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C00-3153-95

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PRESSURE-INDUCED ELASTICITY CHANGES IN V_3Si

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ABSTRACT

The single-crystal elastic moduli of V_3Si have been measured for hydrostatic pressures to 2.5kb and temperatures from 13.5°K to 296°K to determine the influence of volume decreases on the anomalous $C' = (C_{11} - C_{12})/2$ shear mode softening in this A-15 material. Moduli values were obtained by measuring the c-w resonance frequencies of three thin specimens that did not undergo at room pressure the well-known structural transformation exhibited by some V_3Si crystals near 20°K. The measurements show all moduli to be linear in pressure. dB^S/dP , which is nearly constant at 4 for temperatures down to 40°K, is near 7 at 13.5°K. dC'/dP varies from 1 at 296°K to -5 at 13.5°K, vanishing at near 90°K. These results are compared with those obtained earlier for large C' -type shear loads. The possibility of inducing a structural transformation with hydrostatic pressure is discussed.

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INTRODUCTION

Ultrasonic wave velocity measurements by Testardi and Bateman show that cooling the A-15 cubic compound V_3Si from 300°K to 17°K, its superconducting critical temperature, decreases its single-crystal shear modulus, $C' \equiv \frac{1}{2}(C_{11} - C_{12})$, by 90% or more.^{1,2} In some V_3Si crystals the softening of the lattice to $[1\bar{1}0](110)$ type deformation triggers an isovolumetric, continuous phase transformation that begins at 20°K and leaves the lattice tetragonal by two parts in 10^3 at 17°K and below; in other V_3Si crystals this structural transformation fails to occur. Such a transformation is often called the Batterman-Barrett structural transformation.^{3,4}

The shear wave strain amplitudes used in ultrasonic wave velocity measurements, are of the order of 10^{-6} , three orders of magnitude smaller than the structural transformation strains. Patel and Batterman have investigated the influence of large C' type strains on the value of C' by loading V_3Si crystals along $[001]$ and measuring the transverse strain by x-ray methods at temperatures below 35°K.^{5,6} They observed that for strains well below 10^{-4} the crystals were stiffer than predicted by the ultrasonic measurements of Testardi and Bateman and that stresses sufficient to produce strains of 5×10^{-4} not only markedly stiffened the crystals but also completely suppressed the structural transformation in those crystals that transformed when they were not stressed. Thus, at least for large $[1\bar{1}0](110)$ type shear strains, the lattice potential is strongly anharmonic and the shear stress derivative of C' ($dC'/d\epsilon$)

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is positive.

Other measures of lattice anharmonicity are the hydrostatic pressure derivatives of the elastic moduli observed ultrasonically at low temperatures. For a purely harmonic system the moduli should be volume independent, thus pressure independent. Recently,⁷ we discussed very briefly some results we had obtained in measuring the hydrostatic pressure derivative of nontransforming V_3Si by a two transducer version of the ultrasonic continuous wave resonance technique^{8,9,10} at temperatures from 300°K to 13.5°K and at frequencies near 30 MHz. At that time we showed dC'/dP to be strongly negative at temperatures for which Patel and Batterman had observed dC'/dT to be positive. Moreover, we found dC'/dP to be negative for all temperatures below about 90°K and positive at higher temperatures. For temperatures 77°K and above our findings were in general agreement with those of Carcia et al.,¹¹ who had confined their research to the higher temperature range. In this paper we present details of our experiment, results not discussed in our earlier report, and arguments suggesting that the structural transformation might be induced in nontransforming V_3Si by applying hydrostatic pressures.

