Collard and McLellan, 1990) and gold single-crystals (Collard and

McLellan, 1991) The particluar pulse–echo technique utilized in this work has been thoroughly described by Lynnworth (1973) and Papadakis *et al.* (1974).

C. EXPERIMENTAL TECHNIQUES FOR MEASURING LINEAR ELASTIC CONSTANTS

Measurement of the elastic constants of solid materials is one of the most important applications of ultrasonic techniques. Various experimental techniques are described in the literature (Mason, 1958, 1964; Truell *et al.*, 1969; Pohlman, 1967, 1969, 1971 and 1972; Schreiber *et at.*, 1973; Standard Recommended Practice E494–75, 1983). Such measurements include the determination of second–order elastic constants, which yield fundamental information about the binding forces between atoms in crystals. These constants determine the linear elastic relations between stress and strain for solids so that prediction of the response of solid bodies to stresses imposed within the linear elastic range is possible.

Only two elastic constants are required to specify deformation behavior for isotropic materials. These two constants are selected from the Young's modulus (E_Y), shear modulus (G), Poisson's ratio (ν), or the two second–order Lamé constants (λ , μ). Only two of these constants are linearly independent; the others can be determined from these two using (Green, 1973)

$$E_Y = \frac{\mu(3\lambda + 2\mu)}{(\lambda + \mu)}$$

$$\nu = \frac{\lambda}{2(\lambda + \mu)}$$

$$G = \mu$$

Unlike the elastic constants of isotropic materials (polycrystalline aggregates), the elastic constants of single-crystals yield information about the interatomic forces binding solids together, dynamical vibrations of the crystal lattice, lattice specific heats and Debye temperatures (Born and Huang, 1954; de Launey, 1956; Huntington, 1958; Alers, 1965). For cubic single-crystals, three second-order elastic constants are required to determine the linear elastic response.

Before the common use of ultrasonics, elastic constants were determined by static methods — in which the test specimen was subjected to an imposed load and the resulting displacement measured. The results were usually inconsistent because of the high sensitivity needed to create displacements in small specimens, and because the displacement measurements must be within the elastic region. For many solid materials, nonlinear elastic and plastic deformation occurs with very small loads. In such materials, static measurement of second-order elastic constants is virtually impossible (Green, 1973).

These considerations are not applicable to measurement of second-order elastic constants with dynamic ultrasonic techniques. The strains produced in the specimen are extremely small and well within the linear elastic regions. The technique typically involves measurement of wave speeds along selected directions in solid specimens, as well as the specimen density. Advantages of the dynamic method over the static method include (Armstrong, 1971): (1) relative ease of sample preparation and a wide variety of permissible specimen shapes and sizes, (2) greater precision measurements, (3) relative ease of measurement, (4) ready adaptability of techniques to measurements as functions of temperature and pressure, (5) ability to measure elastic constants not measurable with the usual static techniques and (6) use of the same equipment to obtain anelastic data, in some cases simultaneously with elastic measurements.

Static measurements yield the isothermal elastic constants while dynamic methods yield the adiabatic elastic constants. The difference is usually on the same order or smaller than the experimental error associated with the elastic constant measurement, so that it is usually neglected. The difference is given by (Hearmon, 1961)

$$c_{ij}^S = c_{ij}^T + \frac{T V \beta_i \beta_j}{C_\epsilon}$$

where the superscripts S and T indicate elastic constants from dynamic measurements (adiabatic; constant entropy) and static measurements (isothermal; constant temperature), respectively. β_i and β_j are the temperature coefficients of stress at constant strain; T is the absolute temperature (K); and C_ϵ is the specific heat at constant strain.

Determining the adiabatic second-order elastic constants of isotropic solids requires three experimental measurements: (1) the density of the specimen, (2) the speed of propagation of a longitudinal plane wave in any arbitrary direction and (3) the speed of propagation of a transverse plane wave in any arbitrary direction. To insure that the waves used are plane (with little diffraction spread), they must be generated with a transducer that is large (in diameter for circular transducers) compared to the wavelength of the elastic wave to be propagated. The test specimen must have large lateral dimensions compared with the transducer diameter to eliminate mode conversion due to reflection at a lateral surface and guided-wave mode effects, since the equations for calculating elastic constants are based on the assumption of linear elastic wave propagation in an unbounded half-space. Finally, to remain in the linear elastic region, the electrical power applied to the transducer should not be increased beyond the level required to establish an acceptable pulse

train in the test specimen. (Green, 1973)

The second-order elastic constants for unbounded isotropic materials are then calculated using (Green, 1973)

$$\lambda + 2\mu = \rho v_l^2 \quad \text{and} \quad \mu = \rho v_t^2$$

where ρ is the specimen density and v_l and v_t are the wave speeds associated with pure mode longitudinal and pure mode transverse wave propagation along any direction in an isotropic material. The energy-flux associated with both waves is parallel to the wave normal and exhibits no deviation from the propagation direction. Thus, experimental measurement of ρ , v_l and v_t permits calculation of λ and μ . Using these, E_v , G and ν can be calculated (Green, 1973).

Mason (1958) demonstrated that shear waves propagate through cylindrical specimens with a velocity independent of the diameter. The same is not true for longitudinal waves, the velocity of which through the specimen is highly dependent on specimen diameter (boundary conditions). A compressional wave propagating through a long, thin rod represents uniaxial compressions where the displacements are related to the stresses via Young's modulus. Compressional waves propagating through bulk materials, on the other hand, result in displacements arising in the plane normal to the direction of propagation — which are expressed by Poisson's ratio. In bulk specimens, energy is coupled laterally during the passage of extensional (compressional) wave motion. In the limit, as the diameter of the rod is decreased, it becomes a single chain of atoms without cross-coupling. Thus, for thin rods (wires), the wave is propagated with an extensional velocity given by (Schreiber *et al.*, 1973)

$$v_e = \left(\frac{E_Y}{\rho} \right)^{1/2}$$

For a thick rod, the velocity at which a compressional wave propagates through a bounded medium is a function of the ratio of diameter to wavelength. Bancroft (1941) demonstrated that as the ratio of the diameter (d) to wavelength (λ) is increased, the wave propagates with the group velocity and approaches the Rayleigh (surface) wave velocity for thick rods, where a thin rod corresponds to $d/\lambda < 0.1$. However, in bulk samples, the compressional wave is found to travel with the velocity given by the solution of the equation of motion for a longitudinal wave. Thus by keeping the diameter of the specimen small in comparison with the wavelength, the *extensional* velocity rather than the *longitudinal* velocity may be measured. For typical velocities (5,000 – 10,000 m/s) and frequencies of about 10 MHz, the wavelengths are on the order of 100 μm (Schreiber *et al.*, 1973).

The most straightforward method for calculating the second-order elastic constants of cubic single-crystals requires only one single-crystal in the [110] orientation. The specimen density and three separate wave speeds are measured: (1) v_{110e} , extensional wave propagation along the [110] direction, (2) v_{110tf} , (fast) transverse (shear) wave propagation along the [110] direction with particle displacement along $[1\bar{1}0]$ and (3) v_{110ts} , (slow) transverse wave propagation along the [110] direction with particle displacement along [001]. The energy-flux associated with all three waves is parallel to the wave normal and thus does not deviate from the direction of propagation. Measurement of ρ , v_{110e} , v_{110tf} and v_{110ts} permits calculation of c_{11} , c_{12} , and c_{44} using (Green, 1973)

$$c_{11} + c_{12} + 2c_{44} = 2\rho v_{110e}^2$$

$$c_{11} - c_{12} = 2\rho v_{110tf}^2$$

$$c_{44} = \rho v_{110ts}^2$$

In this work, two thin-rod (wire) gold single-crystals were used: one with a [100] orientation and one with a [110] orientation. The specimen density and three separate wave speeds were measured: (1) v_{100e} , extensional wave propagation along the [100] direction, (2) v_{100t} , transverse (torsional) wave propagation along the [100] direction and (3) v_{110e} , extensional wave propagation along the [110] direction (as described above). For plane waves propagating along the [100] axis, the relationships between the three wave speeds and three elastic constants are

$$\begin{aligned} c_{11} &= \rho v_{100e}^2 \\ c_{44} &= \rho v_{100t}^2 \\ c_{11} + c_{12} + 2c_{44} &= 2\rho v_{110e}^2 \end{aligned}$$

D. MEASUREMENT OF POLYCRYSTALLINE ELASTIC CONSTANTS

The experimental technique used has been thoroughly described in an article by Lynnworth (1973), "Ultrasonic measurement of elastic moduli in slender specimens using extensional and torsional wave pulses." The technique was first recommended for *slender* specimens by Bell (1957). Most investigators utilize longitudinal and transverse shear wave pulses for measurement of elastic moduli. However, this technique uses extensional and torsional waves generated by a magnetostrictive transducer so that the Young's and shear modulus can be directly calculated from the measured velocity measurements. We retain for the description and discussion, however, the terminology most commonly used and refer to the torsional waves as "transverse."

1. Specimen Preparation

Twenty grams of MARZ-grade gold (99.999% pure, J.M. Ney Company,

Bloomfield, CT) was cast into a 0.25 cm diameter rod using the lost wax technique. After quenching in room temperature water, the cast gold rod was drawn through a series of stainless steel dies to form a 0.13 cm diameter wire, which was subsequently straightened by rolling between two stainless steel plates. Two specimens, each approximately 8.0 cm long, were cut from the middle of the wire. The ends of each specimen were polished perpendicular to the length, and the final length and diameter of each measured to within 0.001 cm using a linear micrometer (Model 84, Number 505-633-50, Mitutoyo, Japan). The mass of the specimens was measured to within 0.0001 g using an analytical balance (Model H20T, Mettler Instrument Corp., Hightstown, NJ). After ultrasonic cleaning in acetone for 30 minutes, the specimens were annealed at 1000 K for 20 hours at 10^{-6} torr (Sola Basic Type 54357 with a Type 59744A control panel, Lindberg, Watertown, WI).

The two specimens were then welded to 100 cm long, 0.13 cm diameter magnetostrictive lead-in wires (Remendur, Panametrics, Waltham, MA), designed to transmit extensional or transverse (torsional, Lynnworth, 1975) waves with minimal attenuation. The lead-in wires preferentially transmit extensional waves along one direction and transverse waves along the opposite direction. The ends of each lead-in wire are marked according to this directional distinction. One of the two polycrystalline gold specimens was welded to a magnetostrictive lead-in wire so that extensional waves could be transmitted through the specimen; the other gold specimen was welded to a different magnetostrictive lead-in wire so that transverse waves could be transmitted through the specimen. The welding apparatus (Model 1015-C, Weldmatic, Division of Unitek Corporation, Pasadena, CA) was set to deliver 50 watt-sec for each weld.

2. Experimental Apparatus

A schematic illustration of the experimental apparatus is shown in Figure 1. The two polycrystalline gold specimens (welded to the lead-in wires) were placed inside separate 87 cm long quartz tubes (0.2 cm internal diameter; 0.4 cm external diameter) such that the free end of each specimen was 0.3 cm short of one tube end. See Figure 2 for detail. The lead-in wire protruded 21 cm out the opposite tube end. The quartz tubes were then passed through a silicone stopper sealing one end of a larger quartz tube (100 cm long, 4.8 cm internal diameter) such that the specimens were positioned at mid-length of the large quartz tube. The small quartz tubes protruded 21 cm out the large quartz tube end. The large quartz tube was positioned in a furnace (Sola Basic Type 54357 with a Type 59744A control panel, Lindberg) so that both ends of the large quartz tube extended 24 cm out from the furnace chamber and so that the specimens were located in the center of the furnace chamber. The orientation of the specimens/lead-in wires within the quartz tubes and furnace is shown in Figure 2.

A 0.635 cm diameter copper tube was passed through the silicone stopper (adjacent to the two small quartz tubes) and connected to a supply of compressed argon gas (UHP grade, 99.999+%, Lot 071189, Big Three Industries, Inc., Specialty Gas Division, La Porte, TX). See Figure 3. The other end of the large quartz tube was also sealed with a silicone stopper. A K-type (Chromel/Alumel) thermocouple was passed through the second silicone stopper (left side of furnace in Figure 2) and extended to mid-length of the quartz tube (adjacent to the specimens). A digital thermometer accurate to $\pm 1^\circ\text{C}$ (Model 2168A, Omega Engineering Inc., Stanford, CT) was connected to the thermocouple. Another 0.635 cm diameter copper tube was passed through the second silicone stopper, to which was connected a vacuum pump (Duo-seal Model R1402, Welch Scientific Corp., Skokie, IL). A valve to vent

Figure 1

Figure 3

to the outside (valve 3, Figure 3) and a pressure head (Baratron Type 310BHS-1000, MKS Instruments, Burlington, MA) was connected to the line between the large quartz tube and the vacuum pump. A pressure range multiplier (Baratron Type 170M-6B, MKS) and a pressure meter unit (Baratron Type 170M-26B, MKS) was connected to the pressure head to continuously monitor the pressure inside the large quartz tube (around the specimens). All connections with the silicone stoppers, quartz tubes and lead-in wires (except the specimen-containing ends of the small quartz tubes) were sealed with silicone adhesive (Permatex Clear RTV, Part Number 66B, Item Number 80636, Loctite Corp., Automotive and Consumer Group, Cleveland, OH), which was allowed to set 24 hours before the chamber was evacuated.

