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Elastic Constants and Ultrasonic Attenuation of a β-Tungsten-Structure V_3Ge Crystal from 4.2 to 300°K

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The longitudinal and transverse acoustic velocities and the ultrasonic attenuation of a β-tungsten V_3Ge crystal with the β-tungsten structure have been measured by a pulse technique at a frequency of 10 MHz between 4.2 and 300°K. The room-temperature elastic moduli have been determined as $C_{11}=2.966$, $C_{44}=0.6978$, and $C_{12}=1.042$ in units of 10^{12} dyn/cm². Contrary to the behavior of the β-tungsten-structure compounds V_3Si and Nb_3Sn, the adiabatic compressibility of V_3Ge was found to be temperature-dependent. The elastic constant C_{11} exhibits a lattice-softening phenomenon in the temperature interval between 75 and 300°K. The shear modulus $\frac{1}{2}(C_{11}-C_{12})$ displays a minimum at 75°K. At this temperature the longitudinal (in contrast to the shear) attenuation shows a sharp peak. The behavior of the elastic moduli and attenuation is discussed in terms of possible operation of an electron transfer mechanism. In addition, both the longitudinal and the shear attenuation behave anomalously at 168°K. A relaxational process is assumed. The limiting value of the Debye temperature is found to be 487°K. At room temperature, it is 471°K.

INTRODUCTION

CONTRARY to the normal behavior in metals, the shear modulus $\frac{1}{2}(C_{11}-C_{12})$ of the β-tungsten-structure (A-15) compounds V_3Si and Nb_3Sn was found to decrease, and subsequently vanish, with decreasing temperatures. These compounds have high superconducting transition temperatures T_c, 17 and 18°K, respectively. The maximum lattice softening, i.e., decrease in magnitude of the elastic modulus, occurs at temperatures T_m, slightly above T_c.[1-3] X-ray measurements[4-6] revealed the occurrence of a martensitic transformation, from cubic to tetragonal crystallographic structures, at T_m. The variation of the lattice parameters during this transformation is such as to maintain very nearly constant volumes of the unit cells, thus suggesting a second-order phase change.[7] No clear relation was found between T_m and T_c.[6]

The compounds V_3Si and Nb_3Sn exhibit anomalies in the temperature dependence of various physical properties, e.g., magnetic susceptibility and Knight shift,[8] nuclear relaxation times,[9] and electronic specific heat[10,11] was observed at T_c but not at the temperature where the shear modulus $\frac{1}{2}(C_{11}-C_{12})$ assumes minimal values.

The behavior of the physical properties of these compounds was explained in terms of a very narrow electronic d-band structure.[12] It was suggested[13] that their electronic properties are due to an extremely anisotropic band structure, which is a consequence of the particular crystallography emphasizing the one-dimensional chains of atoms in the β-tungsten structure. Experimental confirmation of this model was obtained by observing the behavior of the compounds under uniaxial and hydrostatic pressures.[14] The linear chain model of atoms is unstable against shear deformations defined by the modulus $\frac{1}{2}(C_{11}-C_{12})$. A theoretical approach,[15-18] using the one-dimensional model to calculate the d-band structure in these compounds, and its dependence on temperature and composition, gives reasonably good agreement with experiment.

The unusual behavior of V_3Si and Nb_3Sn at low temperatures does not appear to occur in the isostructural compound V_3Ge, which has a comparatively low superconducting transition temperature ($T_c\approx 6$°K). Earlier elasticity measurements[19] showed that except for a small anomaly in the sound wave velocity near

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room temperature, the behavior is normal at low temperatures.

The objective of the present study was to determine the temperature variation of the three independent elastic constants and the ultrasonic attenuation of a single-crystal V_3Ge, thus gaining additional information that may elucidate the behavior of the β-tungsten compounds. However, the insufficient knowledge about the electronic properties of V_3Ge reported so far, necessarily limits the scope of the discussion.