EXPERIMENTAL PROCEDURE

Modulus values were determined by simultaneously measuring the ultrasonic resonance frequencies of three thin specimens that had been spark-cut from the same single crystal of V_3Si , oriented to within 0.1° in an x-ray diffractometer, lapped flat and parallel, and sandwiched between pairs of 30 MHz, 5mm diameter quartz transducers that had coaxial, evaporated metal electrodes. The crystal, grown by a floating zone process similar to the one described by Greiner and Mason,¹² was a cylinder 7mm in diameter 12mm long and had a [001] longitudinal axis. Each specimen was nominally 1.5mm thick. Two specimens were disks with (100) faces and one was a rectangular plate with (110) faces. Each specimen was checked for the occurrence of the structural transformation at room pressure by inspecting the (600)Copper K_α x-ray reflections for splittings when the temperature was reduced from 32°K to 12°K; none were found, even though the $\alpha_1\alpha_2$ doublet was well resolved, which shows that the specimens were of the nontransforming variety. Pairs of x-cut quartz transducers, transmitters and receivers of compressional waves, were bonded to one disk and the plate with glycerine; resonance frequency measurements on these composite specimens yielded directly values for C_{11} and $\frac{1}{2}(C_{11}+C_{12}+2C_{44}) \equiv C_L(110)$ respectively. A pair of AC-cut quartz transducers, transmitters and receivers of shear waves, were bonded to the remaining disk specimen with Nonaq Stopcock Grease; resonance frequency measurements on this specimen yielded directly values for C_{44} .

The completed composite specimens were mounted together in a three specimen crystal holder with spring-loaded coaxial contacts for the transducers, and the crystal holder was contained in a heavy, beryllium-copper pressure vessel fitted with a pair of threaded end plugs which incorporated Bridgman pressure seals. Indium packing washers were used in each seal. The r-f leads to and from the composite specimens were enclosed in long pressure tubes that passed through these end plugs. Two short lengths of epoxy-filled pressure tubing, mounted at the upper ends of these long tubes and containing enameled copper feed-through wires, served as pressure seals for the r-f leads.¹³ Leads to individual specimens were switched to the terminals of the resonance frequency measuring apparatus with a set of coaxial relays.

The resonance frequency measuring apparatus consisted of a stable r-f signal generator, a frequency counter, and a vector voltmeter. This apparatus, as well as the pressure vessel and crystal holder, the high pressure system, and the temperature control equipment are detailed at length elsewhere.¹⁰ Resonance frequencies of the composites were measured by tuning the signal generator for a maximum voltage indication on the vector voltmeter and reading the frequency off the counter. At least four resonance frequencies, two on each side of the transducer resonance frequency, were measured for each specimen at each pressure and temperature point. The precision of each resonance frequency measurement was 1 part in 10^4 . Resonance frequencies were measured for all three specimens before the pressure or temperature was changed.

The pressure medium was helium, which was pumped into both ends of the vessel through the long pressure tubes to minimize the viscous drag on the leads within the tubes for any total helium flow rate. Pressures were read to ± 0.008 kb with a Heise gauge. Temperatures above 77°K were obtained by containing the vessel in a liquid nitrogen cooled experimental chamber with a self-contained temperature regulator. For experiments at 77°K the vessel was immersed in liquid nitrogen. For experiments at temperatures below 77°K the vessel was suspended inside a helium-vapor-flow dewar, and its temperature was controlled with an automatic temperature regulator which sensed its temperature with a gallium arsenide thermometer and adjusted the current flow through a heat wire wound around the cylindrical surface of the vessel and bonded to it with epoxy resin. The temperature of the vessel, measured with a calibrated gallium arsenide thermometer that was bonded to the bottom of a deep pocket machined in its upper end, was stabilized to $\pm 0.1\%$ at all temperatures. The overall accuracy of the temperature measurements was 0.3°K.

Two sets of experiments were conducted. First, resonance frequency data were taken at room pressure for forty temperatures between 7.8°K and 294°K. Then data were taken as a function of pressure at 296°K, 221°K, 77.3°K, 30.0°K, 20.0°K, and 13.5°K. In processing the resonance frequency data to obtain moduli values, the room pressure value of the density was taken as 5.699 gm/cm^3 and was assumed to be temperature independent; the error introduced by this assumption is only a few parts in 10^3 .¹⁴ The resonance frequency data were corrected by Cook's method¹⁵ for the specimen

shrinkage due to pressure. Values of the adiabatic bulk modulus B^S and the shear modulus C' were computed.

