Pressure Dependence of Elastic Constants and of Shear-Mode Instability in V_3Si and V_3Ge†

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(Received 23 July 1971)

The pressure dependence of the single-crystal elastic constants of V_3Si and V_3Ge has been measured from 77 to 298°K. The first pressure derivative of the shear modulus $c_s = \frac{1}{2}(c_{11}-c_{12})$ is strongly temperature dependent and becomes negative at low temperature. For V_3Ge, an abnormally large second pressure derivative of c_s is found. The results are applied to the calculation of the microscopic and macroscopic Grüneisen parameters and to the pressure dependence of the structural transition in V_3Si.

The anomalous elastic properties[1-3] found in $A15$-structure (β-W) intermetallic compounds have been explained by Barišić and Labbé[4] and by Pytte[5] on the basis of the peak model for the density of states of Labbé and Friedel.[6] In this theory phonon effects are neglected. There is some experimental evidence,[7,8] however, which brings into question the omission of anharmonic phonon effects. The objective of the present note is to present some direct experimental data on the anharmonicity of V_3Si and V_3Ge in the form of the pressure derivatives of the elastic constants and to discuss some implications of these results.

The pressure dependence of the single-crystal elastic constants of V_3Si and V_3Ge has been measured by the pulse superposition method of McSkimin[9] up to 2 kbar at 77 and 195°K for V_3Si and at 77 and 200°K for V_3Ge, and up to 10 kbar at 298°K for both materials. The experimental details will be discussed in a later publication.

Table I presents the first pressure derivatives from the direct measurements of four independent modes, namely, the two longitudinal modes [100] and [110], and the two transverse modes in [110] polarized in $[1\bar{1}0]$ and [001]. In all cases the pressure dependence of the elastic constants was found to be linear within experimental error, except for the [110] shear mode polarized in $[1\bar{1}0]$ in V_3Ge in the range from 0 to 10 kbar, where a strong nonlinearity was found at 298°K. The standard errors of the pressure derivatives from the scatter of the raw data for each run were less than 4% for all cases except the longitudinal mode of V_3Ge at 298°K in the [110] direction (crystal thickness, 4 mm) where the uncertainty due to scatter of the data points is probably responsible for the large inconsistency (14%). The larger than usual inconsistency (9%) which exists for V_3Si at 77°K, where the scatter for all experimental runs was less than 2%, suggests the possibility of a pressure-induced partial transformation to the tetragonal low-temperature phase. This conjecture is corroborated by thermal-expansion measurements on V_3Si which show that this structural transformation is of second order and that the tetragonal phase is present at temperatures well above the transition temperature of 20°K for the structural transformation.[10]

For V_3Ge one obtains for the second pressure

TABLE I. Isothermal first pressure derivatives of adiabatic elastic constants. $c_{11}' = \frac{1}{2}(c_{11}+c_{12})+c_{44}$; $c_s = \frac{1}{2}(c_{11}-c_{12})$; $\Delta \equiv c_{11}' - c_{11} + c_s - c_{44}$.

	T (°K)	$\partial c_{11}/\partial p$	$\partial c_{11}'/\partial p$	$\partial c_s/\partial p$	$\partial c_{44}/\partial p$	$\partial\Delta/\partial p$
V_3Ge	298	5.69	6.37	1.44	1.02	1.10
	200	6.17	...	0.95	0.97	...
	77	4.47	5.71	−0.50	0.82	−0.08
V_3Si	298	5.39	5.59	0.78	1.04	−0.06
	195	...	...	0.88	...	...
	77	3.96	5.29	−0.05	0.77	+0.51

derivative of the shear modulus at 298°K the value $\partial^2 c_s/\partial p^2 = (-5.3 \pm 0.3) \times 10^{-12}$ dyn/cm^2. The linear combinations of third- and fourth-order elastic constants $\gamma_s^{(3)} = \frac{1}{2}(C_{1111mm} - C_{1122mm})$ and $\gamma_s^{(4)} = \frac{1}{2}(C_{1111mmnn} - C_{1122mmnn})$ calculated from these values by using the standard equations[11] are (in 10^{12} dyn/cm^2) $\gamma_s^{(3)} = -13.3$ and $\gamma_s^{(4)} = -1140$. The ratios $\gamma_s^{(3)}/c_s = -15$ and $\gamma_s^{(4)}/c_s = -1250$ are dimensionless measures of the first- and second-order anharmonicity (resulting from third- and fourth-order coupling parameters, respectively) of the shear mode corresponding to the modulus c_s. In alkali halides these ratios are of the order of -10 and $+10^2$, respectively.[12-14]. One may therefore expect that in V_3Ge the first- and second-order anharmonic contributions to other anharmonic properties are approximately equal to, and ten times larger than, those in alkali halides, respectively, and that the second-order anharmonic contributions in V_3Ge are of opposite sign than those in alkali halides.

