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PRESSURE-INDUCED ELASTICITY CHANGES
IN VANADIUM SILICIDE

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A Thesis

Presented to the Faculty of the Graduate School
of Cornell University for the Degree of
Doctor of Philosophy

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by

Ronald Ernulf Larsen

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BIOGRAPHICAL SKETCH

The author was born April 15, 1934 on Staten Island, New York and attended public schools there. He received the B.A. in Physics from Wagner College in 1955 and the M.S. in Physics from Rensselaer Polytechnic Institute in 1960.

Between 1958 and 1966 he was employed in a civilian status as a physicist with the U. S. Army at Frankford Arsenal, Philadelphia, Pennsylvania. During the years 1958 to 1963 he was stationed at Brookhaven National Laboratory, where the focus of his research was radiation enhanced diffusion in alloys. Between 1963 and 1966 he was stationed at Frankford Arsenal, where he was the principle investigator in a study of damage of materials by intense laser beams. In late 1966 he came to Cornell to study under Professor Arthur Ruoff for the Ph.D. in Materials Science. Since then, he has been engaged in research on the influence of high pressure on the elastic properties of solids. A part of this research forms the basis for this dissertation.

The author is a member of the American Physical Society. He has published several scientific papers and has delivered numerous talks before professional societies.

To Arlene

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Many people have contributed their time, efforts, and special talents to this research. To them I offer my most sincere thanks. Professor Arthur Ruoff served as Chairman of my Special Committee and was first to bring to my attention the peculiar elastic behavior of V_3Si . Professors David Seidman and A. J. Sievers were kind enough to serve on my Special Committee. Professor Paul Ho and Dr. J. Paul Day introduced me to the ultrasonic method used in measuring the elastic moduli. Dr. Richard Lincoln was always willing to listen and to offer alternative approaches to experimental problems. Bernard Addis grew the single crystal used in this research. Robert Terry provided general technical assistance. And Arlene Larsen wrote the computer programs and processed the data.

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Chapter I

INTRODUCTION

A. Purpose of this Research

The A-15 (β -tungsten cubic) compound V_3Si softens elastically as the temperature is decreased from 300°K.¹⁻⁴ This behavior contrasts with the stiffening observed in most metals and their compounds. This dissertation describes the author's measurements of the hydrostatic pressure derivatives of the elastic moduli of V_3Si . This research was undertaken to further characterize the anomalous lattice softening.

B. Elastic Softening and Other Anomalies

The elastic moduli of most "ordinary" metals, alloys or compounds increase several percent as a result of a temperature change from 300°K to 4°K. Testardi and Bateman^{1,2} have measured the elastic moduli of V_3Si . For the same temperature decrease, the bulk modulus $[B \equiv \frac{1}{3}(C_{11} + 2C_{12})]$ varies less than 0.5%. The shear modulus C_{44} , which measures the resistance to shearing displacements perpendicular to the $\{100\}$ axes, decreases by about 6%. The shear modulus $C' \equiv \frac{1}{2}(C_{11} - C_{12})$, which measures the resistance to shearing displacements in the $\langle 1\bar{1}0 \rangle$ directions on $\{110\}$ planes, also decreases. For some specimens the total decrease in C' is about 98%; these specimens undergo a second order (or perhaps very weak first order), reversible, apparently isovolumetric, cubic-to-tetragonal martensitic transformation of the type reported by Batterman and Barrett.⁵⁻¹⁷ At the martensitic transformation temperature ($T_m \approx 21^\circ K$) the $\frac{c}{a}$ ratio is 1.00. As the temperature is lowered, $\frac{c}{a}$ increases continuously

until the change is smoothly arrested at a value of 1.0023 at the superconducting critical temperature ($T_c \approx 17^\circ\text{K}$). The rapid C' decrease with decreasing temperature, though partially arrested at T_m , is resumed at T_c . At approximately 14°K and below, C' is only about 2% of its room temperature value. For specimens that do not structurally transform, the arrest in C' is absent at 21°K but the arrest does occur at T_c . C' remains constant at a value of approximately 12% of its room temperature value from T_c to 4°K . Transforming and non-transforming specimens apparently differ from each other in slight variations in concentration or impurity content; transforming type specimens tend to have higher resistivity ratios and minute second phase inclusions.^{3-5,18}

Other high T_c A-15 compounds also elastically soften¹⁹⁻²² and martensitically transform. As in V_3Si , the transformation in Nb_3Sn ^{15,16,23} ($T_m = 43^\circ\text{K}$, $T_c = 18^\circ\text{K}$) is well documented. Recently, striations were seen by Nembach et al²⁴ in an electron microscope investigation of V_3Ga ($T_c = 16.5^\circ\text{K}$) foils below 50°K and were interpreted as transforming lamellae similar to those previously seen by others in Nb_3Sn ¹⁵ and V_3Si ^{5,6,9} below T_m . Furthermore, the high T_c species (including V_3Si) have unusually large temperature dependences of electronic susceptibility, Knight shift,²⁵⁻²⁷ NMR relaxation times²⁸ and electronic heat capacity.²⁹⁻³² These anomalies are insignificant or totally absent in the low T_c species (e.g. V_3Au with $T_c = 0.74^\circ\text{K}$), but as T_c increases, weak anomalies begin to appear (e.g. V_3Ge , with $T_c = 6^\circ\text{K}$, has some weak anomalies in the elastic moduli³³ and in magnetic properties^{26,27} but no pronounced elastic

softening nor a structural transformation).

C. Theory of the Anomalies

The several theories that now explain, with varying degrees of success, the structural transformations and the other anomalies in the high T_c A-15 compounds have evolved from the early (1960) proposal of Clogston and Jaccarino.²⁵ They suggested that the strong temperature dependences in Knight shift and susceptibility arise from the location of the Fermi level at, or very close to, an extremely narrow peak in the density of states function for the three d bands of the transition metal atoms in the A-15 structure. The positions of these atoms are shown in Figure 1. The non-transition metal atoms (e.g. tin in Nb_3Sn and silicon in V_3Si) lie on a BCC lattice coincident with the corners of the cubes in this figure; the atoms are not shown in the figure. Weger³⁴ (1964) pointed out that applying a tight binding approximation to the transition metal three d wave functions should yield a band structure that would have the Clogston-Jaccarino property and also would account for anomalies in the NMR relaxation times and for the unusually large electronic heat capacity. Since the transition metal atoms in the A-15 structure are relatively closely spaced ($a/2$) on relatively widely spaced (a) lines that lie along the three cube edge directions, the standard theoretical procedure of restricting the interactions to nearest neighbors emphasizes the one-dimensional character of the transition metal sub-lattice and results in a triply degenerate d band. Such a model should, according to Weger, not only yield the large temperature sensitivity

Figure 1. Two unit cells of the V_3Si structure. The silicon atoms, which occupy the cube-corner and body-centered positions, are not shown.

of the electronic properties but also a large anisotropy in these properties.

Labbe and Friedel³⁵⁻³⁷ have developed a detailed d band tight binding approximation model incorporating nearest neighbor interactions in the three-dimensional chain lattice of V_3Si and applied it, with success, to predict the structural transformation in V_3Si . Bonnerot et al³² have applied the Labbe-Friedel model to specific heat measurements, with reasonable success. Labbe^{38,39} has treated the magnetic anomalies with this model. Barisic and Labbe⁴⁰ have extended the theory to predict the lattice softening and change in C' . In the Labbe-Friedel-Barisic model, the s bands of the silicon and vanadium atoms are responsible for the cohesive properties. Two of the three d bands (each band with degeneracy 3, as in Weger's model) are completely filled. The Fermi level is located just above the bottom edge of the uppermost d band, placing it at a point of extremely rapid change in the density of states. If the lattice expands along the $[100]$ direction and contracts along the $[001]$ and $[010]$ directions (keeping the volume constant), the deformation reduces the degeneracy of the electron spectrum and a large change in the density of states occurs at the Fermi level. For a certain range of initial Fermi level (determined by temperature and "fixed" parameters such as electronic charge) there is a decrease in free energy leading to a first order martensitic transformation. Although the theoretical $C'(T)$ curve predicts a large softening of C' in the temperature range $300^\circ K$ to $21^\circ K$ and the vanishing of C' at $21^\circ K$, the fit of this curve to the experimental data is otherwise

only fair. The region below 21°K is not analyzed. The theory is cumbersome to apply because of the many numerical integrations.

To make the theory manageable, Cohen, Cody and Halloran⁴¹ replaced the sharply peaked function (which comes from the tight binding approximation) with a step function density of states. The calculated elastic moduli temperature dependence for Nb₃Sn fits the experimental data extremely well above T_m ;^{22,41} Rehwald finds the fit to be somewhat poorer below T_m .²²

Very recently Pytte⁴² presented a dynamical theory. He starts with a Hamiltonian describing the interaction between static strain and the acoustic phonons in the triply degenerate d bands. Elastic moduli changes are obtained from coupled equations of acoustic phonons and the electron density function. The computed C' moduli fit the temperature dependence data extremely well for both Nb₃Sn and V₃Si. Furthermore, by merely reducing the density of states from 6.1 states/ev to 5.3 states/ev and leaving other parameters unchanged, the computed C'(T) curve switches from a fit to the data of structurally transforming specimens to that of non-transforming specimens.⁴³

D. Influence of Stress on the Anomalies

To be able to predict even more interesting (and perhaps useful) properties in V₃Si (and hopefully in other high T_c A-15 compounds) it is helpful to have direct knowledge of the angular and radial dependences of the interatomic potentials. At temperatures well below the Debye temperature (Θ_D for V₃Si 200°K-500°K),^{2,30} the usual thermal (phonon-phonon) contribution to the free energy

(Helmholz) of strain is small. Since the elastic moduli are expansion coefficients of the free energy in the strains, measuring the elastic moduli at low temperatures as a function of hydrostatic pressure maps out changes in the interatomic potential arising from changes in interatomic distance. The shear contributions to the potential are obtained by measuring the moduli as a function of static pure shear stress (but more realistically, uniaxial loading stress).

The influence of high shear stress loading on the compliances (therefore the moduli) was investigated By Patel and Batterman.^{7,8} Using a spring and plunger they applied fixed stresses (σ_{zz}) up to 0.6 kb along the $[001]$ axis of a thin bar specimen of V_3Si and measured (by x-ray diffraction) the transverse strain as the specimen was cooled. Then

$$\frac{d\epsilon_{yy}}{d\sigma_{zz}} = \frac{1}{3B} - \frac{1}{2C'}$$

Near 20°K, $B \approx 2$ Mb, $C' \approx 0.1$ Mb (using Testardi and Bateman's data).^{1,2} Since $B \gg C'$,

$$\frac{d\epsilon_{yy}}{d\sigma_{zz}} \approx -\frac{1}{2C'}$$

Patel and Batterman find that (1) a stress of 0.3 kb to 0.4 kb, large enough to produce a strain above T_m comparable with the transformation strain, is sufficient to suppress that transformation.

(2) At 25°K ($T > T_m$) the modulus C' is slightly greater than that calculated from Testardi and Bateman's^{1,2} ultrasonic measurements, but above 0.3kb applied stress, the stiffening is substantial.

(3) For a fixed stress of 0.6 kb (enough to suppress the structural transformation) a specimen which would not transform in the unstressed condition was softer than one that would transform in the unstressed state.

The general anisotropy implied by Testardi and Bateman's^{1,2} findings for the elastic moduli agrees with the electrical resistivity measurements of Weger et al⁴⁴ on V_3Si under uniaxial loads and hydrostatic pressurization. Above T_c (their $T_c = 16.6^\circ K$, unstressed) over the temperature range $17^\circ K$ to $20^\circ K$, a uniaxial stress of 1 kb along the $[001]$ axis reduces the resistivity by 5%; T_c is reduced by $0.5^\circ K$. The same magnitude stress along the $[111]$ direction has negligible effect on the resistivity and on T_c itself. There is no effect on the resistivity (sensitivity of measurement $\sim 0.2\%$) or on T_c (to $\pm 0.05^\circ K$) for hydrostatic pressures up to 0.4 kb. This report appeared about one year before Batterman and Barrett^{5,6} discovered the martensitic transformation. It is therefore unknown if this material was actually the transforming type. Weger et al⁴⁴ suggest that the stress in the $\langle 100 \rangle$ direction broadens the Clogston-Jaccarino peak, reducing the density of states at the Fermi level. This reduction results in the lowering of T_c , and a lowering of the resistance due to less impurity scattering from s to d states. Muller and Sauer⁴⁵ (1964), reported a linear decrease in T_c of $0.021^\circ K/kb$. Their specimens were in the form of layers formed on the surfaces of vanadium wires and pressure was produced by the ice-bomb technique. Smith⁴⁶ (1970) has pointed out that these two aspects of their technique jeopardize their claim of hydrostatic

pressures in the V_3Si itself. Instead, Smith applied pressure to bulk specimens with an n-pentane and isoamyl alcohol mixture. This mixture is an excellent hydrostatic medium. He finds that T_c is essentially linear in pressure to 24 kb and that its pressure derivative is $0.03 \text{ } ^\circ K/kb$. Using a similar pressurizing method, Neubauer⁴⁷ obtained a pressure derivative of $0.023 \text{ } ^\circ K/kb$ for pressures to 18 kb.