Extensional (Model 5010-E5-RMV, Panametrics) and transverse (torsional) (Model 5010-T10-RMV, Panametrics) magnetostrictive transducers were connected to the free ends of the lead-in wires protruding from the small quartz tubes, through which extensional and transverse waves were to be propagated, respectively (Lynnworth, 1975). The transducers were connected to two separate channels of a four-channel intervalometer (Model 6468-27-10-S, Version P.3.G., Panametrics) by coaxial cables, as shown in Figure 4. The intervalometer was programmed to transmit and receive acoustic wave pulses and measure transit time to ± 10 nsec in up to four different specimens at the same time, though only two channels were used for this work. The intervalometer was connected to a two-channel oscilloscope (Tektronix 465, Beaverton, OR) with coaxial cables: the intervalometer receiver monitor to oscilloscope channel 1 and the intervalometer window to oscilloscope channel 2. The intervalometer and oscilloscope triggers were also connected, as shown in Figure 4.

Figure 4

Intervalometer and Oscilloscope Connections

3. Intervalometer Parameters and Settings

Using the oscilloscope to monitor the acoustic wave forms, two echos were located for each specimen, as shown in Figure 5. The first echo (Figure 5-A) represented the specimen/lead-in wire weld joint and the second echo (Figure 5-B) represented the flat, polished, free end of the specimen. Narrow (50 μ sec) windows, viewed on channel 2 of the oscilloscope, were then positioned below the two echos of interest by entering appropriate information with the intervalometer numeric keypad. For round trip transit time measurement of extensional and transverse waves through the polycrystalline gold specimens, the information entered into the intervalometer is presented in Table I.

Initial τ values were set to monitor acoustic wave round trip transit time. The alternate τ -setting is to monitor sound speed. The *Receiver window 0* width was set at 50 μ sec to monitor the first echo (representing the weld joint between the lead-in wire and the specimen), as shown in Figure 5(A). This window completely enclosed the first echo, but was small enough to avoid overlapping echos from the end of the specimen; and to avoid sensing spurious echoes. The *Receiver window 1-8* width was set at 50 μ sec to monitor the second echo (representing reflections from the flat, polished free end of the specimens), also shown in Figure 5(B). The *Averaging factor* was set at 5 so that 512 actual round trip transit time measurements (wave repetitions) were averaged to determine the round trip transit time recorded. The *Number of zones* was set to 1. *Zone 0 length* represents the lead-in wire.

The *Zone 0 threshold*, which must be between -100% and +100%, was set to +80%. The (+) sign indicates the polarity of the peak to be monitored, which is determined by the impedance of the lead-in and specimen. The impedance is determined using: $Z_e = \rho v_e A$ and $Z_t = \rho v_t J$, where $J = \pi r^4/2$ for round wires of radius r , density ρ , sound velocity v and cross-sectional area A ; the subscripts e and

Figure 5

Receiver Window Locations for Specimen/lead-in
Weld Joint and Specimen End

Table I
Intervalometer Parameters and Settings
for Polycrystalline Gold Specimens

Parameter	Extensional	Transverse
Channel number	1	2
Channel active	yes	yes
Transducer frequency	100 kHz	100 kHz
Initial τ values	time	time
Receiver window 0 width	50 μ sec	50 μ sec
Receiver window 1–8 width	50 μ sec	50 μ sec
Averaging factor	5	5
Number of zones	1	1
Zone 0 length	1000 mm	1000 mm
Zone 0 threshold	+80%	+80%
Zone 0 zero-crossing	right	right
Receiver window midpoint	420 μ sec	630 μ sec
Zone 1 length	74.38 mm	84.58 mm
Zone 1 threshold	+80%	+80%
Zone 1 zero-crossing	right	right
Receiver window midpoint	500 μ sec	760 μ sec

t indicate extensional and transverse waves, respectively. Since the cross-sectional areas of the specimen and lead-in wire were equivalent, the impedance was a function of the density and sound velocity only. The specimen impedance was less than the lead-in wire impedance for extensional and transverse waves, so that positive polarity echos from the lead-in/specimen interface and specimen end were monitored. The threshold value of 80% was recommended by the manufacturer.

Round trip transit time measurements of the selected echos are made at the point the echo crosses the zero line (from positive to negative polarity), so that the *zero-crossing* to the left or right of the echo maximum could be selected. The right *Zone 0 zero-crossing* was selected for extensional and transverse measurements on the manufacturer's recommendation. The *Zone 0 Receiver window midpoint* was selected by monitoring the echo wave forms on the oscilloscope. The round trip transit time of acoustic waves through the lead-in wire was approximately 420 μsec and 630 μsec for extensional and transverse waves, respectively, so the receiver window midpoints were set at these values.

Zone 1 parameters represent the specimens welded to the lead-in wires. The previously measured specimen lengths were entered for *Zone 1 length*, and the *Zone 1 threshold* set to +80%, as with *Zone 0*, because the specimen impedance was less than the impedance of the lead-in wire. The right *Zone 1 zero-crossing* was selected on the manufacturer's recommendation. The *Zone 1 Receiver window midpoint* was selected by monitoring the round trip transit time of acoustic waves through the lead-in wire and the specimen. This transit time was measured to be approximately 500 μsec and 760 μsec for extensional and transverse waves through the polycrystalline gold specimens.

4. Transit Time Measurement at Room Temperature

The round trip transit time of acoustic waves through the specimen only (the desired information) is the difference between the round trip transit time through the lead-in wire/specimen combination and the round trip transit time through the lead-in wire only. The intervalometer was set to automatically calculate the round trip transit time of extensional waves through the specimen only, which was read directly from the intervalometer display. The temperature of the specimen was recorded from the digital thermometer attached to the thermocouple inside the large quartz tube.

5. Transit Time Measurements at Elevated Temperatures

After extensional and transverse wave round trip transit times were measured at room temperature, valves 1 and 3 were closed, valves 2 and 4 opened (see Figure 3, and the vacuum pump was turned on. When the pressure inside the large quartz tube approached zero, valve 2 (connecting the vacuum pump to the quartz tube) was closed and valve 1 (supplying argon gas to the quartz tube) was slightly opened. As the pressure within the quartz tube approached 760 torr (atmospheric), valve 1 was closed and valve 2 reopened to evacuate the quartz tube again. This process of alternately evacuating the quartz tube and then flushing it with argon was repeated five times over a period of approximately 30 minutes to eliminate air from the quartz tube. After the final flush with argon, valve 4 was closed and the vacuum pump switched off. Valve 1 was gradually opened to permit argon to enter the quartz tube until the pressure was slightly above atmospheric, at which time valve 3 (connecting the quartz tube to the outside exhaust) was opened. The argon gas exhausted to the outside first passed through oil in a flask so the rate of argon gas flowing through the quartz tube could be visually monitored (as bubbles through the

oil). The regulator valve on the argon gas tank was adjusted to insure a slow, steady flow of argon gas passed through the quartz tube during the experiment and to insure that atmospheric pressure was maintained around the specimens.

The furnace was then turned on and the temperature set to 473 K (200°C, the lowest setting). One hour later, when the deviation indicators on each furnace section indicated zero (i.e. thermal equilibrium was attained), the acoustic wave round trip transit time through the specimens and the specimen temperature were recorded. The furnace was then set to 523 K (250°C) and 30 minutes later (after thermal equilibrium) the round trip transit time and temperature were again recorded. This process of incrementally increasing the temperature, waiting for thermal equilibrium and then recording the temperature and round-trip transit time was repeated up to ≈ 1275 K. Measurements were made at ≈ 50 K intervals, except at higher temperatures (above 1000 K) where measurements were made in ≈ 10 –20 K intervals.

As the temperature increased, the length of the lead-in wire and specimen increased due to thermal expansion. Associated with this increase in length was an increase in the round trip transit time. Since the receiver window midpoints were set for the room temperature lead-in and specimen lengths, the echos of interest tended to shift out of the 50 μsec receiver windows at elevated temperatures — which prevented transit time measurements. To maintain the echos within the 50 μsec measurement windows, several adjustments of *Zone 0* and *Zone 1 Receiver window midpoints* were required as the furnace temperature was increased. At approximately 973 K, the extensional *Receiver window midpoints* (intervalometer channel 1) were set at 440 and 520 μsec for *Zone 0* and *Zone 1*, respectively. At approximately 1100 K, these windows were set at 450 and 540 μsec . At approximately 700 K, the transverse *Receiver window midpoints* (intervalometer

channel 2) were set at 650 μsec and 800 μsec for *Zone 0* and *Zone 1*, respectively. At approximately 1100 K, these windows were set at 680 μsec and 830 μsec .

Following the highest temperature round trip transit time measurements, the furnace temperature was decreased in 50 K intervals and transit time measurements made as the specimen cooled back to 473 K. The *Receiver window midpoints* were adjusted, as necessary, during cooling as the lead-in wire and specimen length decreased. When the specimen reached thermal equilibrium at 473 K, the furnace was switched off. Transit time and temperature measurements were then made at approximately 25 K intervals as the specimen slowly cooled to room temperature.

6. Calculation of Elastic Moduli from Transit Time Measurements

As 100 kHz frequency acoustic waves were used, the thin-line approximation was valid (50 – 400 kHz) for Young's modulus (E_Y) determination from transit time measurements. E_Y is related (Mason, 1958) to the velocity of extensional acoustic waves (v_e) through the specimen by

$$v_e = \left(\frac{E_Y}{\rho} \right)^{1/2} \left[1 - \left(\frac{\pi \sigma_y r}{\lambda} \right)^2 \right]$$

where ρ is the specimen density, σ_y is Poisson's ratio, r is the specimen radius and λ is the wavelength. For 100 kHz waves, $[(\pi \sigma_y r)/\lambda]^2 < 0.004$, so this term was neglected. The velocity of transverse waves (v_t) through the specimen is related to the shear modulus (G) by

$$v_t = K_t \left(\frac{G}{\rho} \right)^{1/2}$$

where K_t is a correction factor for the cross-sectional shape of the specimen. For specimens round in cross-section, the shape correction factor is unity. Thus the general expressions for calculating E_Y and G are

$$E_Y = \rho v_e^2 \quad \text{and} \quad G = \frac{\rho v_t^2}{K_t^2}$$

The room temperature density (ρ_{RT}) of the polycrystalline gold specimens was calculated from the measured specimen mass (m), room temperature length (l_{RT}) and room temperature radius (r_{RT}) using (Standard Test Method C559-79, 1983):

$$\rho_{RT} = \frac{m}{\pi r_{RT}^2 l_{RT}}$$

The room temperature extensional and transverse wave velocities were calculated using

$$v_e = \frac{2 l_{RT}}{t_e} \quad \text{and} \quad v_t = \frac{2 l_{RT}}{t_t}$$

where t_e and t_t are the round trip transit times of extensional and transverse waves through the polycrystalline gold specimens. Thus, at room temperature the elastic moduli of the polycrystalline gold specimens were calculated using

$$E_Y = \rho_{RT} \left(\frac{2 l_{RT}}{t_e} \right)^2$$

and

$$G = \frac{\rho_{RT}}{K_t^2} \left(\frac{2 l_{RT}}{t_t} \right)^2$$

The increase in specimen length at higher temperatures due to thermal expansion significantly affects the accuracy of E_Y calculations, so some correction is required. Since the coefficient of linear thermal expansion is not linearly dependent on temperature (Goldsmith *et al.*, 1961) and is thus not accurate for correcting the specimen length for the wide temperature range used, a more precise quadratic expression reported by Papadakis (1972) was used to correct the specimen length at all temperatures, given by

$$l = l_{RT} + l_{RT}[(B_0 \times 10^{-3}) + (B_1 \times 10^{-6})T + (B_2 \times 10^{-9})T^2]$$

or

$$l = l_{RT}[(B_0 \times 10^{-3}) + (B_1 \times 10^{-6})T + (B_2 \times 10^{-9})T^2 + 1]$$

where B_0 , B_1 and B_2 are tabulated quadratic coefficients for crystalline materials and T is the temperature of measurement in °C. The values and units of these coefficients for gold are: $B_0 = -0.357$; $B_1 = 14.208 \text{ } T^{-1}$; and $B_2 = 2.654 \text{ } T^{-2}$.