EXPERIMENTAL

The V_3Ge single crystal used in this investigation was lent to one of us (M. W.) by L. R. Testardi of Bell-Telephone Laboratories. The crystal was in the form of a parallelepiped with two pairs of flat and parallel faces, {001} and {110}, suitable for high-accuracy ultrasonic work.

A pulse technique was employed at a single frequency of 10 MHz. Experimental details and method of sound velocity and ultrasonic attenuation determination were described elsewhere.[20] Dow Corning Compound 7, applied as a very thin layer, served as an ultrasonic couplant for both longitudinal and shear wave propagation between 4.2 and 300°K. C_{11}, C_{12}, and C_{44} are the three independent elastic constants of a cubic crystal and ρ is the measured crystal density (6.858 g cm^{-3}), by means of a fluid displacements method. No corrections were made for the acoustic path-length changes with temperature. For the isostructural V_3Si the total change,[2] over the temperature interval between 4.2 and 300°K, was found to be about 3 parts in 10^3. The estimated error in the absolute values of the elastic moduli, as manifested by the internal consistency of the three elastic constants calculated from the four measured sound velocities, is 0.3%. The relative point-to-point precision is better by a factor of 3. The ultrasonic attenuation was determined to within 1% and the temperature to 0.5°K.

RESULTS

The room-temperature values of the three independent elastic constants are

$$C_{11}=2.966\times 10^{12}\ \text{dyn/cm}^2,$$

$$C_{44}=0.6978\times 10^{12}\ \text{dyn/cm}^2,$$

$$C_{12}=1.042\times 10^{12}\ \text{dyn/cm}^2.$$

The temperature dependence of these constants is illustrated in Fig. 1. With decreasing temperature, from 300°K, C_{11} decreases slowly, thus exhibiting to some extent the lattice softening phenomenon.[19] The minimum value of C_{11} is attained at 75°K. Between 6 and 75°K, C_{11} displays a sharp increase (about 7%) in its magnitude. No anomalies in the elastic constants were observed in the vicinity of the superconducting transition temperature of V_3Ge.

TABLE I. Sound velocities measured in crystallographic directions.

Mode	Propagation direction	Polarization direction	Sound wave velocities
Longitudinal	[001]	[001]	$(C_{11}/\rho)^{1/2}$
Shear	[001]	[110]	$(C_{44}/\rho)^{1/2}$
Longitudinal	[110]	[110]	$(C_{11}+C_{12}+2C_{44}/2\rho)^{1/2}$
Shear	[110]	$[1\bar{1}0]$	$(C_{11}-C_{12}/2\rho)^{1/2}$

The C_{44} constant (Fig. 1) does not show any lattice softening. However, the increase in C_{44} with decreasing temperature in the interval between about 160 and about 300°K is very shallow. This is not a characteristic behavior of metals. Below 160°K, C_{44} increases almost linearly with decreasing temperature, and subsequently approaches the ordinate (0°K) with zero slope, as required by the third law of thermodynamics.

The elastic constant C_{12} (Fig. 1) behaves quite differently compared to C_{11} and C_{44}. Its temperature variation shows a flat maximum at 75°K, followed by a steep decrease at lower temperatures. The maximum value of C_{12} is at the temperature where C_{11} is minimal.

The shear mode propagated in the [110] direction with the $[1\bar{1}0]$ polarization, i.e., $\frac{1}{2}(C_{11}-C_{12})$, is shown in Fig. 2. It displays a minimum at 75°K, but does not