Non-hydrostatic stresses modify the electronic heat capacity of V_3Si . Kunzler, Maita, Levinstein and Ryder³¹ stressed cylindrical specimens of single-crystal V_3Si by fitting them with copper bands at room temperature and then cooling the composite structures. Differential thermal contraction produced the stress, which clearly had a significant shear component. All specimens had $[001]$ cylinder axes, and both transforming and non-transforming material was tested. They observed that stress decreased the heat capacity at temperatures below T_c and increased it at temperatures above T_c in both materials. They also reported that an anomaly in the heat capacity that originated at $21^\circ K$ and extended down in temperature in the transforming specimen was almost completely suppressed by stress. Furthermore, the increase in heat capacity at temperatures above $25 \text{ } ^\circ K$ is significantly larger for transforming specimens.

E. Scope of this Dissertation

This dissertation describes the author's experimental study of the influence of hydrostatically applied stress, thus of pure lattice volume reduction, on the anomalous elastic softening in non-transforming V_3Si . The results contrast with those reported by Patel and Batterman for uniaxial loading, thus for shear strains. Since a general deformation is composed of both shear strain and volume change, the research to be des-

cribed and the uniaxial work are in a sense complementary, together providing a complete description of the influence of stress on the softening anomaly in V_3Si .

In the present study the moduli were obtained by measuring the ultrasonic resonance frequencies of three thin specimens cut from the same small single-crystal of V_3Si . A continuous-wave resonance method was used because the specimens were far too thin to allow resolution of individual pulse echos. Each specimen, which had finely ground parallel faces, was sandwiched between a pair of 30 MHz quartz transducers, one serving as a transmitter of ultrasound and the other as a receiver. Resonances in the neighborhood of 30 MHz were measured. The crystallographic orientations of the specimens and their transducers were selected so that a different pure mode vibration would be excited in each specimen. To simplify the experimental procedures, shear modes requiring accurate alignment of the transducer shear direction were not used. Thus $C' \equiv \frac{1}{2}(C_{11} - C_{12})$ was not measured directly because this would have required orienting two shear transducers on the specimen. Instead, its value was computed from the measured values of C_{44} , C_{11} , and $\frac{1}{2}(C_{11} + C_{12} + 2C_{44})$. In this set of moduli, C_{44} controls an isotropic shear mode, which means that the shear transducers need not be oriented, and the other two control compressional modes. The adiabatic bulk modulus (B^S) was also computed from values of the directly measured moduli.

Modulus measurements were conducted as a function of applied helium gas pressure for temperatures from several degrees below the superconducting critical temperature, the apparent lower temperature limit of the softening anomaly in non-transforming V_3Si , to room temperature. This critical

temperature is 17°K . Measurements were also performed at room pressure as a function of temperature over a slightly wider temperature range to check and calibrate the apparatus and to document the softening for these specimens.

Since the ultrasonic pulse methods are the most commonly used ways of measuring the single crystal elastic moduli of materials in laboratories, the reader may have little knowledge of the continuous-wave resonance method. Therefore, the resonance method is described and the relevant equations are derived in Chapter II. This chapter also contains a succinct presentation of the macroscopic theory of elastic moduli and a discussion of wave propagation.

All aspects of the preparation of specimens are described in Chapter III. These include: crystal growing, specimen orientation and fabrication, specimen thickness measurements, the selection of transducers and their frequency calibration, the bonding of transducers to the specimens, and the inspection of the specimens by x-ray diffraction methods for evidence of a structural transformation.

One by-product of this research is a versatile elastic modulus measuring system. Before the beginning of this study, research in the author's laboratory on the elastic properties of solids under pressure had been confined to "typical solids", that is those whose moduli were only slightly sensitive to temperature changes. But the moduli of V_3Si are extremely temperature sensitive. The available temperature controlling system would have allowed experiments at temperatures above 77°K . But a temperature capability of 4°K to 300°K was necessary for the research on V_3Si . An ultrasonic pulse set-up was available in the laboratory. But the available specimens were so small that it was of no use in the

research on V_3Si . The new system uses a transmission-type c-w resonance apparatus. All three specimens are mounted together in a single pressure vessel, and resonance frequencies of all three are measured in sequence at each pressure and temperature. This procedure minimizes temperature differences between the specimens. The temperature of the vessel can be varied from $4^{\circ}K$ to $300^{\circ}K$, and temperatures are stabilized to better than 0.1%. This degree of stability permitted the pressure dependences of the moduli of V_3Si to be measured precisely. This system is described in detail in the first half of Chapter IV. The remainder of Chapter IV is devoted to the resonance frequency measurements on V_3Si , data processing procedures, and an analysis of experimental errors.

The experimental results are presented in Chapter V. Both the temperature dependences and the pressure dependences of the moduli are shown graphically. The pressure derivatives are tabulated. Only C' , C_{44} , and B^S are shown, for they are the relevant moduli for this research. But the directly measured moduli are tabulated in Appendix C for reference.

The results are discussed in Chapter VI. Among the topics considered are the temperature dependences of the pressure derivatives, the influence of stress on the moduli, and the possibility of inducing a structural transformation in V_3Si with pressure.

Chapter. II

MEASUREMENT THEORY

In this research the elastic moduli were measured by a two-transducer version of the continuous-wave (c-w) ultrasonic resonance technique. Data were taken as a function of hydrostatic pressure on thin, single-crystal specimens. This chapter develops the equations used to compute the moduli from the resonance frequencies.

The chapter begins with a brief introduction to Hooke's Law and wave propagation in single-crystals. These basics are followed by a thorough analysis of the c-w resonance method used in this research. The resulting equations are then modified for shortening of the specimens under pressure.

A. Elastic Moduli Basics and the Mode Propagation Equations

The strain amplitudes used in measuring the moduli by ultrasonics are small. For small strains (ϵ_j) the stresses (σ_i) are given by Hooke's Law, which may be written as:⁴⁸

$$\sigma_i = \sum_j C_{ij} \epsilon_j ,$$

where i and j range from 1 to 6. The C_{ij} are the elastic moduli. They form a 6×6 , symmetrical matrix. For cubic crystals the following relations apply provided the coordinate system is coincident with the cubic axes:

$$C_{11} = C_{22} = C_{33} ,$$

$$C_{12} = C_{21} = C_{31} = C_{13} = C_{23} = C_{32} ,$$

$$C_{44} = C_{55} = C_{66} ,$$

and all other C_{ij} are identically zero.

The application of hydrostatic pressure leaves the shape of a cubic crystal unchanged. Thus, the form of the modulus matrix is invariant to pressure for this case. For the same reason the equations relating the elastic

moduli of a cubic crystal to its ultrasonic wave velocities are invariant to hydrostatic pressure.

At any temperature and pressure the observed values of the moduli of a material depend upon the thermodynamic constraint imposed by the modulus measuring method. For ultrasonic methods, expansion and contraction of the material occurs so rapidly that the heat of deformation cannot flow to and from the strained regions. Thus the moduli are measured by an adiabatic process. They are called the adiabatic elastic moduli and are denoted by a superscript S on the usual modulus symbol. For a static method, however, the measuring process is clearly isothermal. A superscript T on the modulus symbol denotes that it is an isothermal elastic modulus.

The relations between the adiabatic and isothermal moduli are:⁴⁹

$$c_{11}^T = c_{11}^S - \frac{\Delta}{1 + \Delta} B^S \quad (2.1)$$

$$c_{12}^T = c_{12}^S - \frac{\Delta}{1 + \Delta} B^S \quad (2.2)$$

$$c_{44}^T = c_{44}^S \quad (2.3)$$

$$c_{ij}^T = c_{ij}^S \quad (2.4)$$

$$B^T = \frac{B^S}{1 + \Delta}, \quad (2.5)$$

where

$$B^S = \frac{1}{3}(c_{11}^S + 2c_{12}^S), \quad (2.6)$$

which is the adiabatic bulk modulus.

$$\Delta \equiv \frac{9\alpha^2 T B^S}{\rho c_p}, \quad (2.7)$$

where T is the absolute temperature, ρ is the density, α is the linear thermal expansivity, and c_p is the specific heat at constant pressure.

A few comments on these relations should be made. Notice that Δ decreases as the temperature is reduced. At room temperature its value is normally between 0.001 and 0.1. But its value may be several orders of magnitude smaller at low temperatures. Thus the differences between isothermal and adiabatic moduli are very small at low temperatures. This is fortunate because the absence of thermal expansivity and heat capacity data precluded the computation of Δ for V_3Si . But not knowing Δ really causes little difficulty, for the focus of this research is C' . And from these relations one sees that the adiabatic and isothermal values of this modulus are identical. Furthermore, the isothermal and adiabatic values of C_{44} are identical. To simplify the notation, the superscripts T and S will not be used on C_{44} and C' .

Although elastic moduli can be measured by a static loading method, a more accurate way is to send ultrasound through the material and measure its wave velocity. The adiabatic elastic moduli determine the velocity (v) of a stress wave propagating in the direction $\hat{k}$ with a specified polarization. Thus, the effective elastic modulus for that propagation mode can be determined by measuring the wave velocity.

There are two general ways of measuring the wave velocity. Both require that the specimen have a pair of flat, parallel faces. A transducer, usually a thin disk of crystalline quartz with evaporated metal electrodes, is bonded to one of these faces with a thin film of viscous oil or cement. This transducer is excited with an r-f signal generator, thereby causing it to inject plane ultrasonic waves into the specimen. If the generator is pulse-modulated, the ultrasonic pulses thus generated echo between the parallel faces of the specimen. The wave velocity of the ultrasound within the pulse envelope is determined by measuring the round-

trip time of the pulse echoes. If the generator emits a continuous-wave (c-w), standing waves can be set up between the parallel faces of the specimen by adjusting the frequency of the generator. The wave velocity is determined by measuring the frequencies of the resonances.

A clear advantage of the c-w resonance method over the pulse method is that it may be used on very thin specimens. Because the V_3Si specimens were far too thin to allow resolution of pulse echoes, the c-w method was chosen for this research.

A single transducer can serve as both transmitter and receiver of ultrasound. In the pulse method these functions alternate rapidly, with the transducer first emitting a strong pulse and then receiving a string of much weaker echoes before emitting another strong pulse. But in the c-w method the resonance are buried in the excitation signal at the transducer. They can be detected with a Q-meter⁵⁰ or r-f bridge⁵¹ if they are sufficiently strong. But they may be weak.

A better way to observe the c-w resonances is to use a separate receiving transducer. It is bonded to the opposite face of the specimen and connected to a sensitive r-f voltmeter. A sharp voltage peak is observed as the signal generator is tuned through each resonance. If the r-f leads to the transducers are thoroughly shielded to avoid pick-up of the excitation signal by the voltmeter, even very weak resonance peaks can be observed. This arrangement was selected for this research.

The equations that relate the elastic moduli to the wave velocities have been derived elsewhere.⁵² Briefly, the wave equation is written in tensor notation, Hooke's Law is substituted into it with the strains expressed in terms of the particle displacement components (u_i), and plane wave solutions are assumed. This procedure yields an eigenvalue equation

that has three solutions for any $\hat{k}$.

If $\hat{k}$ lies along either $\langle 100 \rangle$, $\langle 110 \rangle$, or $\langle 111 \rangle$ directions in the cubic crystal, each solution is particularly simple:

$$\rho v^2 = C, \quad (2.8)$$

where C denotes a C_{ij} or a simple, linear combination of C_{ij} 's. The particle displacements, that is the eigenvectors ($\hat{u}$), lie either parallel with or perpendicular to $\hat{k}$. Thus each wave is either a pure shear wave or a pure compressional wave. ρ is the density of the crystal.

Table I lists all the pure mode axes for any cubic crystal, the mode equations, the particle displacement directions, and the types of transducers required for transmitting and receiving the ultrasound. The parallel faces of the specimen should be oriented accurately perpendicular to k . X-cut quartz transducers are used for compressional modes and AC-cut for shear modes.

To measure all three elastic moduli, three modes are selected from Table I. Of these, at least one must be a shear mode. Modes (1), (2), and (3) were selected for this research. Only mode (3) is a shear type. When this shear mode is used the shear axes of the transducers need not be aligned with a special crystallographic direction on the specimen. And not having to align the transducers considerably simplifies the bonding procedure.

Velocity measurements normally are conducted at frequencies between 5 and 50 MHz. At lower frequencies, diffraction of the ultrasound impairs the accuracy of the measurements. At higher frequencies the surface finish of the specimen faces is very important, and the transducers are very thin and thus quite fragile. All velocity measurements for this research were

Table I: Pure Mode Equations

Mode	$\rho v^2 =$	$\hat{k}$ (Propagation)	$\hat{u}$ (Displacement)	Quartz Transducer Cut
(1)	c_{11}	100	100	X
(2)	$\frac{1}{2}(c_{11} + c_{12} + 2c_{44}) \equiv c_{L(110)}$	110	110	X
(3)	c_{44}	100	in (100) plane	AC
(4)	$\frac{1}{2}(c_{11} - c_{12}) \equiv c'$	110	$\bar{1}\bar{1}0$	AC
(5)	c_{44}	110	001	AC
(6)	$\frac{1}{3}(c_{11} + 2c_{12} + 4c_{44})$	111	111	X
(7)	$\frac{1}{3}(c_{11} - c_{12} + c_{44})$	111	in (111) plane	AC

performed near 30 MHz.