The radius of the specimens was also corrected for thermal expansion because as the radius increases, the volume increases. An increase in specimen volume will be accompanied by a decrease in specimen density, which is a factor in calculating E_Y and G . The specimen radius at any elevated temperature (r) was corrected from the measured room temperature radius, r_{RT} , using

$$r = r_{RT} + r_{RT}[(B_0 \times 10^{-3}) + (B_1 \times 10^{-6})T + (B_2 \times 10^{-9})T^2]$$

or,

$$r = r_{RT}[(B_0 \times 10^{-3}) + (B_1 \times 10^{-6})T + (B_2 \times 10^{-9})T^2 + 1]$$

The density of the specimen may be expressed in terms of the mass, radius and

length using: $\rho = m/\pi r^2 l$. Since mass is conserved, the specimen density will decrease as the specimen volume increases due to thermal expansion. If the terms in the brackets of the expressions above are represented by

$$\xi \equiv \left[(B_0 \times 10^{-3}) + (B_1 \times 10^{-6})T + (B_2 \times 10^{-9})T^2 + 1 \right]$$

Young's modulus was calculated for the wire-shaped specimens at any temperature substituting for ρ and v in: $E_Y = \rho v_e^2$, or

$$E_Y = \left(\frac{m}{\pi r^2 l} \right) \left(\frac{2l}{t_e} \right)^2$$

so that

$$\begin{aligned} E_Y &= \frac{4 m l^2}{\pi r^2 l t_e^2} \\ &= \frac{4 m [l_{RT} \xi]^2}{\pi [r_{RT} \xi]^2 l_{RT} \xi t_e^2} \\ &= \frac{4 m l_{RT}^2}{\pi r_{RT}^2 l_{RT} t_e^2} \frac{\xi^2}{\xi^3} \\ &= \frac{m}{\pi r_{RT}^2 l_{RT}} \frac{4 l_{RT}^2}{t_e^2} \frac{1}{\xi} \end{aligned}$$

or, finally

$$E_Y = \rho_{RT} \frac{4 l_{RT}^2}{t_e^2} \frac{1}{\xi}$$

This expression was used with the room temperature measurements of m (g), l (cm), r (cm) and ρ (g/cm³) to calculate the Young's modulus from the measured extensional wave round trip transit times (t_e) at the various temperatures. The units were converted from dynes/cm² to N/m² (Pa). Using similar calculations, the shear modulus of the polycrystalline gold specimen was calculated from the measured transverse wave round trip transit times at elevated temperatures using

$$G = \frac{\rho_{RT}}{K_t^2} \frac{4l_{RT}^2}{t_t^2} \frac{1}{\xi}$$

7. Regression Fits of Elastic Moduli Measurements

The calculated values of E_Y and G were plotted versus temperature for $300 \leq T \leq 1275$ K and fourth-order polynomials determined for these plots by regression analysis (least squares fitting). First-order (linear) regression was used to determined straight line fits for the calculated values of E_Y and G for $300 \leq T \leq 750$ K. These straight lines (E_L and G_L) were extrapolated into the high-temperature region of the plots. The *modulus defect* is the deviation of the data plots (E_Y and G) from the high-temperature extrapolation of the linear plots (E_L and G_L). The general form of the fourth-order polynomial fits to the polycrystalline data is

$$(E_Y, G) = \alpha + \beta T + \gamma T^2 + \delta T^3 + \epsilon T^4$$

where the regression coefficients are represented by α , β , γ , δ and ϵ . The general form of the first-order (linear) fits to the data is

$$(E_L, G_L) = \alpha + \beta T$$

E. MEASUREMENT OF SINGLE-CRYSTAL ELASTIC CONSTANTS

1. Specimens

Gold single-crystals (0.13 cm diameter $\times$ 8.0 cm long) were obtained commercially: one oriented in the [100] direction (J2564, Atomergic Chemetals Corp. Farmingdale, NY) and one oriented in the [110] direction (J2565, Atomergic). The orientations were verified by the supplier to $\pm 0.5^\circ$ using Laue back-reflection x-ray diffraction. The room temperature length, width and mass of each single-crystal was measured as with the polycrystalline gold specimens. The single-crystals were then welded to two separate (new) magnetostrictive lead-in wires for extensional wave transit time measurement, as previously described.

2. Experimental Apparatus

The same experimental apparatus was used to measure the single-crystal elastic constants, except new, small quartz tubes were utilized for the specimen/lead-in wires. Silicone adhesive was reapplied to the connections, as previously described.

3. Intervalometer Parameters and Settings

The parameters entered into the intervalometer were the same as with the polycrystalline gold specimen, except for the initial specimen lengths and receiver window midpoints. The receiver window midpoints were adjusted as necessary as the specimen temperature was increased (or decreased) during measurements.

4. Transit Time Measurement at Room Temperature

The round trip transit time was measured at room temperature using the technique previously described for polycrystalline specimens.

5. Transit Time Measurement at Elevated Temperatures

Round trip transit time of extensional waves through each single-crystal was measured up to ≈ 1275 K, as described for polycrystalline specimens.

After measurement of the extensional wave round trip transit times, the single-crystals were detached from the lead-in wires. The end of the [100] crystal that was previously welded to the lead-in wire was repolished to remove remnants of the weld joint. The end of the lead-in wire was also polished to remove remnants of the weld joint. The length and mass of the [100] crystal was then remeasured. It was reannealed and then rewelded to the opposite end of the same lead-in wire for transverse wave measurements. Round trip transit times of transverse waves through the [100] single-crystal were then measured up to ≈ 1275 K.

6. Calculation of Elastic Constants from Transit Time Measurements

The round-trip transit time measurements were used to calculate the v_e and v_t in the [100] crystal and v_e in the [110] orientation crystal. These velocities were then used to calculate the single-crystal elastic constants (c_{ij}) using

$$c_{ij} = \rho v^2$$

where the c_{ij} are c_{11} , c_{12} and c_{44} (for crystals of cubic symmetry), ρ is the density, v is the velocity of extensional (v_e) or transverse (v_t) acoustic wave propagation. The extensional and transverse wave velocities in the [ijk] – directions, for particular crystal orientations, are related to the c_{ij} by (Musgrave, 1970)

$$c_{11} = \rho (v_{100e})^2$$

$$c_{44} = \rho(v_{100t})^2$$

$$c_{12} = 2 \left[\rho(v_{110e})^2 \right] - c_{11} - 2c_{44}$$

or

$$c_{12} = 2c_{110e} - c_{11} - 2c_{44}$$

where

$$c_{110e} \equiv \left[\rho(v_{110e})^2 \right]$$

and v_{100e} is the extensional wave velocity in the [100] direction, v_{100t} is the transverse wave velocity in the [100] direction and v_{110e} is the extensional wave velocity in the [110] direction. The quantity $c_{110e} \equiv [\rho(v_{110e})^2]$ and the elastic constants c_{11} and c_{44} were obtained directly from the round trip transit time measurements.

7. Regression Fits of Single-Crystal Elastic Constant Measurements

The values of c_{11} , c_{44} and c_{110e} , calculated from round trip transit time measurements, were plotted versus temperature for $300 \leq T \leq 1275$ K. Fourth-order polynomials were determined for these three plots by regression analysis. The polynomial equations for c_{11} , c_{44} and c_{110e} were combined to calculate c_{12} at 25 K intervals over the same temperature range. The bulk modulus (B) was calculated at 25 K intervals for $300 \leq T \leq 1275$ K from the fourth-order fits to the c_{ij} using

$$B = \frac{c_{11} + 2c_{12}}{3}$$

Fourth-order polynomials were then fitted to the plots of c_{12} and B versus temperature for $300 \leq T \leq 1275$ K.

First-order (linear) regression was used to determined straight line fits for the calculated values of c_{11} , c_{44} , c_{110e} , c_{12} and B for the temperature range $300 \leq T \leq 750$ K. These straight lines were extrapolated into the high-temperature region of the plots. The *modulus defect* is the deviation of the data plots from the high-temperature extrapolation of the linear plots. The general form of the fourth-order polynomial fits to the data is

$$(c_{ij}, c_{110e}, B) = \alpha + \beta T + \gamma T^2 + \delta T^3 + \epsilon T^4$$

where the regression coefficients are represented by α , β , γ , δ and ϵ . The general form of the first-order (linear) fits to the data is

$$(c_{ij_L}, c_{110e_L}, B_L) = \alpha + \beta T$$

F. AVERAGING OF SINGLE-CRYSTAL ELASTIC CONSTANTS

The single-crystal c_{ij} (obtained from the fourth-order polynomial fits) were averaged at 25 K intervals to estimate the elastic properties of polycrystalline aggregates. Several averaging methods were used. The most straightforward of these methods were proposed by Voigt and Reuss (Hearmon, 1956), given by

$$E_V = \frac{(c_{11} - c_{12} + 3c_{44}) (c_{11} + 2c_{12})}{2c_{11} + 3c_{12} + c_{44}}$$

$$G_V = \frac{c_{11} - c_{12} + 3c_{44}}{5}$$

$$E_R = \frac{5 c_{44} (c_{11} - c_{12}) (c_{11} + 2c_{12})}{c_{11}^2 + c_{11}c_{12} - 2c_{12}^2 + 3c_{44}c_{11} + c_{44}c_{12}}$$

$$G_R = \frac{5c_{44} (c_{11} - c_{12})}{4c_{44} + 3(c_{11} - c_{12})}$$

where the V and R subscripts indicate the Voigt and Reuss methods for determining Young's modulus (E_V and E_R) and shear (G_V and G_R) modulus. The arithmetic and geometric averages of the Voigt and Reuss averages were also calculated from the single-crystal c_{ij} , as suggested by Hill (1952), at 25 K intervals using

$$G_{VRH-g} = (G_V G_R)^{1/2} \quad \text{and} \quad G_{VRH-a} = \frac{1}{2} (G_V + G_R)$$

where G_{VRH-a} and G_{VRH-g} represent Hill's arithmetic and geometric averages of the Voigt and Reuss shear modulus averages. Hill's averaging technique was also applied to Young's modulus (E_{VRH-a} and E_{VRH-g}) at 25 K intervals.

The Young's and shear moduli determined by Voigt (E_V and G_V) and Reuss (E_R and G_R) averaging of the single-crystal elastic constants were plotted versus temperature for $300 \leq T \leq 1275$ K. The arithmetic and geometric averaging methods proposed by Hill were also plotted (E_{VRH-a} , E_{VRH-g} , G_{VRH-a} , G_{VRH-g}). Fourth-order polynomials were determined for these eight plots by regression analysis. For comparison, high-temperature measurements of E_V for polycrystalline Au reported by Köster (1948), along with the measured values of E_V for polycrystalline Au reported in this work, are included on the graphs.

The single-crystal c_{ij} (obtained from the fourth-order polynomial fits) were also averaged at 300 K according to the method proposed by Ledbetter and Naiman (1974)

$$E_{LN} = \frac{3 G_{LN}}{1 + (G_{LN}/3B)}$$

and at 25 K intervals using the method proposed by Aleksandrov (1966)

$$G_A = (c_{44})^{3/5} \left(\frac{c_{11} - c_{12}}{2} \right)^{2/5}$$

G. TRANSIT TIME MEASUREMENT OF EXTENSIONAL AND TRANSVERSE WAVES THROUGH SINGLE-CRYSTALS AT DIFFERENT FREQUENCIES

The measurement of acoustic wave round trip transit time through the single-crystals was repeated at 50 kHz, 200 kHz and 500 kHz frequencies at selected temperatures to determine if dispersion occurred. The round trip transit time of transverse waves through the [100] crystal and extensional waves through the [110] crystal were measured and the corresponding elastic constants (c_{44} and c_{110e} ; though c_{110e} is not a true elastic constant) calculated as previously described. The variation with frequency was well within the experimental error for all calculated values at all temperatures of measurement.

III. EXPERIMENTAL RESULTS

A. SPECIMEN MEASUREMENTS AT ROOM TEMPERATURE

The room temperature specimen dimensions, mass, density, sound velocity and wavelength of sound waves are listed in Table II for polycrystals and single-crystals. The [100] crystal is listed twice because the length and mass decreased after it was separated from the extensional lead-in wire and the end polished before welding it to the transverse lead-in wire.

Table II
Room Temperature Specimen Dimensions
Mass, Density, Sound Velocity and Wavelength

	l (cm)	d (cm)	m (g)	ρ (g/cm ³)	v (m/s)	λ (cm)
E_Y	7.438	0.13	1.9030	19.276	1991	1.991
G	8.458	0.13	2.1640	19.283	1171	1.171
[100] _e	8.068	0.13	2.0693	19.323	1947	1.947
[100] _t	7.789	0.13	1.9983	19.329	1361	1.361
[110] _e	7.959	0.13	2.0417	19.327	2083	2.083

l = length
 d = diameter
 m = mass
 ρ = density
 v = sound velocity
 λ = wavelength

B. POLYCRYSTALLINE SPECIMENS

1. Regression Analysis

The coefficients for the first-order (linear) and the fourth-order polynomial regression fits to these plots are presented in Table III.