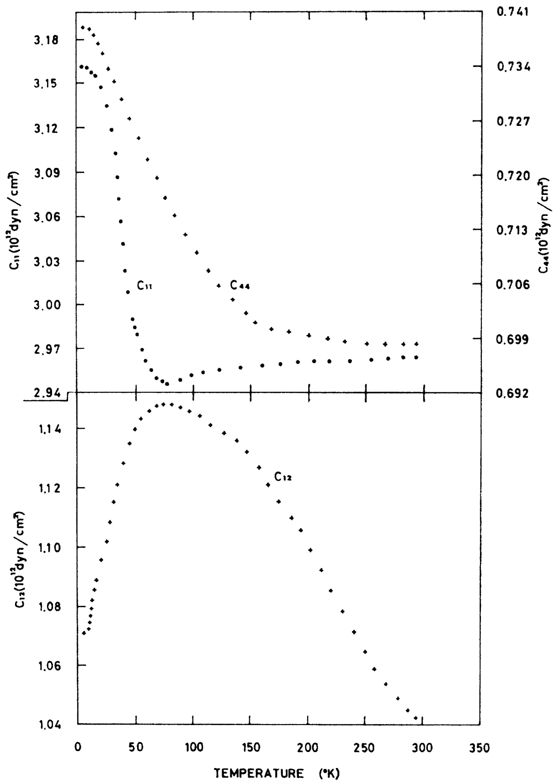

FIG. 1. Temperature variation of the elastic constants (C_{11}, C_{44}, and C_{12}) of single-crystal V_3Ge.

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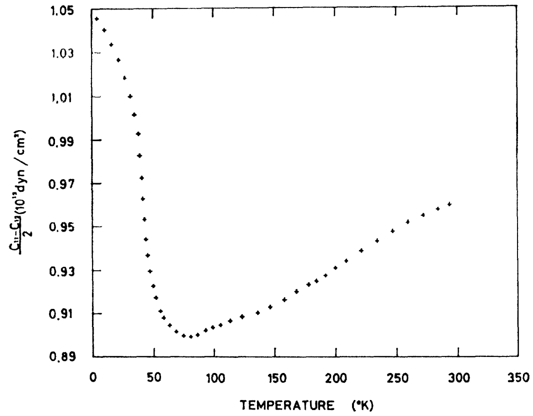

FIG. 2. Temperature variation of the shear modulus $\frac{1}{2}(C_{11}-C_{12})$ of single-crystal V_3Ge.

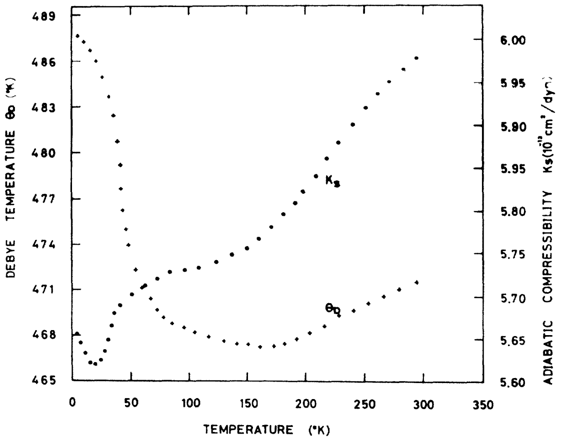

FIG. 3. Temperature variation of the adiabatic compressibility (K_S) and the Debye temperature (Θ_D) of single-crystal V_3Ge.

vanish as was the case in V_3Si[2] and Nb_3Sn.[3] The over-all decrease in $\frac{1}{2}(C_{11}-C_{12})$ from 300 to 75°K is only about 5.5%. Below 75°K the modulus $\frac{1}{2}(C_{11}-C_{12})$ increases rapidly with decreasing temperature similarly to the constant C_{11}.