B. Analysis of the C-W Resonance Method

In this research each velocity was determined by measuring the resonance frequencies of a composite consisting of a specimen, two transducers, and two bonds. The equations for the velocity and elastic modulus in terms of these frequencies are developed in this section. Using a similar procedure, Bolef and Menes have derived the corresponding equations for the single-transducer arrangement.⁵⁰

For a completely isolated specimen of thickness l_s the wavelength of ultrasound at resonance frequency $\nu'_{s,n}$ is

$$\lambda_{s,n} = \frac{2l_s}{n}, \quad (2.9)$$

where $n = 1, 2, 3, \dots$ (all integers). n is the number of half waves between the parallel faces of the specimen at resonance. The wave velocity is given by

$$v = \lambda_{s,n} \nu'_{s,n}. \quad (2.10)$$

Therefore,

$$v = \frac{2l_s}{n} \nu'_{s,n}, \quad (2.11)$$

where

$$n = \frac{\nu'_{s,n}}{\Delta \nu'} \quad (2.12)$$

and

$$\Delta \nu' \equiv \nu'_{s,n+1} - \nu'_{s,n}.$$

In actual resonance frequency experiments the measured quantities are the composite resonance frequencies, the $\nu'_{c,n}$'s. And n is the number

of half waves that would lie between the faces of the specimen if the specimen were isolated and resonating at frequency $\nu_{S,n}$. $\nu_{S,n}$ is computed from $\nu_{C,n}$ by transmission line theory in Appendix A. The final result (Eq. A.5) is

$$\nu_{S,n} = \nu_{C,n} \left\{ 1 - 2 \frac{\left[\frac{m_B}{m_S} - \frac{m_T}{m_S} \left(\frac{\nu_{C,n} - \nu_T}{C,n} \right) \right]}{1 - R \nu_{C,n} (\nu_{C,n} - \nu_T)} \right\}, \quad (2.14)$$

where

$$R = \frac{4\pi^2 m_T m_B}{(\rho_B v_B)^2}$$

and $m = \rho l$. The subscripts C, S, B, and T denote the composite, specimen, bond, and transducer. Notice that the correction to $\nu_{C,n}$ is minimum if $\nu_{C,n}$ equals ν_T , the fundamental resonance frequency of each transducer. Thus the influence of this correction term is minimized by taking resonance frequency data as close to ν_T as the frequency spacing of the resonances will allow.

Eq. (2.14) is unwieldy as it stands. Let us examine the relative sizes of its terms with the hope of eliminating some of them. In this research the specimens were about 0.2 cm thick. The bonds were about 3×10^{-4} cm thick; but this number is uncertain by 50% because the thickness was measured at room temperature, where the bonds were liquid. The density of V_3Si is 5.7 g/cm³, and its moduli are of the order of 1 Mb. For minimum error v should be computed from the two resonance frequencies neighboring ν_T ; thus, δv should not be larger than $\nu_{C,n} - \nu_T$. Using Eqs. (2.8) and (2.11) through (2.13), one finds that

$$2m_B/m_S \sim 5 \times 10^{-4},$$

$$2m_T/m_S \sim 5 \times 10^{-2},$$

$$n \sim 30,$$

$$\Delta \mathcal{V} \sim 1 \text{ MHz},$$

$$R \mathcal{V}_{C,n} (\mathcal{V}_{C,n} - \mathcal{V}_T) \sim 0.1,$$

and

$$\frac{m_B}{m_S} - \frac{m_T}{m_S} \left(\frac{\mathcal{V}_{C,n} - \mathcal{V}_T}{\mathcal{V}_{C,n}} \right) \sim 10^{-3}.$$

With these numbers as guides, Eq. (2.14) may be simplified considerably. m_B/m_S is not only small but it is invariant to pressure or temperature change. Thus it certainly could be set equal to zero in this research, which was directed at measuring changes in the moduli. The term containing R , a second order correction to $\mathcal{V}_{C,n}$, was also set equal to zero. With these two simplifications the expression for $\mathcal{V}_{S,n}$ reduces to

$$\mathcal{V}_{S,n} = \mathcal{V}_{C,n} + 2 \frac{m_T}{m_S} (\mathcal{V}_{C,n} - \mathcal{V}_T), \quad (2.16)$$

where m_T/m_S is independent of pressure and temperature.

n is computed by inserting Eq. (2.16) into Eqs. (2.12) and (2.13).

The result is

$$n = \frac{\mathcal{V}_{C,n} + 2 \frac{m_T}{m_S} (\mathcal{V}_{C,n} - \mathcal{V}_T)}{\left(1 + 2 \frac{m_T}{m_S} \right) \delta \mathcal{V}}, \quad (2.17)$$

where

$$\delta \mathcal{V} \equiv \mathcal{V}_{C,n+1} - \mathcal{V}_{C,n}. \quad (2.18)$$

Using Eq. (2.16) rather than Eq. (2.14) in this computation causes less than 0.03 error in n for the parameters chosen above.

The numerical values of the n 's computed with Eq. (2.17) will not be exact integers because of resonance frequency measurement errors and the approximations used in deriving this equation. But n itself must be an integer. Thus each n computed with this equation must be rounded to the nearest integer to find the actual n .

Once the integer n 's of the resonances have been determined, the wave velocity (v) is calculated with Eqs. (2.11) and (2.16). Because the second order correction to $\mathcal{V}_{C,n}$, which appears in Eq. (2.14), is absent from Eq. (2.16) the computed values of $\mathcal{V}_{S,n}/n$, thus the computed values of v , decrease slowly with increasing n . But notice that this correction term vanishes at $\mathcal{V}_{C,n} = \mathcal{V}_T$. Thus an accurate value for v can be obtained by using Eq. (2.16) to compute $\mathcal{V}_{S,n}/n$ values for the composite resonances neighboring $\mathcal{V}_T$ and then linearly interpolating between these two values to find an effective $\mathcal{V}_{S,n}/n$ value at $\mathcal{V}_{C,n} = \mathcal{V}_T$. If this effective value is denoted as X , the velocity and elastic modulus are given by

$$v = 2/X, \quad (2.19)$$

and

$$c = 4\ell^2 X^2 \rho, \quad (2.20)$$

where ρ and ℓ are the density and thickness of the specimen at the experimental pressure and temperature. A sample numerical computation appears in Appendix B.

$\mathcal{V}_T$ is the fundamental resonance frequency of each transducer when it is isolated from the specimen. It is measured at ambient pressure and

temperature and then corrected to the experimental pressure and temperature. The correction factors for X-cut⁵³ and AC-cut⁵⁴ quartz transducers have been published by McSkimin and Andreatch.

C. Specimen Thickness Change Under Pressure: Cook's Method

Cook has developed a self-consistent scheme to correct the measured values of the moduli for the reduction in the thickness of the specimen due to pressure.⁵⁵ This scheme is applied here to the c-w resonance method.

For a cubic crystal the fractional thickness change produced by a pressure change dP is

$$\frac{d\lambda}{\lambda} = -\frac{1}{3} \frac{dP}{B^T}, \quad (2.21)$$

which may be written as

$$\frac{d\lambda}{\lambda} = -\frac{(1 + \Delta)dP}{c_{11}^S + 2c_{12}^S} \quad (2.22)$$

by using Eqs. (2.5) through (2.7). Now define a function ϕ by

$$\phi \equiv \frac{\lambda(0)}{\lambda}, \quad (2.23)$$

where $\lambda(0)$ is the thickness of the specimen at room pressure. In terms of ϕ , Eq. (2.20) may be written as

$$c = 4\rho(0)\lambda^2(0)x^2\phi, \quad (2.24)$$

where $\rho(0)$ is the density of the specimen at room pressure. ϕ is determined by inserting Eq. (2.23) into Eq. (2.22), solving for $d\phi$ and integrating it over pressure. Modes (1), (2), and (3) of Table I were used to determine the values of the elastic moduli in the research.

For this set of modes the expression for ϕ is

$$\phi = 1 + \frac{1}{4\rho(0)\ell_2^2(0)} \int_0^P \frac{(1 + \Delta)dP}{4x_2^2 - 4g_3^2x_3^2 - g_1^2x_1^2} \quad (2.25)$$

where $g_3 = \frac{\ell_3}{\ell_2}$ (2.26)

and $g_1 = \frac{\ell_1}{\ell_2}$ (2.27)

The subscripts on the ℓ 's, x 's, and g 's denote the mode. g_1 and g_3 are independent of pressure. The integral in Eq. (2.25) is evaluated by numerical techniques.

D. Summary of the Computation Methods

The elastic modulus at the experimental pressure and temperature is given by Eq. (2.24), where $\rho(0)$ and $\ell(0)$ are the density and thickness of the specimen at room pressure. x and ϕ are computed by the following procedure:

- (1) An approximate n is computed with Eq. (2.17) and this number is rounded to the nearest integer to find the actual n , which must be an integer. n 's are computed for several resonances neighboring ν'_T . The n for any resonance must be 1 greater than the n for the next lower frequency resonance.
- (2) $\nu'_{S,n}$ is computed with Eq. (2.16) for the two resonances nearest ν'_T . ν'_T is the unloaded, fundamental resonance frequency of each transducer at the experimental pressure and temperature.

(3) $\mathcal{V}'_{S,n}/n$ is computed for these two resonances. X is the effective value of $\mathcal{V}'_{S,n}/n$ at $\mathcal{V}'_{C,n} = \mathcal{V}'_T$. It is determined by linear interpolation.

(4) ϕ is computed with Eq. (2.25), which applies when modes 1, 2, and 3 are used to measure the moduli. These modes were used in this research.

In this research C_{11} , C_{44} , and $C_{L(110)}$ were measured directly. Expressions for C' and B^S in terms of these moduli are obtained by solving simultaneously the first three mode equations listed in Table I. These expressions are:

$$C' = C_{11} + C_{44} - C_{L(110)} \quad (2.28)$$

$$B^S = \frac{1}{3} \left[4 \left(C_{L(110)} - C_{44} \right) - C_{11} \right] \quad (2.29)$$

$$B^S = C_{11} - \frac{4}{3} C' \quad (2.30)$$

$$B^S = C_{L(110)} - C_{44} - \frac{1}{3} C'. \quad (2.31)$$

Chapter III

SPECIMEN PREPARATION TECHNIQUES

Three specimen-bond-transducer composites were prepared for the resonance frequency measurements on V_3Si . All three specimens were fabricated from the same single-crystal of non-transforming V_3Si . This chapter describes the preparation procedures.

The chapter opens with descriptions of the crystal growing technique, the fabrication of specimens, and the measurement of specimen thicknesses. X-ray inspection of the specimens for signs of a structural transformation is covered next. And the last part deals with frequency calibration of the transducers and with the bonding procedures.

A. Single-Crystal Growth and Etching Procedures

A single crystal of V_3Si was grown for this research by B. F. Addis of the Crystal Growing Facility of the Department of Materials Science and Engineering at Cornell University. The crystal was cylindrical, $\frac{1}{2}$ inch long, and $\frac{1}{4}$ inch in diameter. Its longitudinal axis was parallel to the $[100]$ crystallographic direction to within two degrees.

This crystal was produced by a two-step process similar to the one described by Greiner and Mason.¹⁸ In the first step, a homogeneous polycrystalline bar is formed by induction-melting a slightly silicon-rich mixture of the pure components in a water-cooled copper boat.⁵⁶ In the second step, floating-zone passes are made on the bar to induce the growth of a single-crystal. The excess silicon in the initial charge compensates for selective vaporization of silicon from the melts.

The starting materials were 99.9% pure vanadium produced by Atlantic Equipment Engineers and 40 ohm-centimeter quality silicon produced by Union Carbide. A charge of 25.2 atomic percent silicon and 74.8

atomic percent vanadium was contained in water-cooled copper boats and melted by r-f induction heating under an atmosphere of Matheson Research Grade argon. To promote homogeneity the charge was broken up after solidification, mixed, and remelted. This process was repeated three times. The finished bars were $\frac{1}{4}$ inch in diameter and 8 inches long.

A polycrystalline bar was mounted vertically in the floating-zone apparatus, enclosed with a fused quartz tube, and blanketed with slowly flowing, pure argon. Power from a 375 kHz generator was coupled into the bar with a two-turn coil that encircled the quartz tube. The coil was raised at a constant speed of 0.006 inch per minute by a motor-driven screw mechanism. Several passes of the zone through the bar were required to obtain a grain large enough to serve as a seed. This grain was oriented by x-ray diffraction, fused to the end of another polycrystalline bar in the floating-zone apparatus, and a single pass was made to grow the crystal provided for this research.

The zone-passed region of this bar was lightly sandblasted to remove glazing, etched, and inspected visually for grain boundaries and inclusions. Neither type of defect was observed over a $\frac{1}{2}$ inch length. The etchant consisted of equal parts by volume of hydrofluoric acid and hydrogen peroxide (30%).

B. Crystal Orientation and Specimen Fabrication

Three thin specimens were fabricated from the single crystal, two with (100) faces and one with (110) faces. Fabrication was carried out with special orienting and lapping equipment in the X-Ray Laboratory (B. W. Batterman) of the Department of Materials Science at Cornell. Specimen blanks were cut from the oriented crystal with the spark-cutting machine at the Crystal Growing Facility (B. F. Addis).