In Fig. 1 the pressure derivatives of the bulk modulus B (average of the values calculated from the two longitudinal moduli) and of the two shear moduli c_{44} and c_s (directly measured values) are plotted versus temperature. The error bars of the bulk modulus reflect the inconsistencies of Table I. The resulting curves are extrapolated to lower temperatures as indicated by the dotted lines.

The microscopic Grüneisen parameters $\gamma_\lambda(\bar{N})$ ($\lambda = 1, 2, 3$; $\bar{N}$ = propagation direction) and the macroscopic Grüneisen parameters γ_0 and γ_∞ corresponding to the low-temperature and high-temperature limits, respectively, have been calculated from the pressure derivatives of the elastic constants on the basis of the anisotropic elastic continuum model.[15,16] In the spirit of the quasiharmonic approximation all input data should be referred to 0°K. For V_3Ge the elastic-constant data of Rosen, Klimker, and Weger[3] at 0°K and the pressure derivatives extrapolated to 0°K according to Fig. 1 have been used. For V_3Si, because of the complications associated with the transition to the superconducting state near 17°K, the Grüneisen parameters for V_3Si have been calculated from elastic constants[1] and their pressure derivatives extrapolated to 20°K. Because of the unusually strong temperature dependence of the elastic data, the calculations of the Grüneisen parameters were also carried out with room-temperature input data.

In Fig. 2 the orientation dependence of the microscopic Grüneisen parameters (mode γ's) between the three principal symmetry directions is shown for V_3Si. As a consequence of the negative value of $\partial c_s/\partial p$ and the small value of c_s, one of the transverse branches shows a deep minimum of -5.48 in [110]. In the vicinity of [111] both transverse mode γ's are negative, and a second minimum with a negative mode γ of -1.35 occurs between [111] and [001]. For V_3Ge the

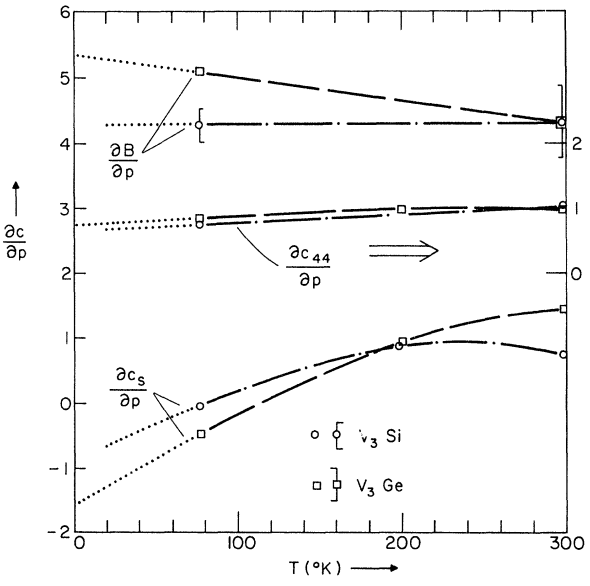

FIG. 1. Pressure derivatives of elastic constants versus temperature.