2. Data Presentation

The round trip extensional wave transit time measurements made on the polycrystalline specimens for $300 \leq T \leq 1275$ K, along with the calculated values of E_Y and G , are presented in Tables IV and V, respectively (pages 73 and 74). The plots of E_Y ($\circ$) and G ($\square$) for this temperature range are presented in Figures 6 and 7, respectively (pages 87 and 88). The smooth curves connecting the data points in these two plots are the fourth-order polynomials fitted to the data by regression analysis. First-order (linear) regression fits to the calculated values of E_Y and G for $300 \leq T \leq 750$ K are represented by the dashed lines that extend to the left and right ordinate axes of each figure.

C. SINGLE-CRYSTAL SPECIMENS

1. Regression Analysis

The coefficients for the first-order (linear) and the fourth-order polynomial regression fits to c_{11} , c_{44} , c_{110e} , c_{12} and B are presented in Table III (page 72).

2. Data Presentation: c_{11} , c_{44} and c_{110e}

The round trip extensional wave transit time measurements made on the [100] and [110] single-crystal specimens for $300 \leq T \leq 1275$ K, along with the calculated values of c_{11} , c_{44} and c_{110e} are presented in Tables VI, VII and VIII, respectively (pages 75 – 77). The plots of c_{11} (Δ), c_{44} (∇) and c_{110e} ($\diamond$) for this temperature range

are presented in Figures 8, 9 and 10, respectively (pages 89 – 91). The smooth curves connecting the data points in these plots are the fourth–order polynomials fitted to the data by regression analysis. First–order (linear) regression fits to the calculated values of c_{11} , c_{44} and c_{110e} for $300 \leq T \leq 750$ K are represented by the dashed lines that extend to the left and right ordinate axes of each figure.

3. Calculated Elastic Properties: c_{12} and B

Plots of the fourth–order polynomials calculated for c_{12} and B from the regression fits to experimentally obtained values of c_{11} , c_{44} and c_{110e} , are presented in Figures 11 and 12, respectively (pages 92 and 93). The apparent non–linear behavior (increasing values) in the low–temperature region is due to the curve–fitting procedure and not the data. First–order (linear) regression fits to c_{12} and B for $300 \leq T \leq 750$ K are represented by the dashed lines that extend to the left and right ordinate axes of each figure.

D. AVERAGING OF SINGLE–CRYSTAL ELASTIC CONSTANTS

1. Regression Analysis

The coefficients for the fourth–order polynomial regression fits to E_V , G_V , E_R , G_R , E_{VRH-a} , E_{VRH-g} , G_{VRH-a} , G_{VRH-g} and G_A , obtained by averaging the measured Au single–crystal elastic constants, are presented in Table IX (page 78).

2. Data Presentation

The fourth–order polynomial regression fits to E_V , E_R , E_{VRH-a} and E_{VRH-g} , obtained by averaging the measured Au single–crystal elastic constants, are plotted as heavy, solid lines in Figure 13 (page 94). For comparison, the measurements of E_V (○) for polycrystalline Au reported in this work, and the measurements of E_V (●)

for polycrystalline Au reported by Köster (1948) are also plotted in Figure 13.

The fourth-order polynomial regression fits to G_V , G_R , G_{VRH-a} and G_{VRH-g} , obtained by averaging the measured Au single-crystal elastic constants, are plotted as heavy, solid lines in Figure 14 (page 95). Values of the Aleksandrov averages, G_A ($\circ$), in 100 K intervals, obtained from the fourth-order polynomial regression fits to the measured Au single-crystal elastic constants, are also plotted in Figure 14. The values of G_A are essentially the same as those of G_{VRH-a} , as can be seen from Figure 14 and the regression coefficients for G_A in Table IX. For comparison, the measurements of G ($\square$) for polycrystalline Au reported in this work are also plotted in Figure 14.

E. TRANSIT TIME MEASUREMENTS AT DIFFERENT WAVE FREQUENCIES

The c_{ij} calculated from transit time measurements in the two single crystals at 50 kHz, 200 kHz and 500 kHz frequencies are presented in Table X and plotted in Figure 15 (page 96). The calculated values for each frequency at each temperature were within the experimental error, indicating that dispersion did not occur in the single crystals.

Table III
Regression Coefficients for Polynomial and
Linear Fits to Gold Elastic Moduli/Constants

	α	β ($\times 10^{-4}$)	γ ($\times 10^{-7}$)	δ ($\times 10^{-10}$)	ϵ ($\times 10^{-13}$)
E_Y	0.8486	-2.6726	-0.6579	1.8372	-1.3490
E_L	0.8454	-2.6459			
G	0.2853	-0.5019	-1.0286	1.3848	-0.7448
G_L	0.2923	-0.9094			
c_{11}	2.0353	-4.1584	1.6783	-0.7636	-0.5013
c_{11L}	2.0261	-3.4002			
c_{12}	1.7429	-3.9784	0.4360	2.5998	-1.8631
c_{12L}	1.6957	-2.3393			
c_{44}	0.4500	-0.2878	-2.7952	3.1533	-1.3190
c_{44L}	0.4653	-1.3723			
c_{110e}	2.3391	-4.3562	-1.7381	4.0714	-2.5012
c_{110eL}	2.3307	-4.3353			
B	1.8404	-4.0384	0.8501	1.4787	-1.4092
B_L	1.8104	-2.7885			

Table IV
Round Trip Transit Time and Calculated
Young's Modulus for $300 \leq T \leq 1275$ K

T (°C)	T (K)	t (μ sec)	EY ($\text{N/m}^2 \times 10^{-11}$)
23	296	74.596	0.76661
35	308	74.744	0.76559
79	352	75.338	0.75308
92	365	75.513	0.74945
128	401	76.079	0.73795
167	440	76.594	0.72764
193	466	76.922	0.72116
225	498	77.346	0.71293
256	529	77.727	0.70562
305	578	78.443	0.69226
351	624	79.110	0.68014
357	630	79.103	0.68020
399	672	79.801	0.66790
437	710	80.324	0.65882
452	725	80.743	0.65184
484	757	81.120	0.64545
530	803	81.991	0.63132
538	811	82.161	0.62863
575	848	82.881	0.61736
618	891	83.849	0.60275
623	896	83.969	0.60097
663	936	84.901	0.58744
707	980	86.011	0.57193
713	986	86.261	0.56856
752	1025	87.368	0.55386
773	1046	88.158	0.54377
796	1069	88.921	0.53425
824	1097	89.856	0.52293
850	1123	90.899	0.51075
870	1143	91.736	0.50129
880	1153	92.206	0.49610
896	1169	92.905	0.48851
909	1182	93.406	0.48317
925	1198	94.323	0.47368
930	1203	94.656	0.47031
938	1211	95.166	0.46521
953	1226	95.971	0.45731
965	1238	96.786	0.44954
976	1249	97.580	0.44216
981	1254	98.041	0.43797
992	1265	98.872	0.43055
1006	1279	100.156	0.41946

Table V
Round Trip Transit Time and Calculated
Shear Modulus for $300 \leq T \leq 1275$ K

T (°C)	T (K)	t (μ sec)	G (N/m ² $\times 10^{-11}$)
22	295	144.500	0.26427
41	314	144.784	0.26317
82	355	145.900	0.25900
95	368	146.050	0.25842
113	386	146.450	0.25694
135	408	146.900	0.25529
154	427	147.326	0.25374
171	444	147.683	0.25245
174	447	147.717	0.25232
196	469	148.605	0.24923
218	491	148.994	0.24785
231	504	149.397	0.24647
244	517	149.515	0.24603
253	526	150.004	0.24439
300	573	151.292	0.24007
353	626	152.500	0.23609
383	656	153.227	0.23374
418	691	154.381	0.23013
434	707	154.695	0.22913
453	726	155.486	0.22674
475	748	156.136	0.22477
536	809	158.300	0.21844
586	859	160.122	0.21332
606	879	160.787	0.21148
630	903	161.885	0.20854
642	915	162.445	0.20706
697	970	165.011	0.20048
710	983	165.528	0.19918
755	1028	168.442	0.19219
800	1073	171.652	0.18492
849	1122	175.097	0.17756
891	1164	179.904	0.16806
939	1212	184.611	0.15946
975	1248	189.684	0.15094
982	1255	190.842	0.14909
990	1263	191.718	0.14771
1004	1277	194.383	0.14365

Table VI
Round Trip Transit Time and Calculated
 c_{11} for $300 \leq T \leq 1275$ K

T (° C)	T (K)	t (μ sec)	c_{11} (N/m ² × 10 ⁻¹¹)
21	294	82.858	1.92636
35	308	83.011	1.91887
79	352	83.269	1.90577
92	365	83.390	1.89989
130	403	83.600	1.88929
167	440	83.819	1.87839
183	456	83.987	1.87043
223	496	84.226	1.85870
256	529	84.439	1.84839
275	548	84.652	1.83856
305	578	84.830	1.82999
351	624	85.106	1.81681
399	672	85.581	1.79531
431	704	85.861	1.78269
475	748	86.134	1.77012
498	771	86.292	1.76297
522	795	86.630	1.74853
555	828	86.815	1.74012
580	853	87.095	1.72821
608	881	87.197	1.72334
650	923	87.805	1.69831
671	944	88.103	1.68622
700	973	88.402	1.67398
723	996	88.630	1.66470
741	1014	88.900	1.65407
755	1028	89.150	1.64439
773	1046	89.413	1.63420
800	1073	89.785	1.61989
825	1098	90.093	1.60810
835	1108	90.245	1.60239
850	1123	90.421	1.59572
870	1143	90.902	1.57829
880	1153	91.075	1.57201
887	1160	91.277	1.56485
909	1182	91.562	1.55449
930	1203	91.946	1.54092
938	1211	92.122	1.53481
952	1225	92.370	1.52617
967	1240	92.816	1.51111
990	1263	93.197	1.49812
1006	1279	93.570	1.48575
1012	1285	93.822	1.47761

Table VII
Round Trip Transit Time and Calculated
 c_{44} for $300 \leq T \leq 1275$ K

T (°C)	T (K)	t (μ sec)	c_{44} ($\text{N/m}^2 \times 10^{-11}$)
21	294	114.466	0.42446
41	314	114.788	0.42196
87	360	115.569	0.41600
120	393	116.210	0.41123
132	405	116.359	0.41010
164	437	116.911	0.40604
174	447	117.132	0.40445
219	492	117.949	0.39859
249	522	118.634	0.39382
274	547	119.219	0.38982
324	597	120.000	0.38446
350	623	120.593	0.38053
383	656	121.540	0.37442
418	691	122.258	0.36983
434	707	122.550	0.36797
496	769	123.935	0.35942
525	798	124.598	0.35543
561	834	125.330	0.35108
583	856	125.821	0.34821
605	878	126.495	0.34438
619	892	126.785	0.34273
630	903	127.056	0.34120
660	933	128.023	0.33589
711	984	129.447	0.32824
723	996	129.803	0.32638
755	1028	131.017	0.32017
789	1062	132.300	0.31380
802	1075	132.745	0.31163
816	1089	133.115	0.30982
831	1104	133.988	0.30571
847	1120	134.800	0.30195
857	1130	135.153	0.30032
889	1162	136.760	0.29313
895	1168	137.147	0.29144
914	1187	138.180	0.28700
939	1212	139.550	0.28126
943	1216	139.872	0.27994
954	1227	140.428	0.27767
963	1236	141.000	0.27538
975	1248	141.957	0.27161
986	1259	142.513	0.26944
999	1272	143.752	0.26475

Table VIII
Round Trip Transit Time and Calculated
 c_{110e} for $300 \leq T \leq 1275$ K

T (°C)	T (K)	t (μsec)	c_{110e} (N/m ² × 10 ⁻¹¹)
21	294	76.422	2.2041
35	308	76.507	2.1988
79	352	76.893	2.1754
95	368	76.954	2.1715
130	403	77.177	2.1578
164	437	77.468	2.1405
183	456	77.580	2.1337
219	492	77.877	2.1163
256	529	78.153	2.1002
305	578	78.517	2.0792
330	603	78.687	2.0694
357	630	78.905	2.0571
380	653	79.066	2.0480
417	690	79.351	2.0320
452	725	79.612	2.0176
484	757	79.850	2.0045
538	811	80.252	1.9827
580	853	80.677	1.9605
614	887	80.918	1.9477
650	923	81.231	1.9315
673	946	81.558	1.9152
700	973	81.781	1.9039
722	995	82.122	1.8874
741	1014	82.326	1.8774
755	1028	82.486	1.8697
773	1046	82.712	1.8588
788	1061	82.913	1.8494
811	1084	83.185	1.8365
835	1108	83.605	1.8173
850	1123	83.765	1.8099
870	1143	84.111	1.7943
887	1160	84.347	1.7837
896	1169	84.518	1.7762
909	1182	84.704	1.7680
929	1202	85.129	1.7498
938	1211	85.247	1.7446
952	1225	85.534	1.7325
965	1238	85.812	1.7208
976	1249	86.114	1.7084
981	1254	86.204	1.7047
990	1263	86.464	1.6942
1006	1279	86.912	1.6762