The temperature variation of the adiabatic compressibility $K_S=3/(C_{11}+2C_{12})$ and of the Debye temperature Θ_D is shown in Fig. 3. The total reduction in K_S, between 4.2 and 300°K, is about 4%. This is a normal behavior of metals. Significant features in the temperature dependence of K_S are a plateau between about 50 and 170°K, and a minimum at 20°K. The Debye temperature was calculated by means of the De Launay method.[21] The temperature variation of Θ_D is similar in character to that of the elastic constants. The limiting $\Theta_D{}^0$ value of Θ_D (at 0°K), as determined from the elasticity measurements in the present study, was found to be 487°K, significantly higher than 405°K calculated from specific-heat measurements.[22] Figure 3 shows that the room-temperature value of Θ_D is 471°K, in good agreement with the value quoted by Testardi,[19] 472°K. It should be noted that Testardi has employed Anderson's averaging method[23] for the calculation of Θ_D. In general, $\Theta_D{}^0$ determined from elastic measurements is higher than that derived from specific-heat data.[20] The latter method suffers from the difficulty in estimating the electronic contribution to $\Theta_D{}^0$, whereas the elastic constants method does not.

Figure 4 shows the temperature variation of the ultrasonic attenuation. The longitudinal (α_l) and shear (α_t) attenuation are of the ultrasonic waves propagated in the [100] direction. The attenuations in the [110] direction (not shown) were found to exhibit similar features. A sharp peak in α_l is formed at about 75°K, where the shear modulus $\frac{1}{2}(C_{11}-C_{12})$ is at its minimum value. In contrast, the shear wave attenuation, Fig. 4, increases monotonically in this temperature interval.

DISCUSSION

The contribution of the electronic state to the adiabatic elastic constants (Appendix) can be calculated by expanding the internal energy as a power series in the strain components, and retaining the second-order terms. Thus,

$$\begin{aligned}
-\delta F=&\sum_{ij} e_{ij}\sum_{m}\int dE(E-E_F)\frac{dn^m(E)}{dE}\frac{\partial E^m}{\partial e_{ij}}f(E-E_{F'}T)+\tfrac{1}{2}\sum_{ijkl} e_{ij}e_{kl}\sum_{m}\int dE(E-E_F)\frac{dn^m(E)}{dE}\frac{\partial^2 E^m}{\partial e_{ij}\partial e_{kl}}f(E-E_{F'}T)\\
&+\tfrac{1}{2}\sum_{m}\int dE(E-E_F)\frac{d^2n^m(E)}{dE^2}\left(\sum_{ij}\frac{\partial E^m}{\partial e_{ij}}e_{ij}\right)^2 f(E-E_{F'}T)+\frac{1}{2n(E_F)}\left(\sum_{ij}e_{ij}\sum_{m}\int dEf(E-E_{F'}T)\frac{dn^m(E)}{dE}\frac{\partial E^m}{\partial e_{ij}}\right)^2\\
&+\frac{E_F}{n(E_F)^2}\left[\sum_{ij}e_{ij}\sum_{m}\int dE\frac{dn^m(E)}{dE}\frac{\partial E^m}{\partial e_{ij}}f(E-E_{F'}T)\right]\\
&\times\left[\frac{dn(E_F)}{dE}\sum_{kl}\sum_{m'}\left(\int dE\, e_{kl}\frac{dn^{m'}(E)}{dE}\frac{\partial E^{m'}}{\partial e_{kl}}f(E-E_{F'}T)-n(E_F)e_{kl}\frac{dn^{m'}(E_F)}{dE}\frac{\partial E_F{}^{m'}}{\partial e_{kl}}\right)\right].
\end{aligned}$$

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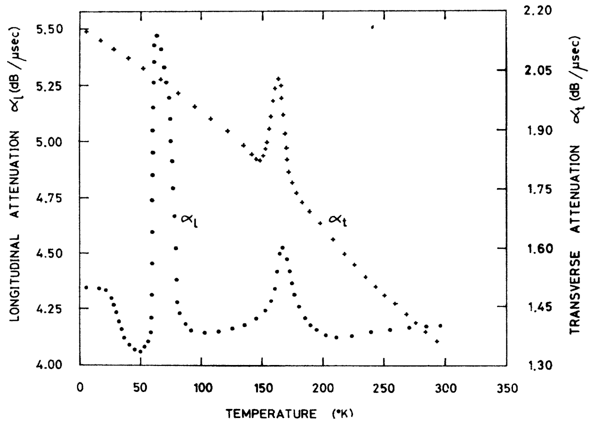

FIG. 4. Temperature variation of the longitudinal (α_l) and shear attenuation of ultrasonic waves propagated in the [100] direction of single-crystal V_3Ge.

