Lattice Instability of High-Transition-Temperature Superconductors. II. Single-Crystal V_3Si Results

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Sound-velocity measurements in V_3Si have shown that the modulus $(C_{11}-C_{12})/2$ for [110] shear waves with $[1\bar{1}0]$ polarization falls from a value at room temperature typical of the metallic state to near-zero magnitude in the superconducting state, while the bulk modulus $(C_{11}+2C_{12})/3$ is constant to 0.5% in the same temperature interval. The attenuation of the soft shear mode increases markedly on cooling. A large increase in attenuation for all modes occurs with the structural transformation at 21°K reported by Batterman and Barrett. The transformation, triggered by the small shear stiffness, is arrested with the onset of the superconducting state. The distortions of the structural transformation are found to be comparable in magnitude with the thermal strains resulting from the soft shear mode. The behavior of the high-frequency phonons involved in the superconductivity is not known, although the specific-heat and electrical-resistivity data indicate that they may be stiffer than the near-liquidlike low-frequency phonons. The lattice instability may result from a very strain-sensitive structure in the density-of-states distribution near the Fermi level. The unusual elastic behavior reported here for V_3Si is probably characteristic of most high-temperature superconductors.

INTRODUCTION

THE highest temperature for the occurrence of superconductivity known today is approximately 18°K. Except for a range of composition in the NbN-NbC system, all of the materials which are superconducting in the range 14°K to 18°K share the β-tungsten (A-15) crystal structure. These materials also exhibit unusual behaviors in a number of their physical properties[1–6] which seemingly stem from those characteristics which are responsible for the high-temperature superconductivity. There is now, in consequence, the growing speculation that with increasing T_c the anomalous behavior of these materials may become incompatible with the occurrence of superconductivity.

The unusual behavior of elastic softening on cooling has now been observed in most of the high-temperature superconductors (see previous paper). In this article we give the results and some analysis of the ultrasonic measurements[7] of the elastic moduli of single-crystal V_3Si ($T_c\sim17$°K). The results provide a basis for understanding the structural instability in this (and perhaps similar) superconductors. They may also be used to raise the question of whether the lattice stability of high-T_c superconductors is jeopardized by those conditions favorable to high-temperature superconductivity. More obscure (and perhaps more important) is the significance of the unusual phonon behavior for the occurrence of superconductivity in these materials.

EXPERIMENTAL METHOD

The V_3Si single crystals used in these studies were grown by a floating-zone process.[8] Two pairs of plane-parallel faces, {001} and {110}, were prepared on the specimen.

Shear waves and longitudinal waves were propagated in both directions. Resonant piezoelectric transducers, ac-cut quartz for shear waves, and X-cut quartz and Z-cut tourmaline for longitudinal waves, were used to excite the ultrasound. The transducers were bonded to the sample with Nonaq,[9] DC 200 series silicone fluid[10] 1000 cS, or Plexol.[11] The latter two fluids provide the thin bond which is essential for accuracy in the velocity measurements.[12]

The ultrasonic velocity and attenuation for the individual modes were measured over the temperature range 300 to 4.2°K. Table I lists the relations between the three independent elastic moduli, C_{11}, C_{12}, and C_{44}, the density ρ, and the ultrasonic-wave velocities of the modes measured in these experiments. The McSkimin pulse-superposition technique[12] was used to

TABLE I. Elastic moduli for several mode velocities in a cubic crystal.

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

[1] W. E. Blumberg, J. Eisinger, V. Jaccarino, and B. T. Matthias, Phys. Rev. Letters **5**, 169 (1960).
[2] A. M. Clogston and V. Jaccarino, Phys. Rev. **121**, 1357 (1961).
[3] A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y. Yafet, Phys. Rev. Letters **9**, 262 (1962).
[4] M. Weger, Rev. Mod. Phys. **36**, 175 (1964).
[5] F. J. Morin and J. P. Maita, Phys. Rev. **129**, 1115 (1963).
[6] M. Weger, B. G. Silbernagel, and E. S. Greiner, Phys. Rev. Letters **13**, 521 (1964).
[7] L. R. Testardi, T. B. Bateman, W. A. Reed, and V. G. Chirba, Phys. Rev. Letters **15**, 250 (1965).
[8] E. S. Greiner and H. Mason, Jr., J. Appl. Phys. **35**, 3058 (1964).
[9] Fisher Scientific Company; see H. J. McSkimin and E. S. Fisher, J. Appl. Phys. **31**, 1627 (1960).
[10] Dow Corning Company; see H. J. McSkimin, J. Appl. Phys. **24**, 988 (1953).
[11] Rohm and Haas Company, di-2-ethylhexylsebacate.
[12] H. J. McSkimin, J. Acoust. Soc. Am. **33**, 12 (1961).

measure the wave velocities. The shear waves were measured at 20 and 60 Mc/sec, and the longitudinal waves were measured at 20, 40, 60, and (along [001] at 20.4°K) 120 Mc/sec. No correction was made for the length change with temperature (~3 parts in 10^3 over the temperature interval studied). The accuracy of length-independent ratios of elastic moduli was estimated to be 0.1%.