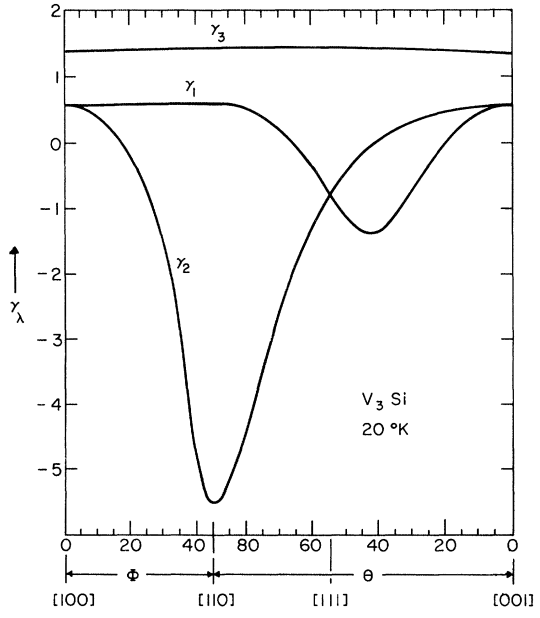

FIG. 2. Microscopic Grüneisen parameters $\gamma_\lambda(\bar{N})$ versus direction.

general pattern is similar and the minimum value of the transverse mode in [110] is -1.49.

The low-temperature limit γ_0 and the high-temperature limit γ_∞ of the macroscopic Grüneisen parameter were calculated from the elastic data at 0°K (V_3Ge), 20°K (V_3Si), and 298°K (V_3Ge and V_3Si) by numerical evaluation of the mode average and are listed in Table II. Also included[17] are the thermal Grüneisen parameter $\gamma_{th}=\beta B^S/\rho c_p$, calculated from the volume thermal expansion coefficient β measured by Testardi[18] and room-temperature density values of $\rho=5.71$ (V_3Si) and 6.85 (V_3Ge). The vibrational specific heat c_p at 30°K was calculated from the expression bT^3 with the coefficient b given by Testardi *et al.*[19] (Table II), whereas at 298°K it was calculated from the elastic Debye temperatures 533°K (V_3Si) and 468°K (V_3Ge) calculated from the room-temperature elastic constants. At 298°K an error arises from the well-known discrepancy between the thermal and elastic Debye temperatures, but this should not drastically affect the thermal Grüneisen parameters. For both materials the high-temperature limit γ_∞ based on room-temperature elastic data agrees roughly with, and is 21% to 26% smaller than, the room-temperature values of γ_{th}. The discrepancy should primarily be due to the omission of the optical modes and of dispersion in the anisotropic continuum model. For V_3Ge the thermal value γ_{th} based on Testardi's thermal-expansion data[18] shows at 30°K an abnormally large negative value of -6.68. As the low-temperature elastic limit $\gamma_0=0.013$ should be correct in the quasiharmonic approximation, the discrepancy may be due to one or several of three causes: First, the actual values of $\partial c_s/\partial p$ at $T=0$°K are considerably more negative than those obtained by extrapolation (Fig. 1); second, some optical-mode γ's or acoustic-mode γ's in the dispersive range are even more negative than the zone-center acoustic-mode γ's, so that γ_{th} shows a deep negative minimum near 30°K, but does rise again at still lower temperatures to the elastic limit γ_0; third, anharmonic contributions to the zero-point motion are so large as to substantially lower the low-temperature elastic limit γ_0. For V_3Si the low-temperature elastic limit (calculated from elastic data at 20°K) has the abnormally large negative value of -1.89. In view of the elastic stiffening due to the superconducting transition it is doubtful whether this limit will actually be reached even in samples which do not undergo the structural transition to the tetragonal low-temperature phase.

From the pressure and temperature derivatives of the shear modulus it is possible to calculate Born's stability limit[20] for the structural transition in V_3Si which for cubic crystals is defined by the vanishing of the shear modulus $c_s(p, T_L)=0$. Expanding c_s up to linear terms in p and T_L gives for the pressure coefficient of the stability limit $\partial T_L/\partial p=-(\partial c_s/\partial p)_T(\partial c_s/\partial T)_p^{-1}$. With the extrapolated value of $(\partial c_s/\partial p)_T=-0.65$ and with[19] $\partial c_s/\partial T=10$ kbar °K^{-1} one obtains $\partial T_L/\partial p=+0.065$ °K kbar^{-1}. Since for alkali halides the pressure coefficient of the stability limit agrees quite closely with the pressure coefficient of the melting temperature,[14] one may expect that the above value is a good approximation to the pressure coefficient of the structural transition temperature in V_3Si. Surprisingly, this value is also of the same order as the pressure coefficient of the superconducting transition temperature (0.036°K kbar^{-1} as experimentally determined by Smith.[21] The initial slope obtained from a (more reasonable) quadratic fit to Smith's data is 0.052°K kbar^{-1}, in even better agreement with the value derived above. This corroborates earlier suggestions[19] that in V_3Si the superconducting transition temperature is determined by the soft transverse branch in [110].