Here, e_{ij} are the strain components $i, j, =x, y, z$; $n^m(E)$ is the density of states of the mth electronic band. $f(E-E_F,T)$ is the function $\{1+\exp[(E-E_F)/k_BT]\}^{-1}$. When the density-of-states function contains singularities, care should be exercised to take the limits properly. The summation is over the relevant bands (say, the conduction bands or some specific d band). The first term is the pressure (positive or negative), which is balanced by an opposite term because of the ion cores (filled bands), etc. The physical nature of the second-order terms can be demonstrated if one assumes $T=0$°K, and that the shift of the bands with strain $\partial E_m/\partial e_{ij}$ is independent of the energy. Then the derivatives can be taken out of the integral, and partial integration performed:

$$\delta F=-\sum_{ij} e_{ij}\sum_{m}\left\langle\frac{\partial E^m}{\partial e_{ij}}\right\rangle n^m-\tfrac{1}{2}\sum_{ijkl} e_{ij}e_{kl}\sum_{m}\left\langle\frac{\partial^2 E^m}{\partial e_{ij}\partial e_{kl}}\right\rangle n^m$$
$$-\tfrac{1}{2}\sum_{ijkl} e_{ij}e_{kl}\sum_{m} n^m(E_F)\left\langle\frac{\partial E^m}{\partial e_{ij}}\right\rangle$$
$$\times\left(\left\langle\frac{\partial E^m}{\partial e_{kl}}\right\rangle-\sum_{m'}\frac{n^{m'}(E_F)}{n(E_F)}\left\langle\frac{\partial E^{m'}}{\partial e_{kl}}\right\rangle\right),$$

where n^m is the total number of electrons in band m, and $n^m(E_F)$ is the density of states at the Fermi surface. It is seen that the second term gives a contribution also for filled bands. The ion-core contribution can be represented by a term of this sort, if desired. The last term gives a contribution to the elastic constants proportional to the density of states at the Fermi level. It is seen that when $\partial E^{m'}/\partial e_{kl}$ is independent of m', i.e., all bands shift under strain in the same way, this term vanishes. Furthermore, this term always yields a negative (or zero) contribution to the elastic constants, i.e., always causes softening.

As suggested by Barisic and Labbé,[7] a particularly important case is that of a high density of states at a point of high symmetry, where the energy bands are degenerate and the degeneracy is lifted by strain. Since a hydrostatic strain does not change the symmetry, it does not lift the degeneracy, and therefore there is no softening in the adiabatic compressibility. For a cubic crystal, there is a softening in the $\frac{1}{2}(C_{11}-C_{12})$ shear modulus if the degeneracy is lifted by a strain in the [100] direction and a softness in C_{44} if the degeneracy is lifted by a strain in the [111] direction. At point $\Gamma(\mathbf{k}=0)$, levels may be singly degenerate (symmetries such as A_1, A_2, etc.), doubly degenerate (symmetry such as E), or triply degenerate (symmetries such as T_1, T_2). The symmetry of the wave function under the operations of reflection in a plane, or rotation by 180°, are not relevant to the elastic constants, since these symmetries are not affected by homogeneous strain. Thus, states T_1 and T_2 behave alike.