The apparatus is illustrated in Figure 2. There are several major components:

(1) X-Ray Diffractometer. The diffractometer table rotates about a vertical axis. The angle of rotation can be set to within 0.01° . A heavy V-block, which supports one of two types of specimen "barrel-holders" during the orienting procedure, rides in a track fastened to this table. A General Electric x-ray tube with a copper target supplies a primary beam that is a vertical line in cross-section.

(2) Bond Barrel Holder. This specimen holder is a cylinder with a tiltable stage mounted on one of its end faces. The stage is held against a three-point kinematic support by a coil-spring and drawbar mechanism that is located within the cylinder. One of the support pins is fixed, and the other two are adjustable in height. The tilt of the stage is set with a pair of Allen screws that press against the bottoms of the moveable pins. Once the tilt has been set, the stage is locked by tightening the drawbar with the knurled knob located at the screw-end of the cylinder. The cylinder has been machined for a close-tolerance slip-fit in the Lapping Bell, which is described below.

(3) Straight Barrel Holder. This specimen holder is not shown in Figure 2. It is essentially a solid, precisely machined, right circular cylinder. Its diameter has been machined for a close-tolerance slip-fit in the Lapping Bell. One end of the cylinder is smooth, flat, and accurately perpendicular to the longitudinal axis of the cylinder. This holder is useful for obtaining an

Figure 2. Specimen fabricating apparatus. (a) Top view of diffractometer. (b) Top view of spark-cutting machine. (c) Side view cross-section of Lapping Bell and plate.

accurately parallel face on a specimen once one face has been oriented and lapped flat.

(4) Spark-Cutting Machine. Cutting proceeds by spark erosion.

The crystal to be cut is mounted on a barrel holder and submerged in kerosene. The barrel holder is clamped in a V-block.

(5) Lapping Bell. This lapping and grinding fixture is a hollow, stepped-diameter cylinder. It is made of hardened steel to inhibit wear. The inner diameter of the upper part of the Bell matches the diameter of either of the barrel holders. The bottom end surface of the Bell is perpendicular to the longitudinal axis of the upper bore of the Bell to within a few hundredths of a degree.

In this research all lapping was performed on a $\frac{1}{4}$ inch thick sheet of plate glass. And the lapping compound was a slurry of 600 mesh, silicon carbide powder in glycerine and water.

Three specimen blanks, each two to three millimeters thick, were spark-cut from the center portion of the single crystal. Two of the blanks were circular disks with (100) faces, and one was a rectangular plate with (110) faces. Accurately parallel surfaces were produced on each disk by orienting and lapping both its faces. The disk was bonded to the stage of the Bond Barrel Holder with a thin film of hard wax. Only one face of the plate was oriented on the diffractometer; after this face was lapped flat, it was bonded to the end surface of the Straight Barrel Holder, and the other face of the plate was lapped flat.

The lapped specimens were etched lightly to remove the cold-worked surface layers and then checked on the diffractometer for misorientation. The etchant was 1 part HF, 1 part H_2O_2 (30%), and 4 parts H_2O . During the orientation checks, the specimens were held to the Straight Barrel

Holder with double-backed Scotch Tape. The misorientation of the disks was 0.05° , and the misorientation of the plate was 0.15° .

C. Thickness and Parallelism Measurements

Specimen thicknesses were measured with a Van Keuren Light Wave Micrometer, a compact, precision micrometer that is readable to 2.5×10^{-5} centimeter (10 microinches). This sensitivity is achieved by using an optical wedge attachment. The wedge, which measures the slight deflection of the micrometer's frame in response to pressure applied by the anvils, allows the thickness of a specimen to be measured at a standard anvil pressure.

The specimens and micrometer were allowed to equilibrate in a temperature controlled laboratory before the specimen thicknesses were measured. The thickness of a specimen was measured at eight points, and the readings were averaged. Temperature was measured with an ordinary mercury thermometer, which rested on the frame of the micrometer. The specimens were manipulated with tweezers to avoid warming them by contact with the hand.

At 296°K , the specimen thicknesses in centimeters were:

$$l_1 = 0.18433 \pm 0.00005$$

$$l_2 = 0.25684 \pm 0.00008$$

$$l_3 = 0.15037 \pm 0.00005$$

The subscripts denote the modes listed in Table I. Non-parallelism of the faces was less than 0.02° .

D. Search for the Structural Transformation

Both disk specimens were checked by x-ray diffraction for evidence of a structural transformation at room pressure. In V_3Si that transforms, the transformation starts near 21°K and stops at 17°K , leaving the crystal

lattice tetragonal instead of cubic. In these diffraction experiments the (600) reflections of the copper $K\alpha_{12}$ doublet were scanned at 32°K and 12°K, thus at well above and at well below the transformation range. Any splitting of the reflection peaks at the lower temperature would have proved that a transformation had occurred.

During these experiments the specimen was mounted in a variable temperature dewar like the one described in Reference 5. A thin layer of G. E. 7031 varnish bonded the specimen to a copper block in the dewar. The temperature of the specimen was adjusted by varying the current to a resistor imbedded in this block. And temperature was read with a calibrated carbon resistor thermometer, imbedded in the same block.

A Siemens diffractometer was used to scan the x-ray reflections. The diffractometer table, driven by a constant speed motor, rotated in the horizontal plane. The base of the dewar rested in a horizontal track that was clamped to a short, vertical shaft at the center of the table. This track, which could be rotated on the shaft and then locked in position, was set perpendicular to the primary x-ray beam. The primary beam, generated by a G. E. copper tube and then collimated and filtered, was $\frac{1}{2}$ inch high and 0.010 inch wide at the specimen. An ordinary 6-32 machine screw, threaded through a vertical plate that closed one end of the track, was used to push the dewar, and thus the specimen, across the primary beam a calibrated distance. To prevent the primary beam from striking those portions of the specimen face that would be outside the active area of the transducer during the resonance frequency measurements, a lead washer with a 0.125 inch hole was varnished to the center of the specimen face. The diffracted beam was sensed by a Geiger tube with a wide open window, and the reflection peaks were displayed on a Mosley

strip chart recorder.

Angles in 2θ from 5° below to 5° above the (600) Bragg reflection of the $\text{CuK}\alpha_1\alpha_2$ doublet were scanned, first at 32°K , then at 12°K . Then the dewar was moved 0.015 inch with the 6-32 screw and both angular scans were repeated. This process was continued until all the unmasked surface of the specimen had been surveyed. The entire experiment was repeated on the other disk.

Neither disk specimen exhibited splitting or broadening of the individual peaks within the doublet when the temperature was lowered to 12°K . Both peaks of the doublet were free of substructure and clearly separated on the strip chart at 32°K and 12°K . The quality of the peaks and the sensitivity of the measuring technique were such that a 20% broadening of a peak could have been observed had it been present. Thus the disks were non-transforming. And since the rectangular plate specimen and the disks had been cut from adjacent material in the same crystal, it is concluded that the plate was non-transforming also.

E. Transducers and Bonding

X-cut and AC-cut quartz transducers resonant at $30\text{ MHz} \pm 1\%$ were purchased from the Valpey Crystal Corporation. Each transducer, several thousandths of an inch thick and 0.200 inch in diameter, had coaxial, evaporated gold-on-chromium electrodes. One electrode covered all of one face of the transducer, wrapped around its edge, and covered a band 0.020 inch wide at the periphery of the other face. The second electrode, 0.125 inch in diameter, was coaxial with this band. A flat had been ground in the edge of each AC-cut transducer perpendicular to the shearing direction; when shear transducers were bonded to a specimen, their flats were aligned to maximize the amplitudes of the resonance peaks.

As one may see by reviewing the analysis of the c-w resonance method in Chapter II, the accuracy of a modulus measurement is influenced by the accuracy of the transducer resonant frequency. The calibration tolerance given by the transducer manufacturer would have been large enough to have impaired the accuracy of the measurements on V_3Si . Thus the transducers were recalibrated.

The calibration procedure was quite simple. The transducer was connected in series with a 1000 ohm carbon resistor and an r-f signal generator, and the voltage across the resistor was measured with a Tektronix Model 585 oscilloscope. The signal generator was tuned for a dip in voltage, which indicates a resonance, and the frequency was read to ± 1 kHz with a Hewlett-Packard Model 5245-L frequency counter.

The calibrated transducers were grouped according to resonant frequency in intervals 100 kHz wide and centered at frequencies from 29.7 MHz to 30.3 MHz. Only transducers from the same group were bonded to a specimen, and the center frequency of the group was assigned as the resonant frequency of both transducers on the specimen. With this procedure the uncertainty in the transducer resonant frequency (± 50 kHz) contributes less than 2 parts in 10^4 to the uncertainty in the absolute value of a V_3Si elastic modulus.

The final step in preparing a composite resonator was to bond a transducer to each face. X-cut transducers were bonded with glycerine to specimens 1 and 2; AC-cut transducers were bonded with Nonaq Stopcock Grease (Fisher Scientific Company) to specimen 3. Nonaq was used with the shear transducers, for it, unlike glycerine, will support shear waves at room temperature as well as at cryogenic temperatures. Glycerine is an excellent bond for compressional transducers at all temperatures and for shear

transducers at temperatures below 200°K .

Two surfaces to be bonded together were wiped with Q-Tips moistened with acetone to remove dust, grit, or vestiges of an old glycerine bond. To clean away Nonaq residue, the surfaces were wiped first with a Q-Tip moistened with water; water, not acetone, desolves Nonaq. Chipping or cracking of the transducer was averted by cleaning it on a smooth, flat surface and manipulating it with a Q-Tip saturated with the solvent.

The transducer, its fully-plated-side-up, and the specimen were placed beside each other on a clean sheet of paper. A very small drop of bonding material was applied to the exposed specimen face with a stiff wire. The bond was formed by picking up the specimen with tweezers, inverting it, and placing it gently on the transducer. Then the specimen was inverted again. Finally, the transducer was positioned and pressed firmly against the specimen with the eraser end of an ordinary pencil.

When a Nonaq bond was to be made, the specimen was warmed with a heat gun before the grease was applied to its surface. Upon touching the warm specimen, the grease would thin to an oil less viscous than glycerine, assuring the thinnest possible bond with this bonding material. Shear resonators assembled with Nonaq that had been thinned in this way produced resonance peaks that were nearly as sharp as those obtained from compressional resonators assembled with glycerine. But shear resonators assembled with unheated Nonaq produced very broad, heavy structured peaks.

As was shown in Chapter II, the sizes of some correction terms in the c-w resonance equations depend on the bond thickness. Thus, an attempt was made to measure the thickness of a bond. Nonaq, rather than glycerine, was chosen for this test because it is fairly stiff at room

temperature. The thicknesses of the transducers, specimen, and composite were measured with the Van Keuren Light Wave Micrometer (see Section C of this chapter), and the average bond thickness was computed from these numbers. To minimize distortion of the bonds, minimum anvil pressure was used. Averaged over three different pairs of Nonaq bonds, the bond thickness found this way was 100 ± 50 microinches (2.5 ± 1.3 microns). This result compares favorably with that reported by Ghafelehbashì for Salol, a crystalline bonding material; his bond thicknesses were less than 100 microinches.⁵⁷

Chapter IV

MODULUS MEASUREMENTS: APPARATUS AND TECHNIQUES

The resonance frequencies of the composites were measured as functions of pressure and temperature, and moduli were computed from these data. Data were taken for pressures to several kilobars and temperatures from ambient to near absolute zero. A complete modulus measuring system, the experimental apparatus is described as a unit in the first section of this chapter, and its subsystems are discussed and illustrated in the next six sections. The data taking and processing procedures are described in the following two sections, and errors are treated in the last section.

A. General Description of the Apparatus

A modulus measuring system was designed for this research. It incorporates c-w resonance apparatus, several temperature controlling systems, a gas pressure generator, a Heise pressure gauge, and a beryllium copper vessel that holds an internally shielded, three-specimen jig. Individual specimens are switched across the terminals of the resonance electronics with a set of coaxial relays. The block diagram of this system is shown in Figure 3.

Two pressure tubes made of hard-drawn, 403 stainless steel carry the transmitting and receiving leads to opposite ends of the vessel. The same tubes carry compressed helium to the vessel. Each tube has a 0.250 inch outer-diameter and a 0.065 inch bore-diameter and contains three, teflon-insulated, stranded copper wires. Both tubes have been electrically grounded, shielding the leads and also providing a common return path to the resonance electronics for the signals. Pressure seals for the r-f leads mount in fittings located at the tops of these tubes. Each seal is an epoxy-filled tube that contains three feed-through wires of enam-

Figure 3. Block diagram of the modulus measuring system. Two pressure tubes feed gas to the vessel and contain the r-f leads. The vessel holds a special 3-specimen jig. The heater winding is used only when the vessel is in the Janis dewar.

eled copper.