TABLE II. Macroscopic Grüneisen parameters γ_0 and γ_∞ calculated from elastic data at 20°K (V_3Si), 0°K (V_3Ge), and 298°K (V_3Si and V_3Ge, in parentheses); and the thermal Grüneisen parameter γ_{th}.

	γ_0	γ_∞	γ_{th} 30°K	γ_{th} 298°K
V_3Si	−1.89	0.11	•••	•••
	(0.90)	(1.08)	•••	1.46
V_3Ge	0.013	0.30	−6.68	•••
	(1.15)	(1.29)	•••	1.63

†Work supported by the U. S. Atomic Energy Commission.

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Polarization Transfer in the Reaction T $(p,n)^3$He at 0° for E_p in the Range 3 to 16 MeV*

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(Received 4 August 1971)

The polarization of the neutrons has been measured for the reaction $T(p,n)^3$He at 0° for conditions where the incident beam is transversely polarized. The neutrons were observed to be highly polarized in the same direction as the incident proton spin, with values of the polarization transfer coefficient $K_y{}^y(0°)$ ranging from +0.39 to +0.83. R-matrix calculations using published ^{4}He level parameters of Werntz and Meyerhof do not agree well with our measurements.

In this Letter we report the first results for a triple-scattering–type observable in the reaction $T(p,n)^3$He, namely, the polarization transfer parameter at 0°. This experiment demonstrates a large transfer of polarization from the incident proton to the outgoing neutron in the process. The data also allow an important comparison to be made with the analysis of Werntz and Meyerhof[1] on the states of ^{4}He.

The reaction was initiated with a transversely polarized proton beam and the transverse polarization of the outgoing neutrons was measured by a second scattering from helium. In this way, the polarization transfer coefficient[2] $K_y{}^y(0°)$ was determined. The coefficient is defined for any angle θ in terms of the M matrix by

$$K_y{}^y(\theta) = [\mathrm{Tr}(M\sigma_y{}^p M^\dagger \sigma_y{}^n)]/[\mathrm{Tr}(MM^\dagger)], \qquad (1)$$

where σ_y is the usual Pauli spin matrix for the nucleons. A right-handed coordinate system with the $+y$ axis parallel to $\vec{k}_{in}\times\vec{k}_{out}$ has been assumed. At 0°, the y axis is undefined and was taken to lie in the horizontal plane and to be normal to $\vec{k}_{in}$. In this reaction, $K_y{}^y(\theta)$ is similar to Wolfenstein's[3] parameter $D(\theta)$ for nucleon-nucleon scattering, except that the outgoing particle is different from the incoming particle. At $\theta=0°$, $K_y{}^y(\theta)$ depends only upon triplet-triplet and singlet-singlet channel spin transitions. For this case, Eq. (1) may be expressed as

$$K_y{}^y(0°) = \frac{2\,\mathrm{Re}[M_{11}{}^*(M_{00}+M_{ss})]}{2|M_{11}|^2+|M_{00}|^2+|M_{ss}|^2}, \qquad (2)$$

where the singlet (M_{ss}) and triplet (M_{11}, M_{00}) M-matrix elements have the form given by MacGregor, Moravscik, and Stapp[4] for n-p scattering. Thus $K_y{}^y(0°)$ is sensitive to few elements of the scattering matrix and as such will provide new information on the four-body system.

Experimentally, a beam of polarized protons produced by the Los Alamos Scientific Laboratory Lamb-shift polarized ion source[5] was accelerated by the model FN tandem accelerator and directed onto a tritium gas target at a pressure of 4.8 atm (absolute). The proton spin polarization vector was oriented parallel to the y axis in the horizontal plane normal to $\vec{k}_{in}$. The y component of the neutron polarization at 0° was measured by scattering the neutrons from a helium polarimeter. Briefly, this polarimeter consisted of a 4.8-mole liquid-helium scintillator operated in fast coincidence with two NE-102 neutron detectors located at scattering angles θ_2(lab) = 115° above and below the helium scintillator. The experimental details