In the present approximation, singly degenerate levels do not contribute to the softening; doubly degenerate levels, split for strain in the [100] direction, but not for strain in the [111] direction, contribute to softening in $\frac{1}{2}(C_{11}-C_{12})$, but not to softening of C_{44}. Triply degenerzte levels split for strain in both directions, and thus may contribute to softness in both $\frac{1}{2}(C_{11}-C_{12})$ and C_{44}. However, quantitatively, it is possible that the contribution to one constant is much larger than to the second; for example, in the linear chain model, $\partial E/\partial e_{xx}$ is due to interactions between nearest-neighbor vanadium d functions, while a nonvanishing $\partial E/\partial e_{xy}$ requires interactions between next-nearest neighbors.[13] Thus, the softening of $\frac{1}{2}(C_{11}-C_{12})$ in V_3Ge, unaccompanied by a softening in C_{44} (Fig. 1), may be due to a doubly degenerate level, or to a triply degenerate level with predominant nearest-neighbor interactions, or even a degeneracy at another high-symmetry point of the Brillouin zone.[24]

A softening in the bulk modulus $\frac{1}{3}(C_{11}+2C_{12})$ should be observed when the softness is due to several inequivalent bands. In that case, the bands may shift with respect to each other under the application of a hydrostatic strain. Thus, it is not surprising that some softness is observed in V_3Ge. This phenomenon is represented by the appearance of a plateau in K_S (Fig. 3), between 50 and 170°K. The temperature variation of K_S in V_3Ge is significantly different from that of V_3Si[2] and Nb_3Sn.[3] In these two compounds, the contribution of the d electrons to K_S vanishes, in the first approximation.[17]

The temperature dependence of the softening phenomenon in the elastic constants has been calculated explicitly for the density-of-states functions[17] $n(E)=(E_0-E)^{-1/2}$ and $n(E)=\text{const}$.[25] In the first case, there is a minimum in the elastic constants at a temperature $k_BT\approx(E_F-F_0)$; in the second, the minimum is at

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0°K. At high temperatures compared with the width of the peak in the density of states, the softening disappears.

For a general density-of-states function, one may expand the energy at low temperatures as a power series in the temperature. (It is probably advantageous to calculate the internal energy, rather than the free energy, because of the adiabatic nature of the sound waves.) In the approximate expressions given here, $n(E_F)$ has to be replaced by

$$n_{\mathrm{eff}}(E_F)=\int \frac{df(E-E_{F'}T)}{dE}n(E)dE\,,$$

thus,

$$n_{\mathrm{eff}}(E_F)=n(E_{F_0})+\tfrac{1}{6}\pi^2\left[\frac{d^2n(E_F)}{dE^2}-\frac{1}{n(E_F)}\left(\frac{dn(E_F)}{dE}\right)^2(k_BT)^2\right].$$

The first correction term is due to "smearing" of the effective electrons over an energy interval k_BT which increases the average density of states when $d^2n(E_F)/dE^2$ is positive and vice versa. The second correction is due to a shift of the Fermi level with temperature in the direction of a lower density of states. Thus, a minimum in the elastic constants at a finite temperature should occur when $n(E_F)d^2n(E_F)/dE^2>[dn(E_F)/dE]^2$, a condition satisfied by the density-of-states function $[n(E)\propto(E-E_0)^{-1/2}]$, selected by Labbé and Friedel.[16]

The temperature of the minimum in the elastic constants depends on the details of the density-of-states function. The minimum should occur at the temperature where $k_BT\approx|E_0-E_F|$. E_0 is the energy at which the density of states has a maximum. At lower temperatures $k_BT<|E_0-E_F|$, therefore the energy level E_0 remains unpopulated. Under such conditions, the softening phenomenon in the elastic constants will disappear. The recovery of the elastic constants of V_3Ge at temperature below 75°K (Fig. 2) can be attributed to such a mechanism.

Noteworthy is the similarity between the temperature of C_{12} in V_3Ge (Fig. 1) and that of the polycrystalline elastic moduli of praseodymium and samarium metals.[26] In these two metals, the anomalous behavior of the moduli was attributed to a possible operation of a temperature-dependent electron interband scattering mechanism.