Temperature is measured with a gallium arsenide thermometer, imbedded in the top of the vessel. To obtain temperatures below 77°K , the vessel is contained in a Model 11DT, Super Vari-Temp Research Dewar, made by Janis Research Company, Stoneham, Massachusetts. This dewar uses liquid helium as its coolant, and the vessel is bathed in helium vapor. Sensing temperature with another imbedded thermometer, an automatic controller adjusts the current flow through a heater winding on the vessel, thereby controlling the temperature of the vessel. For experiments at 77°K the vessel is immersed in liquid nitrogen contained in a deep, glass dewar. And for temperatures above 77°K , the vessel is contained in a Model 6300SD Research Chamber, made by Delta Design, Inc., La Mesa, California. This chamber is cooled with liquid nitrogen supplied by an external, self-pressurizing, storage dewar. An electronic temperature regulator built into the frame of the chamber cyclically opens and shuts a solenoid valve in the nitrogen transfer line, thereby controlling the temperature of the vapor within the chamber and thus the temperature of the vessel. All three methods stabilize temperature to $\pm 0.1\%$, which was adequate for precise modulus measurements on V_3Si .

An overall view of the experimental apparatus is shown in Figure 4. The specimen selector relay box is bolted to the back of the open box that supports the Janis dewar. The Delta Design chamber does not appear in this view.

B. Pressure Vessel

Cross-sectional and overall views of the assembled vessel appear in Figures 5 and 6. The vessel, made of hardened beryllium copper, is a thick-wall cylinder with end plugs that incorporate Bridgeman seals.⁵⁸

Figure 4. View of the experimental area showing (1) resonance electronics, (2) temperature control electronics, (3) Janis dewar, (4) Heise pressure gauge, and (5) gas pressure bench.

Figure 5. Cross section of the pressure vessel.

Figure 6. View of the assembled pressure vessel showing (1) the location of two imbedded gallium arsenide diode thermometers, (2) the heater winding, (3) a mechanical tie point for the heater winding, and (4) the pressure seal extraction clamp. The seal is extracted by backing the threaded end plug against this clamp.

Eighth-inch thick indium washers seal against the pressure tubes and the cylinder. Each washer is sandwiched between anti-extrusion rings made of half-hard beryllium copper. Brass housings that hold electrical connectors for the jig thread onto the pressure tubes. The top of the jig holds a spring-loaded teflon plug containing three spring-contacts. These contacts press against a circular plate consisting of a center conductor and two coaxial conductors. These conductors are insulated from each other by thin bands of epoxy resin. A 4-terminal Amphenol socket in the base of the jig fits onto a mating plug. These electrical connectors are shown in Figures 7 and 8.

The jig is removed from the vessel by extracting the entire bottom end plug assembly from the cylinder. To do this, the retainer plug is unscrewed against a brass clamp that grips the pressure tube. The jig may then be unplugged from the assembly. To mount the jig in the vessel, it is first plugged into the assembly. Then the end plug assembly is inserted into the cylinder, and the retainer plug is tightened with a wrench just enough to cause an initial sealing; the Bridgeman seal tightens itself as the gas pressure is increased.

Round stock of half-hard Berylco 25 for the vessel was purchased from the Beryllium Corporation of America. Each piece was tested ultrasonically for flaws by the Buffalo X-Ray Company, Buffalo, New York; no flaws were found. The cylinder, mushrooms, retainer plugs, and tubing collars were machined roughly to size and shape and then drilled. These pieces were then heat treated to Rockwell C hardness 38. Final machining and threading was done with the metal in this hardened state to make sure that all parts would fit together properly when the vessel was assembled.

The finished cylinder was degreased, and its cylindrical surface

Figure 7. View of the jig and vessel bottom plug assembly showing (1) the V_2Si specimens, (2) the shielded Amphenol connector, (3) the sealing region, (4) the threaded bottom end plug, and (5) the pressure tube containing the three transmitting leads.

Figure 8. View of the jig and vessel top plug assembly showing (1) the indium sealing disk and anti-extrusion rings, (2) the ring contact plate, (3) spring contacts, (4) teflon plug, (5) brass casing of the jig, (6) a sliding transducer contactor, and (7) the threaded top end plug. Both jig and contact plate assembly have symmetrical access windows.

was lightly sandblasted to prepare it for a heater winding. A 25 ohm length of 0.018" diameter manganin wire with enamel and double-silk insulation layers was non-inductively wound on the cylinder. The top and bottom of the winding were mechanically anchored in curved blocks of Berylco 25 that had been epoxied to the curved surface of the cylinder. The winding was bonded to the cylinder by painting it with clear epoxy resin.

Two TG-100-K, gallium arsenide thermometers were purchased from Lake Shore Cryotronics, Inc., Hamburg, New York. One had been calibrated by the manufacturer. They were bonded with General Electric 7031 varnish to the bottoms of two deep pockets that had been machined in the top end face of the cylinder. To shield the thermometers from drafts, the pockets were filled with General Electric RTV silicone rubber.

Long lengths of $\frac{1}{4}$ " x 0.065" pressure tubing were purchased from Harwood Engineering Company, Walpole, Massachusetts. The tube for the bottom of the vessel was shaped by bending it around a pipe. Three lengths of teflon-insulated leadwire were slipped through the bore of each tube. This wire, Type ET 7/38, had been purchased from L. Frank Markel and Sons, Norristown, New Jersey.

The anti-extrusion rings for the Bridgeman seals were machined from half-hard Berylco 25. These rings were individually fitted to the 0.650" bore diameter of the vessel and the outer diameter of the tubing. Indium washers for the seals were punched from 1/8" thick rolled sheet with a special "cookie-cutter" that had been machined from stainless steel tubing.

C. Three-Specimen Jig

The internal construction of the jig is shown in Figure 9. The

Figure 9. Cross section of the specimen jig. The tubes guide the contactors and shield the leads. This wiring order isolates the transmitting leads from the receiving leads. The teflon plug pins center on the rings of the coaxial ring plate.

jig is made primarily of brass. It has three sections, each containing a fixed and a spring-loaded, sliding contactor. Electrical contact to the transducers on the specimens is made with these contactors, which have coaxial electrodes. The center electrode of each is a phosphor bronze spring, and the outer electrode is a narrow ring. A band of epoxy resin 0.005" thick insulates the inner conductor from the outer. Soft solder holds the fixed contactors to the casing of the jig, and two 403 stainless steel tubes guide the sliding contactors. To allow for differential expansion strains, these tubes were not soldered to the brass at any point. But these tubes still make electrical contact with the jig, which is grounded. Thus, they also shield the r-f leads within them. The r-f leads are teflon-insulated, stranded copper wires (Type ET 7/38, made by L. Frank Markel and Sons, Norristown, Pennsylvania). Leads from the transmitting transducers go to a 4-terminal Amphenol socket threaded into the base of the jig. Leads from the receiving transducers go to the spring-loaded, teflon plug in the top of the jig. The wiring order shown isolates these two types of leads from each other. The coil-spring contacts in the plug are guided by brass pins that were pressed into holes drilled in the plug. A metal ring soldered to a recess in the top edge of the jig serves as a retainer for the teflon plug.

The contactors and the coaxial ring plate (see Figure 8) were machined from special coaxial stock in which the brass conductors are insulated from each other by thin layers of epoxy. Coaxial stock was made by the scheme illustrated in Figure 10. Cylinders of brass were machined for a close slip-fit inside one another. Then the center sections of the outer diameters of the inner cylinders were undercut 0.010", leaving bands of metal at the ends as supports. After the parts had been degreased and

STEP 2: EPOXY

STEP 3: RE-MACHINE

Figure 10. Method for fabricating coaxial conductor material.

sandblasted, they were dipped in clear epoxy resin and assembled. The epoxy was allowed to cure at room temperature; an oven cure invariably produced bubbles in the epoxy layers. Finally, the ends of the assembly were cut off, leaving a set of insulated, coaxial cylinders.

D. High Pressure System

The schematic of the high pressure system appears in Figure 11. Tank helium is compressed to pressures up to 5 kb by the first two stages of the Mk. II Gas Bench, a generator built several years ago by the staff of the High Pressure Laboratory at the Department of Materials Science. Helium is carried to the vessel by both pressure tubes, thereby minimizing the flow rate in each tube and thus the viscous drag on the wires within it. Pressure is read with a 0-7.5 kb Heise gauge calibrated to an accuracy of ± 8 bars by the manufacturer. The scale on the gauge can be read to ± 2 bars. Surges during pressure changes are damped by a four foot length of 0.009" bore, 1/8" diameter pressure tubing. Two r-f lead seals are located in fittings atop the $\frac{1}{4}$ " pressure tubes.

Like those described by Goree, McDowell, and Scott,⁵⁹ the r-f lead seals are epoxy-filled tubes that contain fine feed-through wires of enameled copper. The cross-section of a seal is shown in Figure 12. The seals mount in the fittings shown in Figure 13. Insulated with short lengths of heat-shrunk plastic tubing, the soldered joints between the teflon-insulated wires inside the $\frac{1}{4}$ " tubes and these enameled wires are contained in these fittings. The top of each seal threads into an aluminum box that was machined from solid stock. Three BNC receptacles thread into the sides of the box.

The seals were prepared by the following method. Several $2\frac{1}{2}$ " lengths of 3/16" diameter, 0.025" bore tubing (Type 3M, made by Harwood

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Figure 11. Schematic of the high pressure system. The "medium" high pressure section of the laboratory's Mk. II Gas Bench is shown enclosed by dashed lines.

Figure 12. Cross section of a r-f lead pressure seal.

Figure 13. View of hardware atop the upper ends of the vessel pressure tubes showing (1) transmitting lead junction box, containing three 47 ohm terminators, (2) r. f. lead pressure seal, (3) chamber containing spliced leads, (4) receiving lead junction box, (5) r. f. lead pressure seal, and (6) the heater and thermometer lead junction box. The high pressure helium cross-flow line extends to the right.

Engineering Company, Walpole, Massachusetts) were coned, threaded and degreased. Then the bores were etched for 30 seconds in a solution of 45 ml H_2O , 30 ml HNO_3 , 10 ml HF , and 15 ml HCl . The etched tubes were flushed with water, alcohol, and acetone, in that order, and then blown out with dry nitrogen. Three 5" lengths of #34 enameled copper wire were degreased in acetone and then slipped through each tube. Fresh Eccobond 104 epoxy (Emerson & Cuming, Inc., Canton, Massachusetts) was mixed, heated to reduce its viscosity, and degassed briefly under vacuum. Warm epoxy was drawn through the sealing tubes with a vacuum pump. Finally, the epoxy in these tubes was cured by putting the seals in an oven and heating them for 3 hours at $150^{\circ}C$.

To lessen the chance of damaging the teflon-insulated leads inside the long, $\frac{1}{4}$ " pressure tubes, two rules were observed during the experiments on V_3Si : pressure changes were made at rates less than 0.1 kb/minute, and pressures were not allowed to reach the freezing point of helium at any temperature. The freezing points were read from a curve published by Grilly and Mills.⁶⁰ Whenever the freezing-point rule was accidentally violated, making a subsequent pressure change would crack the teflon insulation of the leads and sometimes snap soldered connections or the thin wires that emerge from the bottoms of the r-f lead seals.

E. Janis Helium Dewar

During experiments at temperatures below $77^{\circ}K$, the vessel is suspended inside the Janis Super Vari-Temp dewar. A cross-sectional view of the tail of this dewar appears in Figure 14. Liquid helium from a self-contained reservoir flows through a capillary tube to a heater block in the tail. The flow rate is regulated with a needle valve built into the bottom of the reservoir. The control knob of the valve is located above

Figure 14. Cross section of the lower portion of the Janis Dewar. The liquid helium reservoir is built into the upper portion of the dewar. Heavy, curved arrows denote the helium vapor flow.

the body of the dewar. A small, manually-regulated supply provides current for the heater, which has a resistance of 20 ohms. Helium vapor drifts upward from the heater block, cooling the vessel and pressure tubes before passing out a port at the top of the dewar. A 3-mode controller regulates the temperature of the vessel by adjusting the voltage across the heater winding on the vessel.

To minimize the total helium consumption during an experiment and to minimize the cool-down time, the vessel is chilled in liquid nitrogen before it is lowered into the dewar. Optimum temperature stabilization of the vessel is achieved when the current through the heater block is between 200 and 300 milliamperes and the flow valve is open 10 to 20 degrees in angle; neither setting is critical. Under these conditions, the liquid helium consumption rate is 0.5 to 0.7 liters per hour.

F. Temperature Control Electronics

The wiring diagram of the temperature control electronics appears in Figure 15. The temperature regulation apparatus used when the vessel is in the Janis dewar is shown on the left. The temperature measurement apparatus is on the right. Shielded cable joins the electronics, a chassis mounted in the relay rack, and a minibox screwed to a bracket fastened to the upper end of the center pressure tube (see Figure 13). The small circles on the dashed boxes represent miniature Amphenol connectors. Small diameter, enameled copper wires connect the terminals in the minibox to the vessel heater and thermometers. These wires spiral down the center pressure tube and are held in place with strips of adhesive-backed teflon tape.

Current for the heater is supplied by a Harrison 6824 Power Amplifier, made by Hewlett-Packard (H-P). This amplifier is driven by a

Figure 15. Wiring diagram for the temperature control electronics system. The control thermometer and heater are used only with the Janis dewar. PAR denotes Princeton Applied Research; H-P denotes Hewlett-Packard; L & N denotes Leeds & Northrup. The 100K precision resistor is used to check the current.