Table IX
Gold
Regression Coefficients for
Averages of Single-crystal Elastic Constants
vs. Temperature

	α	β ($\times 10^{-4}$)	γ ($\times 10^{-7}$)	δ ($\times 10^{-10}$)	ϵ ($\times 10^{-13}$)
E_V	0.9298	-0.6561	-3.8281	3.3373	-1.4514
E_R	0.7162	-1.1217	1.7301	-4.4248	1.5745
E_{VRH-a}	0.8230	-0.8889	-1.0490	-0.5437	0.0616
E_{VRH-g}	0.8172	-0.9957	-0.5686	-1.1363	0.2696
G_V	0.3285	-0.2087	-1.4287	1.2193	-0.5191
G_R	0.2491	-0.3539	0.5584	-1.5662	0.5718
G_{VRH-a}	0.2888	-0.2813	-0.4351	-0.1735	0.0264
G_{VRH-g}	0.2865	-0.3197	-0.2552	-0.3975	0.1058
G_A	0.2890	-0.3024	-0.3695	-0.2455	0.0488

Table X
Variation of Elastic Constants
With Wave Frequency

T(K)	$c_{44} (\times 10^{-11} \text{ N/m}^2)$		
	50 kHz	200 kHz	500 kHz
298	0.42349	0.42226	0.42128
597	0.38430	0.38189	0.38362
794	0.35712	0.35837	0.35390
977	0.32784	0.32684	0.32691
1070	0.31135	0.31250	0.31206
1164	0.28919	0.29091	0.28849

T(K)	$c_{110e} (\times 10^{-11} \text{ N/m}^2)$		
	50 kHz	200 kHz	500 kHz
298	2.19742	2.19804	2.19967
597	2.07541	2.07236	2.06900
790	1.99027	1.98766	1.99073
979	1.89264	1.89564	1.89778
1068	1.83372	1.83712	1.83319
1165	1.76130	1.76721	1.76096

F. PREVIOUSLY REPORTED MEASUREMENTS:

POLYCRYSTALLINE GOLD ELASTIC CONSTANTS

Values of E_Y reported in this work are plotted in Figure 13 (page 94) with small (o) symbols. Dynamic values of E_Y obtained from similar measurements using the ultrasonic resonance technique, as reported by Köster (1948), are plotted in Figure 13 with small (•) symbols. As in the previous plots, the dashed lines (E_L) represent first-order (linear) regression fits to the low-temperature ($300 \leq T \leq 750$ K) data, making the high-temperature modulus defect evident for both E_Y plots.

There is obviously good agreement between the values of E_Y reported here and the values of E_Y previously reported by Köster for high temperatures ($T \geq 1000$ K). The agreement is not as good for lower temperatures. This may be due to the thermomechanical history of Köster's Au specimens, since the annealing procedure was not discussed with his results (i.e. there may have been some texture remaining in the specimen from cold working, which would increase the lower temperature values of E_Y). At higher temperatures, due to annealing, this difference would be expected to diminish as it does. The fact that the low temperature plots (E_L) are essentially parallel lends plausibility to this explanation.

The room temperature value of E_Y reported in this work (0.767×10^{11} N/m²) and that reported by Köster (0.791×10^{11} N/m²) are both well within the range of values reported in the literature — though values of E_Y reported in the literature (usually in tables of properties in handbooks) vary considerably. Tracing the original sources of these values to review the techniques employed has proven to be exceedingly difficult and impossible in some cases (Baker, 1991). Many of the values located could be traced back to Köster's work. The room temperature values of E_Y which have been reported are presented in Table XI.

Table XI
Reported Values of Room Temperature
Young's Modulus

$E_Y (\times 10^{-11} \text{ N/m}^2)$	Reference
0.780	Carapella, 1979, 1990
0.745	Lynch, 1989
0.800	Metals Reference Book, 1983
0.745	Bard, 1979
0.786	Albert, 1965
0.745	Roeser and Cochrane, 1961

G. PREVIOUSLY REPORTED MEASUREMENTS:

SINGLE-CRYSTAL GOLD ELASTIC CONSTANTS

Plots of all values of the c_{ij} (c_{11} , c_{12} , c_{44}), c_{110e} , B and polycrystalline elastic moduli (E_Y and G) reported in this work, as calculated from measured transit times in the Au single crystals and regression fits to the data, are presented in Figure 16 (page 97). The plot labeled c_{11} includes values calculated from extensional wave velocity measurements through the $[100]$ -oriented single-crystal for $300 \leq T \leq 1275$ K, as reported in this work, represented by small, hollow (Δ) symbols. Values of c_{11} for $300 \leq T \leq 550$ K, reported by Chang and Himmel (1966), are presented on the same plot and are represented by large, solid (Δ) symbols. Values of c_{11} for $0 \leq T \leq 300$ K, reported by Neighbours and Alers (1958), are also presented on the same plot and are represented by large, hollow (Δ) symbols.

The plot labeled c_{44} in Figure 16 includes values calculated from transverse wave velocity measurements through the $[100]$ -oriented single-crystal for

$300 \leq T \leq 1275$ K, as reported in this work, represented by small, hollow (∇) symbols. Values of c_{44} for $300 \leq T \leq 550$ K, reported by Chang and Himmel (1966), are presented on the same plot and are represented by large, solid (∇) symbols. Values of c_{44} for $0 \leq T \leq 300$ K, reported by Neighbours and Alers (1958), are also presented on the same plot and are represented by large, hollow (∇) symbols.

The plot labeled c_{110e} in Figure 16 includes values calculated from extensional wave velocity measurements in the $[110]$ oriented single-crystal for $300 \leq T \leq 1275$ K, as reported in this work, represented by small, hollow ($\diamond$) symbols. This quantity, which is not a true elastic constant, is used with experimentally obtained values of c_{11} and c_{44} to calculate c_{12} , as previously described. Values of c_{110e} for $300 \leq T \leq 550$ K, calculated from values of c_{11} , c_{12} and c_{44} reported by Chang and Himmel (1966), are presented on the same plot and are represented by large, solid ($\diamond$) symbols. Values of c_{110e} for $0 \leq T \leq 300$ K, calculated from values of c_{11} , c_{12} and c_{44} reported by Neighbours and Alers (1958), are also presented on the same plot and are represented by large, hollow ($\diamond$) symbols.

The fourth-order polynomial representing c_{12} , calculated from the regression fits to experimentally measured c_{11} , c_{44} and c_{110e} reported in this work, is presented as a heavy, solid line labeled c_{12} in Figure 16. Values of c_{12} reported by Chang and Himmel (1966) are indicated with large, solid ($\circ$) symbols. Values of c_{12} reported by Neighbours and Alers (1958) are indicated with large, hollow ($\circ$) symbols.

The fourth-order polynomial representing the bulk modulus (B), calculated from the regression fits to experimentally measured c_{11} and the fourth-order polynomial representing c_{12} reported in this work, is presented as a heavy, solid line labeled B in Figure 16. Values of B calculated from the c_{ij} reported by Chang and Himmel (1966) are represented with large, filled ($\square$) symbols. Values of B calculated from the c_{ij} reported by Neighbours and Alers (1958) are represented with large,

hollow ($\square$) symbols.

As can be seen in Figure 16, the c_{ij} determined experimentally in this work agree exceptionally well with previously reported values for low temperatures. All the c_{ij} are essentially linear functions of temperature between 250 and 850 K, as seen in Figure 16. At very low temperatures ($T \rightarrow 0$ K), as dictated by the Third Law of Thermodynamics, the c_{ij} approach a constant value, with $(\partial c_{ij} / \partial T) = 0$ at this limit.

H. PREVIOUSLY REPORTED MEASUREMENTS:

POLYCRYSTALLINE AND SINGLE-CRYSTAL Al

ELASTIC CONSTANTS

Aluminum is one of the few other *fcc* metals for which the c_{ij} have been measured at elevated temperatures. Values of c_{11} , c_{12} , c_{44} and B for Al up to 930 K, reported by Gerlich and Fisher (1969), are plotted in Figure 17 (page 98). Fourth-order polynomials were calculated for each of these plots using regression analysis for $300 \leq T \leq 925$ K. The fourth-order polynomial is the solid line for each labeled c_{ij} (c_{11} , c_{12} , c_{44}) and for B in Figure 17. The Voigt, Reuss and Hill averaging techniques were applied to the Al c_{ij} reported by Gerlich and Fisher to determine E_V , E_R , E_{VRH-a} and E_{VRH-g} , which are plotted in Figure 18 (page 99). A fourth-order polynomial regression fit to experimentally measured values of E_V for polycrystalline aluminum, reported by McLellan and Ishikawa (1987), is also plotted in Figure 18.

The Voigt, Reuss and Hill averaging techniques were applied to the Al c_{ij} reported by Gerlich and Fisher to determine G_V , G_R , G_{VRH-a} and G_{VRH-g} , which are plotted in Figure 19 (page 100). The Aleksandrov averaging technique was also applied to the Al c_{ij} and values (G_A), represented by ($\circ$) are presented at 100 K

intervals in Figure 19. A fourth-order polynomial regression fit to experimentally measured values of G for polycrystalline aluminum, reported by McLellan and Ishikawa (1987), is also plotted in Figure 19.

From the plots, it is readily seen that the shapes of the corresponding c_{ij} plots for Au (Figure 16) and Al (Figure 17) are similar insofar as there is a pronounced departure from linearity in the c_{11} and c_{12} plots above $0.5 T_m$, while the departure from linearity is much less pronounced in the c_{44} plots.

Fourth-order polynomials were calculated for each plot in Figures 17, 18 and 19, using regression analysis for $300 \leq T \leq 925$ K. The fourth-order polynomial is the solid line for each labeled plot (c_{ij} , B , E_Y , E_V , E_R , E_{VRH-a} , E_{VRH-g} , G , G_V , G_R , G_{VRH-a} , G_{VRH-g} , and G_A). First-order (linear) fits were also calculated for each plot in Figures 17, 18 and 19, using regression analysis for $400 \leq T \leq 700$ K. The linear fits are represented by dashed lines that extend to each ordinate axis in Figures 17, 18 and 19.

The general form for each fourth-order regression fit is

$$(c_{ij}, B) = \alpha + \beta T + \gamma T^2 + \delta T^3 + \epsilon T^4$$

$$(E_Y, E_V, E_R, E_{VRH-a}, E_{VRH-g}) = \alpha + \beta T + \gamma T^2 + \delta T^3 + \epsilon T^4$$

$$(G, G_V, G_R, G_{VRH-a}, G_{VRH-g}, G_A) = \alpha + \beta T + \gamma T^2 + \delta T^3 + \epsilon T^4$$

where α , β , γ , δ and ϵ are the coefficients. The general form for each first-order (linear) fit is

$$(c_{ijL}, B_L) = \alpha + \beta T$$

$$(E_{YL}, E_{VL}, E_{RL}, E_{VRH-aL}, E_{VRH-gL}) = \alpha + \beta T$$

$$(G_L, G_{VL}, G_{RL}, G_{VRH-aL}, G_{VRH-gL}, G_{AL}) = \alpha + \beta T$$

where the L superscript indicates "linear" fits. The regression coefficients of (E_Y , G , B and c_{ij}) and (E_V , E_R , E_{VRH-a} , E_{VRH-g} , G_V , G_R , G_{VRH-a} , G_{VRH-g} , and G_A) are presented in Tables XII and XIII, respectively.