The appearance of an attenuation peak in α_l and its absence in α_t (Fig. 4) may be significant in describing the mechanism responsible for the anomaly in the elastic constants. Longitudinal waves cause local changes in density when propagating through the crystal lattice, while shear (volume-conserving) waves do not. In V_3Si the increase in the ultrasonic attenuations was observed only in samples having a martensitic transformation.[2] However, there is no evidence for a martensitic transformation in V_3Ge. Therefore, the sharp anomaly in α_l (Fig. 4) cannot be related to a crystallographic transition mechanism. Moreover, structural and ordering phase changes are generally accompanied by anomalies in both longitudinal and shear wave attenuation.[19] The behavior of the ultrasonic attenuation, and particularly of α_l, in V_3Ge is consistent with the anomalies in the elastic moduli, Figs. 1 and 2, and indicates the operation of a degeneracy lifting mechanism in the vicinity of 75°K.

An additional feature on the attenuation curves (Fig. 4) is the peaks in both α_l and α_t at 168°K. The elastic moduli (Fig. 1) do not indicate any anomalies at this temperature, although K_S and Θ_D (Fig. 3) show changes in slope in the vicinity of 168°K. The shape of the peaks in α_l and α_t seems to be characteristic of a relaxation phenomenon. Unfortunately, the ultrasonic measurements were performed at a single frequency, and therefore the relaxational character of these anomalies in the attenuation cannot definitely be established.

CONCLUSIONS

The behavior of the elastic moduli and ultrasonic attenuation of V_3Ge was found to be different from other β-tungsten compounds, e.g., V_3Si and Nb_3Sn, in which the shear modulus $\frac{1}{2}(C_{11}-C_{12})$ vanishes in the vicinity of the superconducting transition temperature. In V_3Ge the shear modulus $\frac{1}{2}(C_{11}-C_{12})$ displays a minimum at 75°K, followed by a recovery at lower temperatures. Also, in V_3Ge the modulus C_{44} increases at low temperatures and the increase is of the same order as the changes in the moduli C_{11} and C_{12}.

The theoretical model, presented in this paper, gives an estimate of the contribution of electronic states to the adiabatic elastic constants, if the effect of strain on the shifting of the bands (the deformation potential) is known. The model indicates that for a cubic crystal singly degenerate levels do not contribute to the lattice softening, doubly degenerate levels split for strain in the [100] direction, but not for strain in the [111] direction, thus contributing to the softness of the $\frac{1}{2}(C_{11}-C_{12})$ shear modulus, but not to C_{44}. Triply degenerate levels split for strain in both directions, thus causing softness in both $\frac{1}{2}(C_{11}-C_{12})$ and C_{44} moduli.

A minimum in the shear modulus $\frac{1}{2}(C_{11}-C_{12})$ should occur at a temperature T, where $k_BT\approx|E_0-E_F|$. E_0 is the energy at which the density of states has a maximum. At lower temperatures, the energy level E_0 remains unpopulated, or fully populated, causing the lattice softening phenomenon to disappear. The recovery of the $\frac{1}{2}(C_{11}-C_{12})$ shear modulus in V_3Ge below 75°K is attributed to such a mechanism.

The appearance of the plateau in the adiabatic compressibility between 50 and 170°K, may be due to the presence of several inequivalent electronic bands. In V_3Si and Nb_3Sn the contribution of the d electrons to the isotropic compressibility is small compared with

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that to the anisotropic one. The electronic contribution to the isotropic compressibility in V_3Ge is large, and temperature-dependent.

The longitudinal wave attenuation of V_3Ge displays a sharp peak at 75°K, where the shear modulus $\frac{1}{2}(C_{11}-C_{12})$ is minimal. The shear wave attenuation does not exhibit any anomaly at this temperature. Such a behavior is consistent with operation of an electron transfer mechanism, realized by strain-dependent degeneracy lifting.