Model 150 Cryogenic Temperature Controller, made by Princeton Applied Research Company, Princeton, New Jersey. A 1000 ohm resistor loads the output circuit of the controller. The controller has manual and automatic control modes. The automatic control functions include proportioning, rate, and reset. An uncalibrated gallium arsenide thermometer senses the temperature of the vessel for the controller. This apparatus stabilizes the temperature of the vessel to $\pm 0.1\%$, which was adequate for the research on V_3Si .

The actual temperature of the vessel is measured with a calibrated gallium arsenide thermometer, a diode. Ten microamperes direct-current is passed through the thermometer in the forward direction, and the voltage drop is measured with a Leeds & Northrup K-3 potentiometer. Current is furnished by a constant current supply. Because the thermometer voltage varies from 0.6 at ambient to 1.5 at $4.2^\circ K$, the potentiometer is operated on the 1.6 volt range. In this range, voltage can be measured to within ± 10 microvolts, adequate for detecting temperature changes as small as $0.01^\circ K$.

The current through the thermometer is checked before each temperature measurement. To do this, the voltage across a calibrated, 100K precision resistor (Type WWA-38, made by Dale Electric Company) is measured with the K-3 potentiometer. This resistor has a temperature coefficient of less than 20 ppm/ $^\circ C$, which is insignificant. It was calibrated against a 1000 ohm standard resistor made by Leeds and Northrup. The potentiometer is connected to either the 100K resistor or the thermometer by means of a double-pole, double-throw, toggle switch. The switch and resistor are mounted in a chassis located in one of the equipment racks.

The thermometer had been calibrated by the manufacturer for tem-

peratures from 4.2°K to 300°K in intervals of 1°K to 20°K . Voltages were given to enough significant figures, and the calibration curve was close enough to being linear within these intervals, to allow temperatures to be read to within $\pm 0.01^{\circ}\text{K}$ by interpolation. To facilitate the temperature measurements, a calibration table that listed the voltages for temperatures in intervals of 0.1°K was developed on a computer and printed out. The accuracy of the calibration was checked by submerging the vessel successively in ice water, liquid nitrogen, and liquid helium and measuring the voltage across the thermometer. From these tests the absolute accuracy of the calibration was estimated to be $\pm 0.1^{\circ}\text{K}$, which was adequate for this research.

A 10 microampere constant current supply was constructed for the calibrated thermometer. Its schematic appears in Figure 16. An 8.4 volt mercury cell and the resistors in the base-emitter circuit determine the current through the thermometer. The 25K potentiometer is adjusted to calibrate the supply. The calibrated 100K Dale resistor also appeared in Figure 15. The 2N4250 transistor was selected for its low leakage current, which is less than 2 nanoamperes. The regulation and stability of this supply is $\pm 0.01\%$, which is more than adequate for temperature measurements to within $\pm 0.01^{\circ}\text{K}$.

A view of the temperature control electronics and the Janis dewar appears in Figure 17. The rack on the left contains the apparatus described in this section, a liquid-nitrogen level controller for the dewar, and the power supply for the heater block in the dewar.

G. Resonance Electronics

Apparatus for the c-w resonance method was constructed by Day, Ho, and Ruoff.⁶¹ Completed during the early part of this research, it was

Figure 16. Schematic of the current supply for the calibrated thermometer. The diode symbol denotes the thermometer.

Figure 17. View of the temperature control electronics and Janis dewar showing (1) pressure cross-flow line, (2) helium exhaust port, (3) liquid helium control knob, (4) helium reservoir filler tube, and (5) helium gas flushing line valve.

incorporated into the rest of the modulus measuring system shortly thereafter. The block diagram of this apparatus is shown in Figure 18. H-P denotes equipment by Hewlett-Packard.

Swept-frequency and manually-tuned modes are available. In the sweep mode, the composite is excited with an H-P 675-A sweeping signal generator; the resonance signals are amplified and detected with a H-P 8405-A vector voltmeter, and the resonance frequency spectrum is displayed by a H-P 7004-A X-Y recorder. The generator supplies a d-c voltage proportional to frequency for the X channel, and the voltmeter supplies a d-c voltage proportional to amplitude for the Y channel. The sweep mode is used to check the peaks for substructure; the resonance frequency is ambiguous if a peak has substructure. In the manual mode, excitation is supplied by a H-P 606-B signal generator, and the amplitude of the resonance signal is observed on the amplitude meter of the voltmeter. The frequency of a resonance peak is determined by tuning the generator for a voltage maximum and reading the frequency off a H-P 5245-L frequency counter. This counter can be read to ± 1 Hz at 30 MHz. The mode, sweeping or manual, is selected with a circuit that incorporates a set of coaxial relays. Individual specimens (composites) are switched into the resonance electronics circuit with another set of coaxial relays.

The components of the resonance apparatus are joined by RG-58/U coaxial cable, which has a characteristic impedance of 50 ohms. To provide a proper termination for the lines carrying excitation signals from the generators, the far ends of the three transmitting cables from the specimen selector box were shunted to ground through 47 ohm carbon resistors. These resistors are located in the transmitting lead junction box, atop the center pressure tube (see Figure 13). These terminators

Figure 18. Block diagram of the resonance electronics. The 47 ohm resistors, located in the transmitting lead junction box, are terminators. Both selectors switch with coaxial relays. H-P denotes Hewlett-Packard. The H-P 675-A is used only in checking the resonance peak quality; the H-P 606-B is used in the actual resonance peak frequency measurements.

are necessary; without them the automatic tuning circuit of the vector voltmeter, which is driven by the r-f voltage of the signal generator in use, fails to operate at some frequencies. This failure probably occurs because the standing wave ratio of the non-terminated line is excessive.

H. Resonance Frequency Measurements

The resonance frequencies of a composite were measured by tuning the H-P 606-B signal generator to the maximum amplitude point on each peak and reading the frequency on the counter. Data were taken at frequencies from approximately 27 to 33 MHz. The frequencies of at least two peaks on each side of the transducer resonance frequency were measured. The output of the generator was 1 volt, and the observed maximum amplitudes of the peaks ranged from 1 mv to 100 mv.

Typical X-Y recorder traces of the resonance peaks of V_3Si are shown in Figure 19. The Q of a typical peak was 10,000, which is quite large. That is, the resonance peaks were sharp. Under ideal circumstances the maximum amplitude point of a peak could be located to within ± 0.1 kHz. But even under worst conditions, this point could be located to within ± 1 kHz. Notice that the backgrounds on the traces are negligible and that there is no evidence of cross-talk from the other two composites.

The traces shown in Figure 19 were taken at room temperature. Often, fine structure would appear on the resonance peaks at temperatures below $200^\circ K$. Its appearance was probably caused by crazing of the bonds or distortion of the transducers as a result of thermal stresses; either would produce multiple paths for the ultrasound and thereby give rise to fine structure. Each resonance peak consisted of a strong minipeak (fine structure peak) and one or two weaker minipeaks, all located within about 10 kHz of each other. The number of minipeaks and their relative ampli-

Figure 19. Typical X-Y recorder traces of V_2Si resonance peaks. (a) Peaks for compressional waves propagating in the $[110]$ direction in specimen 2. (b) The peak at 30320.6 kHz displayed on a sweep 100 kHz wide. The specimen was at room temperature and room pressure.

tudes varied slightly with temperature but not at all with pressure. The number and relative amplitudes were different for each resonance peak. But the frequency spacings of the minipeaks within a resonance peak were independent of pressure and temperature. Thus, for the purpose of determining the pressure and temperature dependencies of the moduli, it did not matter which minipeak within a resonance peak was followed during a data taking run. The obvious choice, however, was the minipeak with the greatest amplitude at the beginning of the run.

In pressure runs, the same minipeak could be followed from beginning to end. But in temperature runs, the minipeak that was being followed sometimes changed enough in amplitude to vanish into the main resonance peak, requiring that a new minipeak be selected. And often, a large temperature change moved a main peak through the transducer frequency. Because modulus values are computed from the frequencies of both peaks neighboring the transducer frequency, this event required that the frequency of a new peak be used in this computation from then onward. If this peak had fine structure its frequency was necessarily ambiguous. Thus, small discontinuities should be expected in plots of the modulus versus temperature. These discontinuities will be called fine structure errors.

Two series of experiments were conducted on V_3Si . In the first, the resonance frequencies of the three composites were measured at 40 temperatures between $294^\circ K$ and $7.8^\circ K$. These data were taken at room pressure. In the second, resonance frequency data were taken as a function of pressure at $296^\circ K$, $221^\circ K$, $77.3^\circ K$, $30.0^\circ K$, $20.0^\circ K$, and $13.5^\circ K$. At each point, the resonance frequencies of the three composites were measured in sequence before the pressure or temperature was changed to a new value.

After each pressure or temperature change, the frequencies as well as the pressure and temperature were allowed to stabilize completely before data were taken. Pressures were stable to ± 2 bars, temperatures to $\pm 0.1\%$.

I. Data Processing

Moduli values were computed from the frequency data by procedures summarized in Section D. of Chapter II. These procedures take in account reductions in the specimen size caused by pressure increases. All data were processed by double-precision arithmetic on the IBM 360/65 computer at Cornell.

In the absence of complete thermal expansivity data for V_3Si , the expansivity was assumed to be zero, and the density and specimen thicknesses at room temperature were used in computing moduli values with Eq. (2.24). Recent experiments by Testardi⁶² show that this procedure depresses the low temperature values of the moduli by less than 0.12% relative to their room temperature values. This error has no significant effect on the changes in the moduli induced by pressure. Furthermore, it is negligible compared with the actual changes in the moduli caused by cooling the specimen to low temperatures. The specimen thicknesses used in these computations were listed in Section C of Chapter II. The density, 5.699 g/cm^3 , was computed from the velocity and modulus data for V_3Si at 300°K published by Testardi and Bateman.^{1,2} Its uncertainty is $\pm 0.1\%$.

Because both thermal expansivity and heat capacity data were unavailable, the quantity Δ in Eq. (2.25) was assumed to be zero in computing ϕ , the ratio of the specimen thickness at room pressure to that at the experimental pressure. This was a reasonable procedure, for even if Δ were known to be as large as 0.2, an enormous and thus highly unlikely

value for this quantity, its effect on ϕ and thus on the pressure derivatives on the moduli would have been insignificant. Values of ϕ are tabulated along with values for the directly measured moduli in Appendix C.

J. Error Analysis

Uncertainties in the moduli, temperatures, and pressures are discussed in this section. The fractional errors (%) reported for C' are relative to the value of C' at room temperature. Given in this way, the fractional errors in C' are independent of temperature even though C' varies strongly with temperature.

The only significant sources of error in measuring modulus changes induced by pressure were temperature fluctuations of $\pm 0.1\%$ and uncertainties of ± 1 kHz in locating the maximum amplitude point of each resonance peak or minipeak. These uncertainties also determined the minimum modulus change that could be detected during the temperature dependence experiments. This minimum detectible change will be called the precision of the modulus measurement. The combined effect of these temperature and frequency uncertainties is $\pm 0.01\%$ uncertainty in the directly measured moduli, that is in C_{11} , C_{44} , and $C_{L(110)}$. Computed from these errors, the corresponding errors in B^S and C' are $\pm 0.02\%$ and $\pm 0.05\%$, respectively.

Fine structure, which was defined and discussed in Section H, was the dominant source of error in measuring modulus changes induced by temperature changes. For a minipeak separation of 10 kHz the fine structure error for the directly measured moduli is $\pm 0.07\%$. The corresponding errors in B^S and C' are $\pm 0.14\%$ and $\pm 0.35\%$, respectively. Because the same set of minipeaks could always be followed throughout a pressure run, the fine structure errors do not apply to the pressure dependence measurements.

Several errors contribute to the total uncertainties for the absolute values of the moduli. They are uncertainties in specimen thickness, bond thickness, specimen alignment, thermal expansivity, and specimen density. Also included in the total error are fine structure errors and measurement precisions. Their combined effect is a total uncertainty of $\pm 0.22\%$ for values of the directly measured moduli. The corresponding uncertainties for B^S and C' are $\pm 0.44\%$ and $\pm 1.1\%$, respectively. Total errors are the appropriate uncertainties to use in comparing modulus values obtained by different researchers.

The total uncertainty in temperature includes temperature fluctuations of $\pm 0.1\%$ and uncertainty of $\pm 0.1^\circ\text{K}$ in the thermometer calibration. Combined as random errors, these uncertainties cause a total temperature error given by

$$\delta T = \pm 0.1 \sqrt{1 + (T/100)^2} \quad ^\circ\text{K} \quad (4.1)$$

Thus the error in T varies from 0.3°K at 300°K to $\pm 0.1^\circ\text{K}$ for temperatures below 100°K . Uncertainties computed with this equation have been assigned to the temperature variable in the temperature dependence results and to the temperature parameter in the pressure dependence results.

Pressures were read to ± 0.002 kb on a Heise gauge that had been calibrated to an accuracy of ± 0.008 kb, that is to an accuracy of $\pm 0.1\%$ of full-scale. Because it dominates, the calibration error is the uncertainty in pressure.