Table XII
Regression Coefficients for Polynomial and
Linear Fits to Aluminum Elastic Moduli/Constants

	α	β ($\times 10^{-4}$)	γ ($\times 10^{-7}$)	δ ($\times 10^{-10}$)	ϵ ($\times 10^{-13}$)
E_Y	0.6645	9.8684	-46.812	69.738	-37.901
E_L	0.8060	-3.6672			
G	0.3653	-5.8826	11.795	-12.326	3.6885
G_L	0.3160	-1.6371			
c_{11}	1.0401	6.5038	-26.714	29.262	-11.987
c_{11L}	1.1991	-4.2284			
c_{12}	0.6176	-0.1256	-1.4761	1.1538	-0.4804
c_{12L}	0.6360	-1.0076			
c_{44}	0.2965	0.5862	-4.7533	4.5725	-1.7080
c_{44L}	0.3326	-1.5887			
B	0.7584	2.0842	-9.8889	10.523	-4.3159
B_L	0.8237	-2.0812			

Table XIII
Aluminum
Regression Coefficients for
Averages of Single-crystal Elastic Constants
vs. Temperature

	α	β ($\times 10^{-4}$)	γ ($\times 10^{-7}$)	δ ($\times 10^{-10}$)	ϵ ($\times 10^{-13}$)
E_V	0.7050	4.2968	-20.099	21.235	-8.4798
E_{VL}	0.8335	-4.0877			
E_R	0.6874	5.2759	-22.998	24.699	-9.9800
E_{RL}	0.8296	-4.1536			
E_{VRH-a}	0.6962	4.7863	-21.548	22.967	-9.2299
E_{VRH-aL}	0.8315	-4.1206			
E_{VRH-g}	0.6962	4.7907	-21.561	22.983	-9.2370
E_{VRH-gL}	0.8315	-4.1209			
G_V	0.2624	1.6776	-7.8996	8.3651	-3.3262
G_{VL}	0.3122	-1.5974			
G_R	0.2553	2.0670	-9.0509	9.7413	-3.9209
G_{RL}	0.3104	-1.6218			
G_{VRH-a}	0.2588	1.8723	-8.4753	9.0532	-3.6235
G_{VRH-aL}	0.3113	-1.6096			
G_{VRH-g}	0.2588	1.8742	-8.4809	9.0600	-3.6266
G_{VRH-gL}	0.3113	-1.6097			
G_A	0.2589	1.8688	-8.4648	9.0406	-3.6181
G_{AL}	0.3113	-1.6093

Figure 6

Measured Young's Modulus for Polycrystalline Au

Figure 7
Measured Shear Modulus for Polycrystalline Au

Figure 8
Measured c_{11} for Au Single-Crystal

Figure 9
Measured c_{44} for Au Single-Crystal

Figure 10

Measured c_{110e} for Au Single-Crystal

Figure 11
Calculated c_{12} for Au Single-Crystals

Figure 12
Calculated Bulk Modulus for Au Single-Crystals

Figure 13

Measured Young's Modulus for Polycrystalline Au and
Averaged Au Single-Crystal Elastic Constants

Figure 14

Measured Shear Modulus for Polycrystalline Au and
Averaged Au Single-Crystal Elastic Constants

Figure 15

Frequency Dependence of Extensional and Transverse Wave
Velocity Measurements in Au Single-Crystals

Figure 16

Measured Au Single-Crystal Elastic Constants and
Similar Values Reported by Other Investigators

Figure 17

Measured Single-Crystal Elastic Constants of Al

Reported by Gerlich and Fischer (1969)

Figure 18

Young's Modulus for Polycrystalline Al (McLellan and Ishikawa, 1987) and Averaged Single-Crystal Elastic Constants of Al (Gerlich and Fischer, 1969)

Figure 19

Shear Modulus for Polycrystalline Al (McLellan and Ishikawa, 1987) and
 Averaged Single-Crystal Elastic Constants of Al (Gerlich and Fischer, 1969)

V. DISCUSSION

A primary motivation of this work was to study the relationship between the presence of grain boundaries in *fcc* metals and the observation of a *modulus defect*. Thus, it was important to determine to what extent deviations in polycrystalline E_V and G are due to the intrinsic variation with temperature of the single-crystal c_{ij} , i.e. the crystal lattice. This determination is not straightforward even when the c_{ij} show a linear temperature dependence. As can be seen in Figure 18, even the large E_V modulus defect in polycrystalline Al is not entirely due to grain-boundary relaxation.

The central problem is the translation of c_{ij} data into an equivalent elastic parameter for polycrystalline aggregates. Such quantities may be thought of as the moduli of polycrystalline materials in which grain boundaries are present, but their relaxation is forbidden. The most straightforward of the averaged quantities are the Reuss (E_R and G_R , homogeneous stress) and the Voigt (E_V and G_V , homogeneous strain) averages (Hearmon, 1956), as previously defined. The other methods of averaging c_{ij} to estimate polycrystalline moduli were proposed by Hashin and Shtrikman (1962), Hill (1965), Kröner, Datta and Kessel (1966) and Kröner (1967).

Ledbetter and Naiman (1974) reviewed the various approximations and demonstrated that none is completely satisfactory for the noble metals at room temperature. They did suggest a relationship between c_{ij} and G , based on the assumption that the elastic Debye temperature (θ_D) is not perturbed by the presence of grain boundaries. This model leads to an equation of G ($\equiv G_{LN}$), which is a function only of the density of the material, θ_D and B . Since B is a scalar invariant of the stiffness tensor, G_{LN} is fully defined in terms of θ_D . This method yields excellent agreement with measured values of G for noble metals and many ionic compounds at 300 K. The Ledbetter and Naiman model can be applied to calculate

E_{LN} by

$$E_{\text{LN}} = \frac{3 G_{\text{LN}}}{1 + (G_{\text{LN}}/3B)}$$

Fourth-order polynomial regression fits to $E_{\text{VRH-a}}$ and $E_{\text{VRH-g}}$ of Au, as calculated from the experimentally determined c_{ij} values, are plotted in Figure 13 over the entire temperature range. The calculated value of E_{LN} at 300 K is indicated by the large ($\diamond$) symbol in Figure 13. Higher temperature values are not presented because E_{LN} is essentially temperature-invariant. The Aleksandrov (1966) method for averaging G ($\equiv G_{\text{A}}$) is given by

$$G_{\text{A}} = (c_{44})^{3/5} \left(\frac{c_{11} - c_{12}}{2} \right)^{2/5}$$

At room temperature, G_{A} is within 2% of the values obtained by the Hill arithmetic and geometric averages, as indicated by the large ($\circ$) symbols in Figure 14.

Ledbetter (1989) reviewed the elastic data for copper and concluded, by comparison with experimental values of G for polycrystalline Cu, that the Kröner (1967) method of averaging c_{ij} (E_{K} and G_{K}) is the most reliable, though Kröner's method is algebraically rather complex. E_{K} for Au at room temperature, using the c_{ij} obtained experimentally (in this work), coincides precisely with $E_{\text{VRH-g}}$ at room temperature, as indicated in Figure 13 by the large (Δ) symbol. The diverse methods for averaging c_{ij} result in a wide range of values for any particular metal, as is clearly demonstrated by Ledbetter's review (1989).

At room temperature, Kröner's method (E_{K}) of averaging the measured c_{ij} for Au (reported in this work) agrees very well with Hill's averaging methods, especially

$E_{\text{VR-g}}$. See Figure 13. Also at room temperature, the Ledbetter and Naiman method (E_{LN}) of averaging the c_{ij} for Au agrees very well with experimentally determined values of E_{V} reported here.

At temperatures below 800 K, the values of E_{V} reported here are slightly lower than those previously reported by Köster. The reason for this is not immediately apparent, though room temperature values of E_{V} for Au reported in the literature vary widely (see Table XI). Köster's room temperature values of E_{V} for Au, as well as those reported here, are well within this range. At temperatures above 800 K, Hill's arithmetic and geometric methods ($E_{\text{VRH-a}}$ and $E_{\text{VRH-g}}$) of averaging the c_{ij} for Au reported in this work agree very well with both plots of E_{V} (this work and Köster's) in Figure 13. In particular, above 1000 K the degree of curvature of each plot ($E_{\text{VRH-a}}$, $E_{\text{VRH-g}}$, Köster's E_{V} and E_{V} reported in this work) is remarkably consistent. Since the elastic modulus of the polycrystalline aggregate and the average of the single-crystal elastic constants are so similar at elevated temperatures, it is not surprising that efforts to relate the modulus defect in polycrystalline Au to grain boundary diffusion parameters yields values of Q_{b} which do not agree with experiment (Collard and McLellan, 1991).

A comparison of the curvature of Hill's averaging methods in Figure 13 with the summary of actual c_{ij} plots in Figure 16, reveals another noteworthy phenomenon: $E_{\text{VRH-a}}$ and $E_{\text{VRH-g}}$ are non-linear at all temperatures while the c_{ij} are linear up to approximately 900 K. Thus, the curvature in $E_{\text{VRH-a}}$ and $E_{\text{VRH-g}}$ is due, at least in part, to the averaging methods of E_{V} and E_{R} . Moreover, if the c_{ij} are all strictly linear functions of T , E_{V} and E_{R} are third-order polynomials in T . There is very little variation of G with temperature, as seen in Figure 16 — the modulus defect is small. Unlike E_{V} and E_{R} , G_{V} is linear in temperature if the c_{ij} are linear.

The Voigt and Reuss averages of the c_{ij} of Al are essentially identical for both

E and G , as seen in Figures 18 and 19, respectively. The small, filled symbols represent: E_Y ($\circ$), E_V ($\square$), E_R (Δ), E_{VRH-a} (∇), E_{VRH-g} ($\diamond$) in Figure 18. The same small, filled symbols represent: G ($\circ$), G_V ($\square$), G_R (Δ), G_{VR-a} (∇) and G_{VR-a} ($\diamond$) in Figure 19, except the Aleksandrov averages are plotted in 100 K intervals as large, hollow ($\circ$) symbols. The Aleksandrov values (G_A) are essentially coincident with G_V and G_R . All the single-crystal averaging techniques plotted in Figures 18 and 19 for Al show much less departure from linear behavior than the measured polycrystalline E_Y and G , represented by ($\bullet$) symbols in both Figures 18 and 19. Much of the modulus defect for E_Y and G is undoubtedly due to relaxation of grain boundaries.

Let us now concentrate the discussion on the measurements of Au single-crystal c_{ij} . The variation of c_{ij} with T , at constant pressure (P), as demonstrated by the plots of Au and Al c_{ij} in Figures 16 and 17, may be formally expressed by

$$\left(\frac{\partial c_{ij}}{\partial T} \right)_P = \left(\frac{\partial c_{ij}}{\partial T} \right)_V - B_T \alpha_T \left(\frac{\partial c_{ij}}{\partial P} \right)_T$$

where B_T and α_T are the isothermal bulk modulus and the thermal expansivity. The last term represents the implicit dependence of the c_{ij} on T due to the volume change with temperature. The term $(\partial c_{ij}/\partial T)_V$ is an explicit dependence of the c_{ij} on T (Lazarus, 1949). Gerlich and Fisher (1969), in discussing their results on Al, separated the terms of this equation by substituting data for B_T , α_T and $(\partial c_{ij}/\partial P)_T$. This procedure is complicated by the lack of data at elevated temperatures and knowledge of the behavior of $(\partial c_{ij}/\partial P)_T$ requires a model of $(\partial c_{ij}/\partial T)_V$. In this work we suggest a physical explanation of the observed $(\partial c_{ij}/\partial P)_T$ data using a simple model.

The adiabatic stiffness constants of metals generally depend on the presence of imperfections. And, although elastic waves interact with dislocations in metals (internal friction), this does not occur in well-annealed single crystals at the (elevated) temperatures of interest. Truell *et al.* (1969) presented an excellent discussion of dislocation damping.

At elevated temperatures, the monovacancy concentration (C_{1v}) in Au becomes large ($C_{1v} = 3.5 \times 10^{-4}$ at 1250 K). The first attempt to calculate the effect of point defects (vacancies and self-interstitials) on elastic properties was made by Dienes (1952), who calculated the perturbation in the lattice potential energy (U) due to the introduction of vacancies or interstitials. The lattice was allowed to relax after the defect was introduced. The energy per atom, $U(r)$, was taken as a Born–Mayer interatomic potential,

$$U(r) = U_0(r) e^{-r/q} \quad (1)$$

where $U_0(r)$, the dissociation energy, and q are obtained from the c_{ij} of defect-free crystals. For Cu, Dienes found that a $C_{1v} = 10^{-2}$ would decrease the elastic moduli by ≈ 1.0 %. Thus for vacancies in thermal equilibrium in Cu, the effect would hardly be measurable. Since the early work of Dienes, many other calculations have been made and the topic has been reviewed by Ledbetter and Austin (1985). Dederichs *et al.* (1975) performed a computer simulation calculation using a crystallite containing 2457 atoms interacting with a Morse potential, given by (see page 12)

$$U(r_{ij}) = U_0(r) \left[\exp \left[-2\alpha(r_{ij} - r_e) \right] - 2 \exp \left[-\alpha(r_{ij} - r_e) \right] \right] \quad (2)$$

restricted to first and second nearest neighbors. For Cu, the constants are $U_0(r) = 17.31 \text{ kJ/mole}$ ($= D_0$), $\alpha = 0.2327 \text{ nm}^{-1}$ and $r_e = 0.25706 \text{ nm}$. For monovacancies, the result ($\Delta c_{44}/c_{44} = -3.1 C_{IV}$) predicts an $\approx 0.1\%$ decrease in c_{44} at the melting temperature (Dederichs *et al.*, 1975). Thus, although it is possible (Folweiler and Brotzen, 1959) to monitor the change in E_V of Al during isochronal annealing of quenched-in vacancies, monovacancies in thermal equilibrium are not responsible for the elevated-temperature variations observed in the c_{ij} for Au or Al.