Peaks in both longitudinal and shear wave attenuation, at about 168°K, are presently unaccounted for, but may be due to a relaxation phenomenon.

ACKNOWLEDGMENTS

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APPENDIX

In order to calculate electronic contribution to the elastic constants, following the approximations made in the text, we make use of the following symmetry properties: (a) Under hydrostatic strain, the degeneracy is not lifted. (b) Under volume-preserving strain, the center of gravity of the energy levels has no linear shift with strain, because, for cubic symmetry, such a strain is not invariant under the allowed symmetry operations.

For a triply degenerate level, at point Γ, the wave functions $\Psi_1\Psi_2\Psi_3$ transform like x,y,z or yz, zx, xy. The expressions for the contribution to the elastic constants, are

$$C_{11}^e=-\frac{2}{9}n(E_F)\left(\frac{\partial E^1}{\partial e_{xx}}-\frac{\partial E^1}{\partial e_{yy}}\right)^2=-2C_{12}^e.$$

Here, E^1 is the energy of state Ψ_1; Labbé and Friedel assume $\partial E^1/\partial e_{xx}=0$, but this assumption holds only in a very special case (no crystalline field, only nearest-neighbor interaction) and is not necessary to account for the experimental observations.

When strain is applied in the [111] direction, the triplet splits into a singlet state Ψ_1' and a doublet state Ψ_2', Ψ_3'. Let $e_1=(1/\sqrt{3})(e_{xy}+e_{yz}+e_{zx})$. Then

$$C_{44}^e=-(2/9)n(E_F)\left(\frac{\partial E^1}{\partial e_1}-\frac{\partial E^2}{\partial e_1}\right)^2.$$

For a doubly degenerate level at point Γ, the wave functions Ψ_1'', Ψ_2'' transform like x^2, y^2-z^2, respectively. The expression for the electronic contribution to the elastic constants is

$$C_{11}^e=-\tfrac{1}{4}n(E_F)\left(\frac{\partial E^1}{\partial e_{xx}}-\frac{\partial E^2}{\partial e_{xx}}\right)^2=-2C_{12}^e;\quad C_{44}^e=0.$$

These expressions are the most general ones, allowing for the above-mentioned symmetries, and the approximations mentioned in the text.

As an example of a case where one cannot assume that $\partial E/\partial e_{ij}$ is even approximately constant, and cannot, therefore be taken out of the integral, consider the case of degeneracy at the zone boundary.[27] Assume that on the zone face, $k_x=\pi/a$, two energy levels, E^1 and E^2, are degenerate, and in its neighborhood

$$E_0^1=\left(\frac{\partial E}{\partial k_x}\right)_0\delta k_x,\quad E_0^2=-\left(\frac{\partial E}{\partial k_x}\right)_0\delta k_x,$$

and under strain,

$$[E^m(e_{ij})]^2=(E_0^m)^2+\left[\left(\frac{\partial E_0^m}{\partial e_{ij}}\right)e_{ij}\right]^2.$$

Then, if the Fermi level lies at the degeneracy point, the electronic contribution to the elastic constants is given by

$$n(E_F)\left(\frac{\partial E^1}{\partial e_{ij}}-\frac{\partial E^2}{\partial e_{ij}}\right)^2\ln\left[n(E_F)\left|\frac{\partial E^1}{\partial e_{ij}}-\frac{\partial E^2}{\partial e_{ij}}\right||e_{ij}|\right].$$

This contribution diverges logarithmically for small strain, indicating an instability, as remarked already by Fröhlich.[28] In practice, a degeneracy of this type will exist only on isolated points on the zone faces, and therefore the weak, logarithmic singularity is removed. But the limitations of the approximations made in this paper should be borne in mind.

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[27] H. Jones, *Theory of Brillouin Zones* (North-Holland Publishing Co., Amsterdam, 1960), p. 148.

[28] H. Fröhlich, Proc. Roy. Soc. (London) **223A**, 296 (1954).