Chapter V

EXPERIMENTAL RESULTS

Results of the modulus measurements on nontransforming V_3Si are presented in this chapter. Only B^S , C_{44} , and C' are considered here, for these are the relevant moduli in this research. Values of the directly measured moduli have been tabulated in Appendix C. Errors in all the variables were discussed at length in Section J of Chapter IV.

A. Temperature Dependences of the Moduli

Figure 20 shows the temperature dependence obtained for the adiabatic bulk modulus, B^S , at room pressure. Reducing the temperature of nontransforming V_3Si from $294^\circ K$ to $90^\circ K$ increases its bulk modulus by 0.8%, a change typical for ordinary solids. Lowering the temperature from $90^\circ K$ to $40^\circ K$ reduces the modulus by 0.2%, a change only slightly larger than the fine structure error. Between $40^\circ K$ and $17^\circ K$, the superconducting critical temperature (T_c), the modulus is constant to within the fine structure error, 0.14%. Between $17.0^\circ K$ and $7.8^\circ K$, the lowest temperature used in this research, the modulus is constant to within the precision of the modulus measurements, 0.02%. This dependence is in general agreement with that reported for transforming V_3Si by Testardi and Bateman.^{1,2} In particular, they find B^S to be constant to within 0.5% for temperatures from $300^\circ K$ to $4.2^\circ K$. Furthermore, both room temperature values for B^S agree to within 0.05%.

Figure 21 shows the temperature dependence obtained for C_{44} at room pressure. Decreasing the temperature of nontransforming V_3Si from $294^\circ K$ to T_c decreases this modulus by 5.4%. Any decrease at all would have been anomalous. For temperatures below T_c the modulus is constant to within 0.01%, the precision of the measurements. Testardi and Bateman

Figure 20. Temperature dependence of the adiabatic bulk modulus at room pressure. T_c denotes the superconducting critical temperature.

Figure 21. Temperature dependence of the shear modulus C_{44} at room pressure. T_c is the superconducting temperature. T_m is the structural transition temperature. The dashed curve was obtained by Testardi and Batemen. Dots represent the present data.

find that decreasing the temperature of transforming V_3Si from room temperature to $18.5^\circ K$ decreases C_{44} by 6.0%. Between this temperature and $17.0^\circ K$ the modulus increases by 0.2%. Thus, transforming V_3Si softens slightly more than nontransforming V_3Si does over the same temperature range. Furthermore, their room temperature value for C_{44} is 1% less than was obtained for nontransforming V_3Si .

Figure 22 shows the temperature dependence obtained for C' at room temperature. Decreasing the temperature of the nontransforming V_3Si used in this research reduces its modulus C' by 88%, which is 15 times more decrease than is obtained for C_{44} . For temperatures below $17.0^\circ K$ ($T_c = 17^\circ K$) this modulus is constant to within 0.05%, the precision of the measurements. The decreases in C' measured by Testardi³³ for nontransforming V_3Si are within 2% of those measured in this research. This is reasonably good agreement, for the total uncertainty in the C' values is 1%. However, the curve through the data obtained by Testardi and Bateman for transforming V_3Si is significantly below the curves for nontransforming V_3Si at temperatures below $40^\circ K$, which is considerably higher than the structural transition temperature. And they show a total decrease in C' of at least 98%.

B. Pressure Dependences of the Moduli

Figures 23 through 26 show the hydrostatic pressure dependences obtained for the moduli at temperatures from $296^\circ K$ to $13.5^\circ K$. Computed in Section J of Chapter IV, the precisions of individual modulus values are ± 0.08 kb for C_{44} and ± 0.4 kb for B^s and C' . Because $13.5^\circ K$ is well below T_c , and thus well into the region where the moduli are temperature independent, the dependences obtained for this temperature are judged to be particularly reliable. Straight lines have been fit to the data

Figure 22. Temperature dependence of the shear modulus C' at room pressure. T_c is the superconducting temperature. T_m is the structural transition temperature. The dashed curve was obtained by Testardi and Bateman. The solid curve was obtained by Testardi. Dots represent the present data.

Figure 23. Pressure dependence of the adiabatic bulk modulus at various temperatures.

Figure 24. Pressure dependence of the shear modulus C_{44} at various temperatures.

Figure 25. Pressure dependence of the shear modulus C' at various high temperatures.

Figure 26. Pressure dependence of the shear modulus C' at various low temperatures.

by the method of least squares to obtain pressure derivatives. All moduli are linear in pressure to within the precisions of the measurements.

Most probable values for the pressure derivatives are listed with their standard errors in Table II. These errors are large compared with all other experimental uncertainties.

Table II

The most probable values for the pressure derivatives of the elastic moduli of nontransforming V_3Si as a function of temperature.

$T (^{\circ}K)$	$\frac{dB^S}{dP}$	$\frac{dC_{44}}{dP}$	$\frac{dC'}{dP}$
296.0 ± 0.3	4.48 ± 0.03	0.90 ± 0.00	1.13 ± 0.07
221.0 ± 0.2	4.13 ± 0.10	1.11 ± 0.01	1.28 ± 0.05
77.3 ± 0.1	4.16 ± 0.10	1.00 ± 0.00	-0.58 ± 0.08
30.0 ± 0.1	5.18 ± 0.08	1.02 ± 0.01	-3.58 ± 0.13
20.0 ± 0.1	6.60 ± 0.11	1.21 ± 0.01	-4.74 ± 0.16
13.5 ± 0.1	6.58 ± 0.32	1.38 ± 0.09	-5.04 ± 0.21

Chapter VI

DISCUSSION

A. Temperature Dependences of the Pressure Derivatives

Figure 27 shows how the hydrostatic pressure derivatives for the moduli vary with temperature in nontransforming V_3Si . Smooth curves have been drawn through the data to represent the temperature dependences of these derivatives at intermediate temperatures. dB^S/dP varies from 4.5 at $300^\circ K$ to 6.8 at $13^\circ K$, with most of the increase occurring at below $40^\circ K$. dC_{44}/dP varies from 1 at $300^\circ K$ to 1.4 at $13^\circ K$; thus pressure inhibits the weak anomalous softening of the C_{44} shear mode. dC'/dP varies from 1 at $300^\circ K$ to -5 at $13^\circ K$, vanishing at $90^\circ K \pm 10^\circ K$; thus, at temperatures above $90^\circ K$ pressure inhibits the strong anomalous softening of the C' shear mode, and at temperatures below $90^\circ K$ pressure enhances this softening.

Recently Carcia, Barsch, and Testardi⁶⁴ measured the hydrostatic pressure derivatives of the moduli of transforming V_3Si at $298^\circ K$, $195^\circ K$, and $77^\circ K$. Their results are compared with those for nontransforming V_3Si in Table III. Notice that with specimen cooling from $298^\circ K$ their dC'/dP first increases and then decreases, becoming slightly negative at $77^\circ K$; dC'/dP for nontransforming V_3Si does the same. Furthermore, their data shows that dC'/dP vanishes at about $80^\circ K$, which is within the estimated uncertainty of the temperature for the vanishing of dC'/dP in nontransforming V_3Si .

B. Stress Dependences for the Moduli

Patel and Batterman⁸ have measured C' for static C' -type shear stresses at $25^\circ K$ by loading a V_3Si crystal along $[001]$ and measuring the transverse strain by x-ray diffraction. Details of their measurements

Figure 27. Variation with temperature of the pressure derivatives of the elastic moduli. Smooth curves have been drawn through the data points. See the text for further information.

Table III

Comparison of the pressure derivatives for the elastic moduli of nontransforming and transforming V_3Si at high temperatures.

Temp. (°K)	dB^S/dP		dC_{44}/dP		dC'/dP	
	NonTr [#]	Tr [*]	NonTr	Tr	NonTr	Tr
298	4.48	4.35	0.90	1.04	1.13	0.78
195	4.02	-	1.19	-	1.25	0.88
77	4.16	4.29	1.00	0.77	-0.58	-0.05

[#] Nontransforming - This research.

^{*} Transforming - Carcia, Barsch, and Testardi.

were given in Section D of Chapter I. Even for strains less than 10^{-4} their C' is significantly larger than C' measured ultrasonically, thus with strains of the order of 10^{-6} . Thus C' has a positive C' shear stress derivative. For strains larger than 4×10^{-4} stress is strongly nonlinear in strain. These results contrast with those of this research, which show that for hydrostatic specimen loading at 25°K the modulus C' is linear in stress for pressures to at least 2 kb and that dC'/dP is negative. At 2 kb pressure the volumetric strain is 10^{-3} and the linear strain is 3×10^{-4} . Thus, for strains of the same magnitude, hydrostatic stress reduces C' and shear stress increases C' .

C. Pressure-Induced Structural Transformation

At temperatures for which dC'/dP is negative, applying enough hydrostatic pressure to nontransforming $V_3\text{Si}$ should drive C' to zero and thereby induce the structural transformation. The required pressure, P_{crit} , was computed for 20 temperatures between 85°K and 13°K on the assumption that dC'/dP at each temperature is independent of pressure. Derivative values were read from the dC'/dP curve in Figure 27. Figure 28 shows the result of these computations. The open circles represent P_{crit} for the temperatures at which the pressure derivatives were measured in this research. P_{crit} is 20 kb at 13.5°K and 30kb at 20°K . Pressures of this size can be generated by the method used by Smith⁴⁶ and described briefly in Section D of Chapter I. However, any method used to achieve the required pressure must produce only hydrostatic stress if a transformation is to occur; Patel and Batterman⁷ have shown that only 0.4 kb shear stress is sufficient to completely suppress the transformation in $V_3\text{Si}$ crystals that transform at room pressure.

For temperatures above 14°K the transformation pressure may be

Figure 28. Variation with temperature of the hydrostatic pressure needed to drive the shear modulus C' to zero in nontransforming V_3Si .

somewhat less than P_{crit} . To understand this, recall from Figure 22 that at room pressure transforming V_3Si undergoes the structural transformation at 21°K and that at this temperature C' is 60 kb. At this temperature dC'/dP for nontransforming V_3Si is -4.7 and C' is 140 kb. Thus, a hydrostatic pressure of 17 kb should reduce C' to 60 kb, and this may be sufficient to induce the structural transformation in V_3Si that does not transform at room pressure. Of course, the fundamental criterion for the occurrence of this or any other phase transformation (unless a macroscopic instability is present) is that the Gibbs free energy of the new phase be less than that of the former phase.

APPENDIXES

Appendix A

CALCULATION OF THE SPECIMEN RESONANCE FREQUENCIES FROM THE COMPOSITE RESONANCE FREQUENCIES

Using an acoustic transmission line equivalent circuit developed by Lamb and Williams, Bolef and Menes⁵⁰ have computed the specimen resonance frequencies ($\nu_{S,n}$) from the resonant frequencies ($\nu_{C,n}$) of a composite system consisting of one transducer, a thin coupling film (bond) and a specimen. In this appendix, the general approach of Bolef and Menes has been followed to include an additional transducer and a bond. The elements of the system are assumed to be loss-free so that the usual hyperbolic tangents can be replaced by tangents. The bonds are assumed to have the same thickness and the transducers are assumed to have the same mechanical resonance frequency. The lengths, densities, velocities and phases are denoted by ℓ , ρ , v and ϕ . The specific acoustic impedance ρv is denoted by k . The subscripts S, B, T and C refer to specimen, bond, transducer and composite. The subscripts 1 and 2 refer to the transmitting transducer (the one driven by the signal generator) and the receiving transducer, respectively. The transducers are assumed to be operated close to their half wave resonance frequency (ν_T). Then,

$$\ell_T = \frac{1}{2} \lambda_T = \frac{1}{2} \frac{v_T}{\nu_T} \quad (A.1)$$

The resonance condition for the free (no transducers attached) specimen is

$$\ell_S = \frac{n}{2} \lambda_S \quad \text{where } n = 1, 2, 3, \dots \text{ (an integer)} \quad (A.2)$$

and λ_S is the wave length at resonance.

To apply the transmission line theory, assume that the elements of the composite are assembled in the following way:

Transducer(1) - Bond(1) - Specimen - Bond(2) - Transducer(2)

Following Bolef and Menes, $Z_{T_2'}$ is the impedance looking from the bond(2) - transducer interface into the short circuited transmission line which represents transducer(2). $Z_{B_2'}$ is the impedance looking toward bond(2) from the specimen - bond(2) interface. $Z_{S'}$ is the impedance looking toward the specimen from the bond(1) - specimen interface, and so on. Then the impedance equations are:

$$Z_{T_2'} = jk_T \tan \phi_T \quad (j \equiv \sqrt{-1})$$

$$Z_{B_2'} = k_B(Z_{T_2'} + jk_B \tan \phi_B) / (k_B + jZ_{T_2'} \tan \phi_B)$$

$$Z_{S'} = k_S(Z_{B_2'} + jk_S \tan \phi_S) / (k_S + jZ_{B_2'} \tan \phi_S)$$

$$Z_{B_1'} = k_B(Z_{S'} + jk_B \tan \phi_B) / (k_B + jZ_{S'} \tan \phi_B)$$

$$Z_{T_1'} = k_T(Z_{B_1'} + jk_T \tan \phi_T) / (k_T + jZ_{B_1'} \tan \phi_T)$$

where

$$\phi_B = 2\pi \nu_{C,n} \frac{l_B}{v_B}$$

$$\phi_S = \frac{2\pi \nu_{C,n}}{v_S} l_S$$

$$\phi_T = \frac{2\pi \nu_{C,n}}{v_T} l_T = \pi \frac{\nu_{C,n}}{\nu_T}$$

At the resonance frequency of the composite, $Z_{T_1'} = 0$.