Let us consider the temperature-dependence of the c_{ij} of a crystal free of point defects. Varshni (1970) proposed the form

$$c_{ij} = c_{ij}^0 - \left(\frac{s}{e^{t/T} - 1} \right) \quad (3)$$

where c_{ij}^0 is c_{ij} at 0 K and s and t are constants for a given index pair (i, j) . This relation, using the values of s and t tabulated by Varshni, yields an accurate fit to the c_{ij} for Au between 300 and 900 K. Derivation of the Varshni relation is facilitated by assuming the mean free energy of an atom in a crystal is that of an Einstein solid. If so, this equation essentially relates dc_{ij}/dT to the frequency spectrum of the crystal. Extensive reviews have been published on this topic (Leibfried and Ludwig, 1961; Wallace, 1972). A detailed calculation of dc_{ij}/dT based on the phonon spectrum is beyond the scope of this work, but we will suggest a simple model which is in qualitative agreement with the observations.

The Helmholtz free energy of a strained crystal containing N atoms of original (static) volume V_0 at absolute temperature T is given by (Wallace, 1972)

$$F(\epsilon_i, T) = U_0(\epsilon_i) + \frac{1}{2} \sum_{q=1}^{3N} h\nu_q + kT \sum_{q=1}^{3N} \ln \left(1 - e^{-h\nu_q/kT} \right) \quad (4)$$

where $U_0(\epsilon_i)$ is the internal energy of the crystal with the atoms in their equilibrium positions under the strain ϵ_i , ν_q are the normal mode frequencies, h is Planck's constant, k is Boltzmann's constant and $3N$ is the number of degrees of motional freedom. Voigt notation is used for the components of the strain tensor ϵ_i . By using eqn.4 we make the assumption that conduction-electron free energy and anharmonicity (vibrational wave interactions) are not significant in calculating the free energy.

We may calculate the isothermal stiffness constants from the Helmholtz free energy, eqn.4, using

$$c_{ij}^T \equiv -\frac{1}{V_0} \left(\frac{\partial^2 F}{\partial \epsilon_i \partial \epsilon_j} \right)_T$$

so that

$$c_{ij}^T = \tilde{c}_{ij} + \frac{1}{V_0} \left\{ h \sum_{q=1}^{3N} \frac{\partial^2 \nu_q}{\partial \epsilon_i \partial \epsilon_j} f'(x_q) + \frac{h^2}{kT} \sum_{q=1}^{3N} \frac{\partial^2 \nu_q}{\partial \epsilon_i \partial \epsilon_j} f''(x_q) \right\} \quad (5)$$

where

$$\tilde{c}_{ij} \equiv -\frac{1}{V_0} \left(\frac{\partial^2 U_0}{\partial \epsilon_i \partial \epsilon_j} \right)$$

$$x_q \equiv \frac{h\nu_q}{kT}$$

$$f(x_q) \equiv \frac{x_q}{2} + \ln(1 - e^{-x_q})$$

$$f'(x_q) = \frac{1}{2} + \left(e^{x_q} - 1\right)^{-1}$$

and

$$f''(x_q) = -e^{x_q} \left(e^{x_q} - 1\right)^{-2}$$

The quantities $\tilde{c}_{ij} = 1/V_0(\partial^2 U_0/\partial\epsilon_i\partial\epsilon_j)$ are the elastic moduli in the strictly harmonic approximation where the frequencies ν_q are constant and the thermal expansivity is zero. The $\tilde{c}_{ij}$ are not dependent on temperature. In the quasi-harmonic approximation, the ν_q are not constant and depend on the strain tensor components [$\nu_q = \nu_q(\epsilon_i)$] and the c_{ij}^T become temperature-dependent due to the anharmonic terms of eqn.5.

The simplest way to approximate the spectrum of ν_q is to use Einstein's approximation for specific heat, where all frequencies are assumed to be the same and equal to the Einstein frequency ($\nu_q = \nu_e$ for all q). Rewriting eqn.5 in terms of the Einstein temperature ($\theta_e = h\nu_e/k$) yields

$$F(\epsilon_i, T) = U_0(\epsilon_i) + \frac{3}{2} N h \nu_e + 3 N k T \ln \left(1 - e^{-\theta_e/T}\right)$$

so that

$$c_{ij}^T = \tilde{c}_{ij} + \frac{1}{V_0} \left\{ \left(\frac{\partial^2 \theta_e}{\partial \epsilon_i \partial \epsilon_j} \right) g'(x_e) + \frac{1}{T} \left(\frac{\partial^2 \theta_e}{\partial \epsilon_i \partial \epsilon_j} \right) g''(x_e) \right\}$$

where we set

$$x_q = \frac{h\nu_q}{kT} = x_e = \frac{h\nu_e}{kT} \equiv \frac{\theta_e}{T}$$

$$g(x_e) \equiv 3Nk \left(\frac{x_e}{2} + \ln(1 - e^{-x_e}) \right)$$

$$g'(x_e) = 3Nk \left(\frac{1}{2} + [e^{x_e} - 1]^{-1} \right)$$

and

$$g''(x_e) = -3Nk \left(\frac{e^{x_e}}{(e^{x_e} - 1)^2} \right)$$

so that the isothermal elastic constants are given by

$$c_{ij}^T = \bar{c}_{ij} + \frac{1}{V_0} \left(\frac{\partial^2 \theta_e}{\partial \epsilon_i \partial \epsilon_j} \right) \left[g'(x_e) + \frac{1}{T} g''(x_e) \right] \quad (6)$$

Eqn.6 can be used to calculate the adiabatic elastic constants c_{ij}^S using the conversion

$$c_{ij}^S = c_{ij}^T + \frac{T V \beta_i \beta_j}{C_\epsilon}$$

where C_ϵ is the specific heat at constant strain, given by

$$C_\epsilon = T \left(\frac{\partial S}{\partial T} \right)_\epsilon = T \left(\frac{\partial}{\partial T} \left(- \frac{\partial F}{\partial T} \right) \right)_\epsilon - T \left(\frac{\partial^2 F}{\partial T^2} \right)_\epsilon$$

or, in terms of the Einstein approximation to the Helmholtz free energy,

$$C_\epsilon = \frac{3Nh^2 \nu_e^2}{kT^2} \left(\frac{e^{\theta_e/T}}{(e^{\theta_e/T} - 1)^2} \right) = - \left(\frac{\theta_e}{T} \right)^2 g''(x_e)$$

The thermal stress coefficients, β_i (and β_j) are defined as

$$\beta_i \equiv \left(\frac{\partial \sigma_i^T}{\partial T} \right)_\epsilon = \frac{1}{V_0} \left(\frac{\partial^2 F}{\partial T \partial \epsilon_i} \right)_{T, \Sigma \epsilon}$$

where σ_i^T is the isothermal component of the stress tensor, given by

$$\sigma_i^T \equiv \frac{1}{V_0} \left(\frac{\partial F}{\partial \epsilon_i} \right)_{T, \Sigma \epsilon}$$

Thus, in terms of the Einstein approximation to the Helmholtz free energy, the thermal stress coefficients are

$$\beta_i = \frac{1}{V_0} \left\{ \frac{3N h^2 \nu_e}{k T^2} \left(\frac{\partial \nu_e}{\partial \epsilon_i} \right)_T \left(\frac{e^{\theta_e/T}}{(e^{\theta_e/T} - 1)^2} \right) \right\}$$

or

$$\beta_i = - \frac{1}{V_0} \frac{\theta_e^2}{T} \left(\frac{\partial \theta_e}{\partial \epsilon_i} \right)_T g''(x_e)$$

where $g''(x_e)$ is as previously defined and

$$\left(\frac{\partial \nu_e}{\partial \epsilon_i} \right)_T = \frac{k}{h} \left(\frac{\partial \theta_e}{\partial \epsilon_i} \right)_T$$

Thus, using the expressions for c_{ij}^T , β_i and $C\epsilon$ in terms of the Einstein approximation, and the relation

$$c_{ij}^S = c_{ij}^T + \frac{T V_0 \beta_i \beta_j}{C_\epsilon}$$

the adiabatic elastic constants are:

$$c_{ij}^S = \tilde{c}_{ij} + \frac{3Nh}{V_0} \left(\frac{\partial^2 \nu_e}{\partial \epsilon_i \partial \epsilon_j} \right) \left[\frac{1}{2} + \left(e^{h\nu_e/kT} - 1 \right)^{-1} \right] \quad (7)$$

In the high-temperature limit, $kT > h\nu_e$ and eqn.7 yields the linear dependence of c_{ij}^S on temperature in the quasi-harmonic approximation. This is equivalent to the Varshni relation (eqn.3). In eqn.7, the factor $(\partial^2 \nu_e / \partial \epsilon_i \partial \epsilon_j)$ is a measure of the anharmonicity and is not regarded as a function of temperature. The only temperature dependence of c_{ij}^S comes from the harmonic oscillator term. At moderate temperatures, eqn.7 gives a reasonable account of (dc_{ij}^S/dT) , but it does not explain deviations from linearity at high temperatures. If the quasi-harmonic model is essentially correct and $(\partial^2 \nu_e / \partial \epsilon_i \partial \epsilon_j)$ exhibits only a slight temperature dependence, then the implication is that, despite the non-zero thermal expansivity, the Grüneisen tensor

$$\gamma_i = \frac{1}{C_\epsilon} \left(\frac{\partial S}{\partial \epsilon_i} \right)_T = - \frac{1}{C_\epsilon} \left(\frac{\partial^2 F}{\partial \epsilon_i \partial T} \right)$$

is virtually independent of temperature. However, $U_0(\epsilon_i)$ is a function of temperature and may be calculated by using some interaction model. This modification amounts to replacing the temperature-independent strictly harmonic moduli, $\tilde{c}_{ij}$, by $\hat{c}_{ij}$ — calculated from the new crystal configurations where the

equilibrium distance r_e is now a function of temperature. At moderate temperatures, $\hat{c}_{ij}$ is expected to decrease linearly as T increases — as predicted by Varshni (1970) and observed experimentally for many metals.

A reasonable approximation of the potential energy for *fcc* metals can be calculated by summing $U(r)$ over nearest-neighbors. The $\hat{c}_{ij}$ are calculated (Fuchs, 1936) in this manner in terms of $\left[\frac{\partial U(r)}{\partial r}\right]_{r=r_e}$ and $\left[\frac{\partial^2 U(r)}{\partial r^2}\right]_{r=r_e}$ in the form

$$\hat{c}_{11} = \frac{2\sqrt{2}}{r_e} \left\{ \left(\frac{\partial^2 U}{\partial r^2} \right)_{r_e} + \frac{7}{3r_e} \left(\frac{\partial U}{\partial r} \right)_{r_e} \right\} \quad (8)$$

$$\hat{c}_{12} = \frac{\sqrt{2}}{r_e} \left\{ \left(\frac{\partial^2 U}{\partial r^2} \right)_{r_e} - \frac{7}{3r_e} \left(\frac{\partial U}{\partial r} \right)_{r_e} \right\} \quad (9)$$

$$\hat{c}_{44} = \frac{\sqrt{2}}{r_e^2} \left\{ r_e \left(\frac{\partial^2 U}{\partial r^2} \right)_{r_e} + 3 \left(\frac{\partial U}{\partial r} \right)_{r_e} \right\} \quad (10)$$

where r_e is the equilibrium interatomic distance. Using eqns.8–10, calculation of the $\hat{c}_{ij}$ and B in terms of a given potential function (e.g. eqns.1 or 2) is straightforward. For example, using the Born–Mayer potential (eqn.1)

$$U(r) = D_0 e^{-r/\rho}$$

$$\left(\frac{\partial U}{\partial r} \right)_{r_e} = -\frac{D_0}{\rho} e^{-r_e/\rho}$$

$$\left(\frac{\partial^2 U}{\partial r^2} \right)_{r_e} = \frac{D_0}{\rho^2} e^{-r/\rho}$$

Substituting these into eqns.8–10 we find

$$\hat{c}_{11} = \frac{2\sqrt{2} D_0 e^{-r_e/\rho}}{r_e \rho} \left(\frac{1}{\rho} - \frac{7}{3r_e} \right) \cong \frac{2\sqrt{2} D_0 e^{-r_e/\rho}}{r_e \rho^2} \quad (11)$$

$$\hat{c}_{12} = \frac{\sqrt{2} D_0 e^{-r_e/\rho}}{r_e \rho} \left(\frac{1}{\rho} + \frac{7}{3r_e} \right) \cong \frac{\sqrt{2} D_0 e^{-r_e/\rho}}{r_e \rho^2} \quad (12)$$

$$\hat{c}_{44} = \frac{\sqrt{2} D_0 e^{-r_e/\rho}}{r_e \rho} \left(\frac{1}{\rho} - \frac{3}{r_e} \right) \cong \frac{\sqrt{2} D_0 e^{-r_e/\rho}}{r_e \rho^2} \quad (13)$$

$$B = \frac{8D_0}{3\sqrt{2} r_e \rho^2} e^{-r_e/\rho}$$

where the second terms within parentheses have been neglected because they are small compared to the first.