EXPERIMENTAL RESULTS

Figure 1 shows the temperature dependence of the bulk modulus at room pressure. The precision of the modulus values is 0.15%. Notice that cooling nontransforming V_3Si from room temperature to about 90°K increases B^S by about 1% and that reducing the temperature further has negligible effect on this modulus. This temperature dependence is in general agreement with that reported by Testardi and Bateman for transforming V_3Si . In particular, they find B^S to be constant to within 0.5% over the temperature range 300°K to 4.2°K.

Figure 2 shows the temperature dependence of the shear modulus C_{44} at room pressure. The precision of the modulus values is 0.01%. Decreasing the temperature of nontransforming V_3Si from 294°K to T_C (17°K) decreases this modulus by 5.4%. The occurrence of any decrease is considered anomalous. For temperatures below T_C this modulus is constant to within the precision of the measurements. Testardi and Bateman find that decreasing the temperature of transforming V_3Si from room temperature to 18.5°K decreases C_{44} by 6% and that between the lower temperature and 17.0°K, C_{44} 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 3 shows the temperature dependence obtained for C' at room temperature. Decreasing the temperature of the nontransforming

V_3Si used in this research reduced the modulus C' by 88%, which decrease is 15 times greater than the decrease observed 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 Testardi¹⁶ for nontransforming V_3Si are within 2% of the present values, reasonably good agreement, for the absolute uncertainty of the C' values is about 1%. But the curve for transforming V_3Si is significantly below the curves for nontransforming V_3Si at temperatures below $40^\circ K$, a temperature considerably above the structural transition temperature. Furthermore, the total decrease in C' obtained for transforming V_3Si was at least 98%.

Pressure experiments were conducted at several temperatures from $296^\circ K$ to $13.5^\circ K$, the latter temperature being well below the lower limit of the softening anomaly. The precisions of the individual modulus values at each pressure were $\pm 0.08 kb$ 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 pressure dependences obtained for this temperature are judged to be particularly reliable. In all moduli at all temperatures investigated, the moduli were found to be linear in pressure. To obtain pressure derivatives, straight lines were fitted to the data by the method of least squares. Figure 4 shows the data for $C'(P)$ at all experimental temperatures. Most probable values for the pressure values of the moduli and for the pressure derivatives are shown with their standard errors in

Table I. These random errors are judged to be large compared with all other possible absolute errors.

Table I

The most probable values for the pressure derivatives of the elastic moduli of nontransforming V_3Si and for the elastic moduli at room pressure (in parentheses) as a function of temperature. Moduli units are megabars (10^{12} dynes/cm²).

T(°K)	dB^S/dP (B^S)	dC_{44}/dP (C_{44})	dC'/dP (C')
296.0±0.3	4.48±0.03 (1.759±0.008)	0.90±0.00 (0.817±0.002)	1.13±0.07 (0.849±0.009)
221.0±0.2	4.13±0.10 (1.764±0.008)	1.11±0.01 (0.808±0.002)	1.28±0.05 (0.789±0.009)
77.3±0.1	4.16±0.10 (1.775±0.008)	1.00±0.00 (0.782±0.002)	-0.58±0.08 (0.471±0.009)
30.0±0.1	5.18±0.08 (1.769±0.008)	1.02±0.01 (0.776±0.002)	-3.58±0.13 (0.211±0.009)
20.0±0.1	6.60±0.11 (1.769±0.008)	1.21±0.01 (0.774±0.002)	-4.74±0.16 (0.141±0.009)
13.5±0.1	6.58±0.32 (1.770±0.008)	1.38±0.09 (0.774±0.002)	-5.04±0.21 (0.117±0.009)