After some algebraic manipulation one finds that

$$\tan \theta_S = \frac{2 \tan A}{1 - \tan^2 A} \equiv \tan 2A$$

(the equality is a standard trigonometric relation), where

$$A = \left(\frac{k_B}{k_S} \tan \theta_B + \frac{k_T}{k_S} \tan \theta_T \right) / \left(1 - \frac{k_T}{k_S} \tan \theta_T \tan \theta_B \right)$$

and

$$\theta_B \equiv 2\pi \nu_C \frac{l_B}{v_B}$$

$$\theta_S \equiv n\pi \left(\frac{\nu_{S,n} - \nu_{C,n}}{\nu_{S,n}} \right)$$

$$\theta_T \equiv \pi \left(\frac{\nu_T - \nu_{C,n}}{\nu_T} \right).$$

Therefore,

$$A = \frac{n\pi}{2} \left(\frac{\nu_{C,n} - \nu_{S,n}}{\nu_{S,n}} \right).$$

Solving for $\nu_{S,n}$, one finds that

$$\nu_{S,n} = \frac{\nu_{C,n}}{1 - \frac{2}{n\pi} \tan^{-1} \left[\frac{\frac{k_B}{k_S} \tan \theta_B + \frac{k_T}{k_S} \tan \theta_T}{1 - \frac{k_T}{k_B} \tan \theta_T \tan \theta_B} \right]}. \quad (\text{A.3})$$

Assuming, as in Section B, Chapter II, that $\nu = 30$ MHz, $l_S = 0.2$ cm,

$C_{ij} = 1$ Mb, $l_B \sim 3 \times 10^{-4}$ cm, $\rho_B \sim 1.5$ gm/cm³ and taking as a

worst case $\nu_{S,n+1} - \nu_{S,n} = \nu_{C,n} - \nu_T$, one finds that

$$n = \frac{\nu_{S,n}}{\nu_{S,n+1} - \nu_{S,n}} \approx 30.$$

The argument of the inverse tangent is ≈ 0.1 . Neglecting all terms above the first order in the Taylor expansion of this inverse tangent produces an error of only 3 parts in 10^4 in the inverse tangent and a negligible error of 5 parts in 10^6 in $\nu_{T,n}$. Furthermore expanding ν_S to first order in the second term in the denominator and neglecting higher order terms contribute a negligible error of 4 parts in 10^6 to $\nu_{S,n}$. Performing the above steps, one finds

$$\nu_{S,n} = \nu_{C,n} \left[1 - \frac{2}{n\pi} \left(\frac{\frac{k_B \tan \theta_B + \frac{k_T \tan \theta_T}{k_S}}{1 - \frac{k_T \tan \theta_T \tan \theta_B}{k_B}} \right) \right]. \quad (A.4)$$

Finally, expanding the tangents to first order in their arguments and applying the resonance conditions for the transducer and specimen (A.1 and A.2), one finds

$$\nu_{S,n} = \nu_{C,n} \left(1 - 2 \left[\frac{\frac{m_B}{m_S} - \frac{m_T}{m_S} \left(\frac{\nu_{C,n} - \nu_T}{\nu_{C,n}} \right)}{1 - R \nu_{C,n} (\nu_{C,n} - \nu_T)} \right] \right), \quad (A.5)$$

where

$$R \equiv \frac{4\pi^2 m_T m_B}{(\rho_B v_B)^2} \quad (A.6)$$

and

$$m \equiv \rho l$$

Excluding higher order terms in the expansions of the tangents contributes an error of only 1 part in 10^5 to $\nu_{S,n}$.

Appendix B

SAMPLE MODULUS COMPUTATION

The computation of $C_{L(110)} \equiv \frac{1}{2}(C_{11} + C_{12} + 2C_{44})$ from composite resonance data of V_3Si at room pressure and $14^\circ K$ temperature is outlined in the table below to illustrate the use of the equations and procedures derived in Chapter II. Listed in the far left column of this table are measured resonance frequencies of a composite consisting of specimen #2 and two glycerine bonded X-cut quartz transducers. Corrected for temperature, the transducer fundamental free resonant frequency is 30119 kHz. Room temperature values of the specimen density and length, 5.699 g/cm³ and 0.25684 cm, are used uncorrected for thermal expansion in this computation. This density was calculated from room temperature V_3Si velocity and modulus data published by Testardi and Bateman^{1,2}.

Table B-I. Sample analysis of composite resonance frequency data.
Units: frequencies in kHz and the modulus in kilobars.

$\nu_{C,n}$	Calc. n	n	$\nu_{C,n}/n$	$\nu_{S,n}/n$	X *	$C_{L(110)}$
27607.46	21.01	21				
28874.70	22.03	22	1312.486	1310.582		
30140.96	22.89	23	1310.476	1310.508	1310.509	2582.740
31404.84	23.95	24				

* Interpolation of $\nu_{S,n}/n$ to the transducer resonant frequency.

Appendix C

DIRECTLY MEASURED MODULI VALUES

The adiabatic values of C_{11} , $C_{L(110)}$, and C_{44} for nontransforming V_3Si are tabulated in this appendix. Adiabatic and isothermal values of C_{44} are identical. $C_{L(110)}$ denotes $\frac{1}{2}(C_{11} + C_{12} + 2C_{44})$. Relations between these moduli and C' and B^S are listed at the end of Section D, Chapter II.

Values of the directly measured moduli were computed from resonance frequency data by procedures summarized in Section D of Chapter II. Thermal expansion effects were ignored. Changes in the moduli induced by pressure changes are accurate to $\pm 0.01\%$; changes in the moduli induced by temperature changes are accurate to $\pm 0.07\%$. The precision of the modulus measuring technique is $\pm 0.01\%$. Absolute values of the moduli are estimated to be accurate to $\pm 0.22\%$. Included in this estimate are uncertainties in density, specimen thicknesses, specimen orientations, thermal expansivity, bond thicknesses, and resonance frequencies. Pressures are accurate to ± 0.008 kb. Temperatures below $100^\circ K$ are accurate to $\pm 0.1^\circ K$. Temperatures from $100^\circ K$ to $200^\circ K$ are accurate to $0.2^\circ K$. And temperatures above $200^\circ K$ are accurate to $0.3^\circ K$.

Table C-I. Room pressure values of the directly measured elastic moduli. Thermal expansion effects are neglected. See the text for further information. The units are kilobars.

T (°K)	C_{11}	$C_{L(110)}$	C_{44}
294.4	2890.0	2858.4	816.84
283.7	2881.5	2855.8	815.02
268.9	2868.5	2852.6	813.42
251.0	2851.4	2846.8	811.41
231.8	2830.4	2839.8	809.06
212.4	2804.6	2833.5	806.37
200.9	2787.5	2827.6	804.67
180.5	2750.2	2814.5	801.20
160.0	2708.3	2803.5	797.65
143.7	2669.2	2790.4	794.62
118.9	2593.8	2768.7	789.28
77.3	2402.8	2713.9	781.87
57.8	2271.5	2675.7	778.06
51.3	2223.4	2663.0	777.29
45.7	2179.0	2649.8	776.30
39.7	2141.4	2640.2	775.73
35.1	2097.0	2628.2	775.37
31.8*	2071.6*	2622.2*	775.01*
30.2	2050.1	2616.2	775.46
30.0*	2053.3*	2617.3*	775.90*
29.0*	2043.6*	2614.8*	775.64*

* Sequence of increasing, rather than decreasing, temperatures.

Table C-I. Room pressure values of the directly measured elastic moduli. Thermal expansion effects are neglected. See the text for further information. The units are kilobars. (Continued).

T (°K)	C_{11}	$C_{L(110)}$	C_{44}
28.0*	2033.8*	2612.1*	775.52*
27.0*	2023.1*	2609.5*	775.40*
26.2	2011.8	2606.0	775.25
26.0*	2012.6*	2606.7*	775.18*
25.0*	2001.0*	2603.7*	775.04*
24.0*	1989.0*	2600.4*	774.93*
23.0*	1977.1*	2597.4*	774.67*
23.0	1975.9	2596.7	774.62
22.0	1965.6	2594.0	774.28
21.0	1955.3	2591.4	774.15
20.0	1943.0	2588.4	773.91
19.0	1933.9	2585.7	773.52
17.9	1922.6	2582.5	773.28
17.0	1917.3	2582.4	773.08
16.0	1916.8	2582.5	773.32
15.0	1916.4	2582.6	773.25
14.0	1916.1	2582.7	773.48
13.0	1916.1	2582.6	773.47
12.0	1916.2	2582.7	773.47
10.9	1916.3	2582.8	773.65
7.8	1916.5	2582.8	773.74

* Sequence of increasing, rather than decreasing, temperatures.

Table C-II. Effect of pressure on the directly measured elastic moduli and on the specimen lengths at 296°K. The moduli and pressure are in units of kilobars.

P	$\phi \equiv l_0/l$	C_{11}	$C_{L(110)}$	C_{44}
0.001	1.000000	2891.1	2858.7	816.79
0.292	1.000054	2892.8	2860.4	817.04
0.595	1.000111	2894.9	2862.2	817.33
1.004	1.000189	2897.3	2864.4	817.69
1.501	1.000283	2900.1	2867.4	818.13
1.997	1.000376	2902.9	2870.2	818.57
2.491	1.000470	2906.2	2873.0	819.03

Table C-III. Effect of pressure on the directly measured elastic moduli and on the specimen lengths at 221°K. The moduli and pressure are in units of kilobars.

P	$\phi \equiv l_0/l$	C_{11}	$C_{L(110)}$	C_{44}
0.001	1.000000	2815.3	2834.2	807.53
0.293	1.000055	2817.0	2835.9	807.90
0.595	1.000111	2818.7	2837.6	808.24
1.001	1.000188	2821.4	2840.0	808.69
1.500	1.000282	2824.0	2842.8	809.22
2.003	1.000377	2827.4	2846.0	809.78
2.495	1.000470	2829.6	2848.0	810.31

Table C-IV. Effect of pressure on the directly measured elastic moduli and on the specimen lengths at 77.3°K. The moduli and pressure are in units of kilobars.

P	$\phi \equiv l_0/l$	C_{11}	$C_{L(110)}$	C_{44}
0.001	1.000000	2402.7	2713.8	781.64
0.200	1.000037	2403.3	2714.8	781.76
0.400	1.000074	2404.1	2715.8	782.06
0.600	1.000111	2404.7	2716.8	782.20
0.800	1.000149	2405.4	2717.8	782.59
1.000	1.000186	2405.9	2718.7	782.74
1.200	1.000224	2406.4	2719.6	782.85
1.400	1.000262	2407.6	2720.6	783.07
1.600	1.000299	2408.1	2721.6	783.27
1.800	1.000336	2408.8	2722.9	783.34

Table C-V. Effect of pressure on the directly measured elastic moduli and on the specimen lengths at 30.0°K. The moduli and pressure are in units of kilobars.

P	$\phi \equiv l_0/l$	C_{11}	$C_{L(110)}$	C_{44}
0.015	1.000003	2049.7	2614.4	775.45
0.248	1.000043	2049.6	2615.6	775.80
0.508	1.000092	2050.2	2617.1	775.99
0.762	1.000140	2050.4	2618.5	776.23
1.012	1.000186	2049.6	2619.5	776.51
1.260	1.000233	2050.6	2620.9	776.74
1.506	1.000280	2050.2	2622.0	777.00
1.752	1.000326	2050.2	2623.0	777.25
1.974	1.000368	2050.8	2624.3	777.50

Table C-VI. Effect of pressure on the directly measured elastic moduli and on the specimen lengths at 20.0°K. The moduli and pressure are in units of kilobars.

P	$\phi \equiv l_0/l$	C_{11}	$C_{L(110)}$	C_{44}
0.015	1.000003	1958.9 *	2590.2	773.83
0.198	1.000034	1956.7	2590.4	774.06
0.390	1.000070	1956.5	2591.8	774.32
0.603	1.000110	1957.1	2593.4	774.60
0.804	1.000147	1956.9	2594.6	774.79
1.000	1.000185	1957.0	2595.8	775.01
1.212	1.000225	1956.7	2597.0	775.29
1.395	1.000259	1957.4	2598.1	775.53
1.500	1.000278	1957.0	2598.7	775.65

* May be spurious.

Table C-VII. Effect of pressure on the directly measured elastic moduli and on the specimen lengths at 13.5°K. The moduli and pressure are in units of kilobars.

P	$\phi \equiv l_0/l$	C_{11}	$C_{L(110)}$	C_{44}
0.005	1.000001	1925.5	2582.4	773.74
0.090	1.000015	1925.4	2583.0	773.93
0.205	1.000037	1925.5	2583.6	774.16
0.305	1.000056	1925.4	2584.4	774.19
0.400	1.000073	1925.2	2584.7	774.41
0.520	1.000096	1925.5	2585.7	774.48
0.580	1.000107	1925.4	2586.1	774.56

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