Similarly, using the Morse potential (eqn.2) we find

$$\hat{c}_{11} = \frac{4\sqrt{2} \alpha^2 D_0 K}{r_e} \left((2K-1) + \frac{7}{3r_e \alpha} (1-K) \right)$$

$$\hat{c}_{12} = \frac{2\sqrt{2} \alpha^2 D_0 K}{r_e} \left((2K-1) - \frac{7}{3r_e \alpha} (1-K) \right)$$

$$\hat{c}_{44} = \frac{2\sqrt{2}\alpha^2 D_0 K}{r_e} \left((2K-1) + \frac{3}{r_e \alpha} (1-K) \right)$$

$$B = \frac{16\alpha^2 DK(2K-1)}{3\sqrt{2}r_e}$$

where $K = \exp[-\alpha(r - r_e)]$. The $\hat{c}_{ij}$ can be calculated from eqns.8–10, r_e (from tabulated thermal expansivity), and the adjustable parameters for the given potential model. The Morse interatomic potential is more commonly used than the Born–Mayer approximation.

Dederichs *et al.* (1975) determined values for the Morse potential constants (D , α and r_e^0) using computer simulation of a group of 2457 interacting atoms and fitting calculated values of B , the formation energy for a monovacancy (E_{iv}^f) and the lattice parameter to experimentally measured values for Cu, where r_e^0 is the equilibrium interatomic distance at absolute zero temperature. The values of c_{11} thus calculated are in good agreement with experimentally measured values at 0 K; but the values of c_{12} and c_{44} deviate considerably from experimentally measured values. Values of Cu c_{ij} calculated with the Born–Mayer approximation are in remarkably good agreement with experimentally measured values. Cotterill and Doyama (1967) have presented the Morse potential constants of Au for several truncations. Calculated values for Au c_{ij} deviate considerably from experimentally measured values at 0 K (Neighbours and Alers, 1958).

It is clear from eqn.7 (the quasi-harmonic model with the Einstein approximations) that model calculations using some form for $U(r)$ cannot be expected to yield accurate results for the c_{ij}^S at 0 K. This is because of the non-zero terms in c_{ij}^S which result from the perturbation of the zero-point vibrations when a

strain is applied to the crystal at 0 K. However, we may calculate the temperature dependence of the $\hat{c}_{ij}$ using eqns.8–10 and a suitable interaction model. We begin by rewriting the quasi-harmonic expression (eqn.7)

$$c_{ij}^S = \tilde{c}_{ij} + \frac{3Nh}{V_o} \left(\frac{\partial^2 \nu_e}{\partial \epsilon_i \partial \epsilon_j} \right) \left[\frac{1}{2} + \left(e^{h\nu_e/kT} - 1 \right)^{-1} \right]$$

Using the approximation

$$e^{h\nu_e/kT} = 1 + \frac{h\nu_e}{kT} + \frac{(h\nu_e/kT)^2}{2!} + \dots \cong 1 + \frac{h\nu_e}{kT}$$

we have

$$c_{ij}^S = \tilde{c}_{ij} + \frac{3h\Phi_{ij}}{2\Omega_o} + \frac{3k\Phi_{ij}}{\nu\Omega_o} T \quad (14)$$

where the strain derivative of the frequency is substituted for

$$\Phi_{ij} \equiv \frac{\partial^2 \nu_e}{\partial \epsilon_i \partial \epsilon_j}$$

the atomic volume is

$$\Omega_o \equiv \frac{V_o}{N}$$

and the strictly harmonic model results when the frequencies are constant (and their strain derivatives are equal to zero), i.e.

$$c_{ij}^S = \tilde{c}_{ij} \equiv \frac{1}{V_o} \left(\frac{\partial^2 U}{\partial \epsilon_i \partial \epsilon_j} \right)$$

where the $\tilde{c}_{ij}$ are constant and independent of temperature.

In our first modification to the quasi-harmonic model (eqn.14), we assume that the $\tilde{c}_{ij}$ vary with temperature due to thermal expansion. We express this temperature dependence by introducing into eqn.14 the term

$$\hat{c}_{ij}(T) \equiv \hat{c}_{ij}(0) - \omega_{ij} T \quad (15)$$

where ($\omega_{ij} > 0$) and

$$\hat{c}_{ij}(0) \equiv \tilde{c}_{ij} + \frac{3\hbar^2 \nu_{ij}}{2\Omega_0}$$

and calculate the coefficients ω_{ij} from the Born-Mayer interatomic potential, eqns.11-13. The $\hat{c}_{ij}$ are functions of temperature because they are functions of r_e (as in eqns.11-13), which is a function of temperature through normal (volume) thermal expansion.

Since the $\hat{c}_{ij}$ are functions of temperature (through thermal expansion), the temperature dependence of ν_e must also be considered. Assuming the Grüneisen parameter is volume-independent, we may use the approximation:

$$\gamma = - \left(\frac{V}{\nu_e} \right) \left(\frac{\partial \nu_e}{\partial V} \right)_P$$

from which we find that

$$\left(\frac{\partial \nu_e}{\partial T} \right)_P = \left(\frac{\partial \nu_e}{\partial V} \right)_P \left(\frac{\partial V}{\partial T} \right)_P = \left(- \frac{\gamma \nu_e}{V} \right) V \alpha$$

and by integration

$$\int \frac{d\nu_e}{\nu_e} = - \int \gamma \alpha dT$$

so that

$$\ln \frac{\nu_e}{\nu_e(0)} = - \gamma \alpha T$$

so the temperature dependence of the frequencies may be expressed as

$$\nu_e(T) = \nu_e(0) e^{-\alpha \gamma T} \quad (16)$$

where $\nu_e(0) \equiv \nu_0$ is the value of ν_e at 0 K. Combining eqns.14, 15, and 16 we present a modified quasi-harmonic model

$$c_{ij}^S = \hat{c}_{ij}(0) - \omega_{ij} T + \frac{3k\hbar_{ij} T}{\nu_0 \Omega_0} e^{\alpha \gamma T} \quad (17)$$

At (intermediate) temperatures above that at which classical statistics become valid, but below which the final term in eqn.17 becomes important (i.e. the linear range of the c_{ij} vs. T plots), $e^{\alpha \gamma T} \cong 1$ and c_{ij}^S is approximately linear with respect to temperature. The experimental slope is then

$$\delta_{ij} \equiv \left(\frac{\partial c_{ij}^S}{\partial T} \right)_P = -\omega_{ij} + \frac{3k\hbar_{ij}}{\Omega_0 \nu_0}$$

At elevated temperatures, $e^{\alpha \gamma T}$ becomes significant and may be approximated by

$$e^{\alpha\gamma T} = 1 + \alpha\gamma T + \frac{(\alpha\gamma T)^2}{2!} + \dots \cong 1 + \alpha\gamma T$$

so that

$$c_{ij}^S = \hat{c}_{ij}(0) - \omega_{ij}T + \frac{3k_{ij}T}{\nu_o\Omega_o}(1 + \alpha\gamma T)$$

or

$$c_{ij}^S = \hat{c}_{ij}(0) + \left(\frac{3k_{ij}}{\nu_o\Omega_o} - \omega_{ij} \right) T + \left(\frac{3k_{ij}}{\nu_o\Omega_o} \right) \alpha\gamma T^2$$

We thus obtain the modified quasi-harmonic model in final form:

$$c_{ij}^S = \hat{c}_{ij}(0) + \delta_{ij}T + (\delta_{ij} + \omega_{ij})\alpha\gamma T^2 \quad (18)$$

where δ_{ij} is determined from the linear portion of the experimentally measured plot of c_{ij}^S vs. T . ω_{ij} is obtained from interatomic potential functions, i.e.

$$\omega_{ij} \equiv \left(\frac{\partial \hat{c}_{ij}}{\partial T} \right)$$

From eqn.18, if there is no thermal expansivity ($\alpha = 0$), the quasi-harmonic approximation results. According to the modified quasi-harmonic model (eqn.18), the c_{ij}^S will only exhibit curvature at elevated temperatures for metals with large values of γ . The value for gold: $\gamma_{Au} = 2.93$; the largest value for metals.

Now the coefficients ω_{ij} are obtained in terms of the Born-Mayer potential from eqns.11-13, where the second terms in these expressions may be neglected to a first approximation. For example, from eqn.11 we have

$$\hat{c}_{11} \cong \frac{2\sqrt{2} D_o e^{-r_e/\rho}}{r_e \rho^2}$$

or

$$\hat{c}_{11} = \mathcal{K} \frac{e^{-r_e^0/\rho}}{r_e^0}$$

where

$$\mathcal{K} \equiv \frac{2\sqrt{2} D_o}{\rho^2}$$

so that

$$\hat{c}_{11} = \frac{\mathcal{K}}{r_e^0} e^{-r_e^0(1 + \alpha T)/\rho}$$

$$\hat{c}_{11} = \frac{\mathcal{K}}{r_e^0} e^{-r_e^0/\rho} e^{-r_e^0 \alpha T/\rho}$$

$$\hat{c}_{11} = \frac{\mathcal{K}}{r_e^0} e^{-r_e^0/\rho} \left(1 - \frac{r_e^0 \alpha T}{\rho} \right)$$

from which we find

$$\omega_{11} = \left(\frac{\partial \hat{c}_{11}}{\partial T} \right) = \frac{\mathcal{K}}{r_e^0} e^{-r_e^0/\rho} \left(-\frac{r_e^0 \alpha}{\rho} \right) = -\frac{\mathcal{K} \alpha}{\rho} e^{-r_e^0/\rho}$$

or

$$\omega_{11} = \frac{2\sqrt{2} D_o \alpha}{\rho^3} e^{-r_e^0/\rho} \quad (19)$$

where α = linear expansivity and τ_e^0 is the equilibrium interatomic distance at absolute zero (0 K). Similarly, we find from eqns.12 and 13 that

$$\omega_{12} = \omega_{44} = \frac{\omega_{11}}{2} \quad (20)$$

It is not possible to obtain values of D_0 and ρ from the elastic constants at 0 K in the modified quasi-harmonic model, since the strain derivative of the frequency at 0 K (i.e. $\Phi_{ij}(T = 0)$) is non-zero because of the zero-point vibrational energy. Thus to obtain the ω_{ij} , the experimentally measured plot of c_{12}^S vs. T was fitted to our eqn.18 to obtain ω_{12} by a least-squares regression. δ_{12} was obtained from the linear portion of the same plot. Using the value of ω_{12} , and the relationship given in eqn.20, determination of ω_{11} and ω_{44} was straightforward. The results for Au are:

$$\omega_{11} = 1.527 \times 10^{-5}$$

$$\omega_{12} = 3.044 \times 10^{-5}$$

$$\omega_{44} = 3.044 \times 10^{-5}$$

The results of these calculations are indicated by the heavy solid lines in the high-temperature region of the c_{11} and c_{44} plots in Figure 16. The agreement between the calculated and measured c_{ij} is satisfactory. Eqns.19 and 20 imply that the departure of c_{ij} from linearity at high temperatures should be approximately twice as large for c_{11} as for c_{12} . The equivalent form of eqn.18 has been calculated using the Debye approximation for ν . These calculations are much more tedious, but lead, as expected, to essentially identical results.

It is interesting to note that Au has a value of $\alpha\gamma$ larger than other metals: for Au, $\alpha\gamma = 1.30 \times 10^{-4}$; whereas for W, $\alpha\gamma = 2.40 \times 10^{-5}$. Lowrie and Gonas (1967) have measured the c_{ij} for W up to 2073 K and found small deviations from linearity at elevated temperatures.

VI. CONCLUSIONS

This work has led to two results. The first is a general conclusion that the elastic constants of polycrystalline aggregates may be expected to exhibit large modulus defects — even when the corresponding c_{ij} are strictly linear functions of temperature. Thus the utilization of $E_V(T)$ or $G(T)$ measurements to draw conclusions concerning the properties of grain boundaries is highly questionable.

The second result of this work is that non-linear behavior should be expected in the high temperature region of c_{ij} vs. T plots for metals where the frequency spectrum shows a large dependence on volume. It may well be that Al and the noble metals are quite unique in this respect.

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