DISCUSSION

Figure 5 shows the temperature dependences of the hydrostatic pressure derivatives. Smooth curves have been drawn through the data to represent these temperature dependences. dB^S/dP , near 4 at room temperature, is near 7 at 13°K; thus pressure stiffens the lattice to further volume decreases, with a strong enhancement of this effect occurring at very low temperatures. dC_{44}/dP is near 1 at all temperatures; thus, pressure inhibits the weak anomalous softening of the C_{44} shear mode. dC'/dP varies from 1 at 300°K to -5 at 13°K, vanishing at 90°K±10°K. Thus, at temperatures above 90°K, pressure inhibits the strong anomalous softening of the C' shear mode, and at temperatures below 90°K it enhances this softening. Notice also that the $C'(T)$ and $\frac{dC'}{dP}(T)$ curves are similar in shape. We have no explanation for this similarity but feel that it is worth mentioning in passing.

It was mentioned earlier that Carcia et al. had measured the pressure derivatives of V_3Si at liquid nitrogen temperature and above on a transforming type crystal. Their results are compared with those obtained for nontransforming V_3Si in the present research in Table II. Notice that the temperature dependences of their pressure derivatives are in very general agreement with those obtained during the present research, although there are significant differences in the actual values of the moduli. Thus, it would appear that had they taken data to lower temperatures they would have found dC'/dP to be considerably more negative.

Table II

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

Temp. ($^{\circ}K$)	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, Testardi.

It will be recalled that the experiment of Patel and Batterman showed that large C' type strains stiffen the lattice to C' type shear deformatives, with the effect being particularly strong for strains of 5×10^{-4} and greater at 25°K. In fact, dC'/dT is itself nonlinear in strain (or stress). The results of the present research show that for comparable linear strains induced by hydrostatic pressure stressing C' is not only linear in stress (pressure), but also that the stress (pressure) derivative is negative.

The fact that dC'/dP for nontransforming V_3Si is strongly negative at low temperatures has an interesting implication: The application of sufficient, pure hydrostatic pressure to non-transforming V_3Si should drive C' to zero and thereby induce a structural transformation. Presumably, this transformation would be the Batterman-Barrett structural transformation. The required pressure to do this, P_{crit} , was computed for 20 temperatures between 77°K and 13°K on the assumption that dC'/dP does not vary with pressure at any temperature. Derivative values were read from the dC'/dP curve of Figure 5. Figure 6 shows the results of these computations. The open circles represent P_{crit} for the experimental temperatures. Notice that P_{crit} is 20kb at 13.5°K and 30kb at 20°K. Pressures of this size may be generated by the method described by Smith.¹⁷ However, it is important to emphasize that any method selected to achieve these pressures must produce pure hydrostatic pressure if the transformation is to be

achieved, for the uniaxial loading experiments of Patel and Batterman show quite clearly that only 0.4kb shear stress is sufficient to completely suppress the structural transformation.

Notice that P_{crit} for the structural transformation increases quite rapidly with temperature. We have also plotted the variation of T_c with pressure as computed from the dT_c/dp data published for V_3Si by Smith.¹⁷ Thus we see that it will be very much easier to change T_M (the structural transformation temperature) appreciably by the application of pressure than it will be to shift T_c a comparable amount.

ACKNOWLEDGMENT

The authors acknowledge the support of the United States Atomic Energy Commission and the use of certain of the Cornell Materials Science Center Central Facilities which are supported by the National Science Foundation.

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FIGURE CAPTIONS

- Figure 1: Temperature dependence of the adiabatic bulk modulus at room pressure. T_C denotes the superconducting critical temperature.
- Figure 2: 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 Bateman. Dots represent the present data.
- Figure 3: 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 4: Pressure dependence of C' at six temperatures.
- Figure 5: Variation with temperature of the pressure derivatives of the elastic moduli. Smooth curves have been drawn through the data points. See the text and Table I for further information.
- Figure 6: Variation with temperature of the hydrostatic pressure needed to drive the shear modulus C' to zero in non-transforming V_3Si . Dashed line shows predicted pressure dependence of superconducting temperature T_C .

Fig 4.