Attenuation measurements were made for most of the modes studied although at the higher temperatures the loss was too small to be determined accurately. For the [110] longitudinal wave, detailed measurements were made at low temperatures from 20 to 300 Mc/sec.

RESULTS

Much of the ultrasonic behavior can be related to the occurrence of a low-temperature structural transformation reported by Batterman and Barrett.[13] On cooling below about 21°K (T_m) this crystal undergoes a small continuous deformation of several parts per thousand from a cubic to a tetragonal ($c/a>1$) structure. This transformation is accompanied by the formation of platelike domains which have a thickness of several tenths of a millimeter[14] and which are slightly tilted (~1/10°) from the structure which exists in the cubic phase. It is possible to obtain samples of V_3Si (nominal composition) for which no structural transformation occurs. The differences between transforming and nontransforming samples, which are presumably of a compositional or defect nature, are brought about by variation of the crystal-growth procedure. These differences lead to a variation in T_m among transforming crystals over a range of several degrees about 20°K. They appear not to influence T_c, however, which falls in the range 16.5 to 17°K for all samples. Except where stated otherwise, all results refer to a transforming crystal.

Ultrasonic Attenuation

The temperature dependence of the attenuation of 310-Mc/sec longitudinal waves propagating along [110] is shown in Fig. 1. At the higher temperatures the attenuation is small and slowly increases with decreasing temperature. The losses here are predominantly electronic (free-carrier Joule heating) which increase on cooling because of the increase in electrical conductivity. The dashed curve in Fig. 1 shows the expected behavior for a typical superconductor calculated from standard expressions[15] in the normal and superconducting states. Below 21°K the observed attenuation increases very

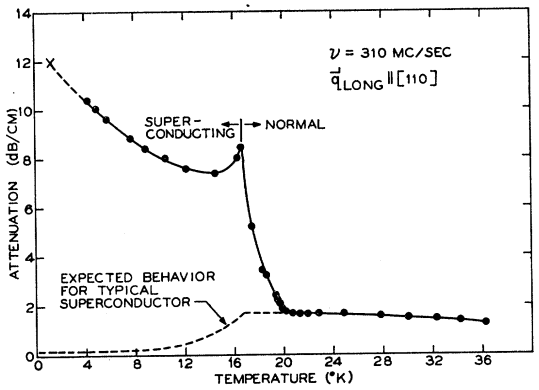

FIG. 1. Temperature dependence of the attenuation of 310 Mc/sec longitudinal waves propagating along [110].

rapidly on cooling, but the increase is sharply arrested with the onset of superconductivity. Below T_c a minimum occurs (partly the result of the decrease in the electronic attenuation) followed by a comparatively slow increase. The general features of the attenuation behavior shown in Fig. 1 are also obtained with the other modes and at other frequencies with the exception that the slow increase in attenuation below T_c is smaller or absent.

The rapid but continuous increase in attenuation below 21°K results from the continuous structural transformation which occurs in that temperature range. A sample for which no structural transformation occurred (determined from x-ray observations) showed no increase in attenuation below 21°K. Although the structural transformation with the accompanying domain formation can provide several possible sources for ultrasonic attenuation, the specific loss mechanism could not be deduced with certainty. For two such possibilities—sound scattering and electron damping of domain-wall motion—no experimental confirmation was obtained. The former must be considered because the sound wavelength at the frequencies used was comparable with the domain thickness. For sound scattering the frequency dependence of the attenuation should vary from ω^4 to ω^0 as the wavelength varies from being long to short compared to the scattering size.[16] The observed frequency dependence of the anomalous low-temperature attenuation shown in Fig. 2 varies from ω^2 (at 30 Mc/sec) to ω (at 300 Mc/sec). This is the general behavior found for many ultrasonic loss mechanisms, but it is a somewhat smaller range in the power-law dependence than expected for scattering losses. These arguments, however, are complicated by the necessary (and possibly invalid) assumption of a single-loss mechanism over the frequency range studied. Since the crystallographic misorientations which occur in the domain structure are quite small (~1/10°), it seems unlikely that they can be the source of such large

[13] B. W. Batterman and C. S. Barrett, Phys. Rev. Letters **13**, 390 (1964); Phys. Rev. **149**, 296 (1966).

[14] M. J. Goringe and U. Valdré [Phys. Rev. Letters **14**, 823 (1965)] have found a 250 Å substructure in the transformed state.

[15] W. P. Mason, *Physical Acoustics and the Properties of Solids* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1958), pp. 326–330.

[16] Reference 15, pp. 206–209.

scattering losses. Approximate numerical estimates of the domain scattering losses, obtained from standard expressions,[16] are in support of this.

Electron damping of the domain-wall motion (impressed by the sound wave) could lead to large differences in losses between the normal and superconducting states. However, the attenuation arising from the structural transformation just above T_c is neither eliminated nor appreciably reduced in the superconducting state. There were, furthermore, no observable amplitude-dependent effects in the attenuation (similar to that found for dislocation damping in superconductors[17]) with a 20-dB variation in the input power level both above and below T_c. The attenuation which results from the structural transformation may be due to a conversion of tetragonal phase produced by the sound wave (an acoustic analog of critical opalescence).

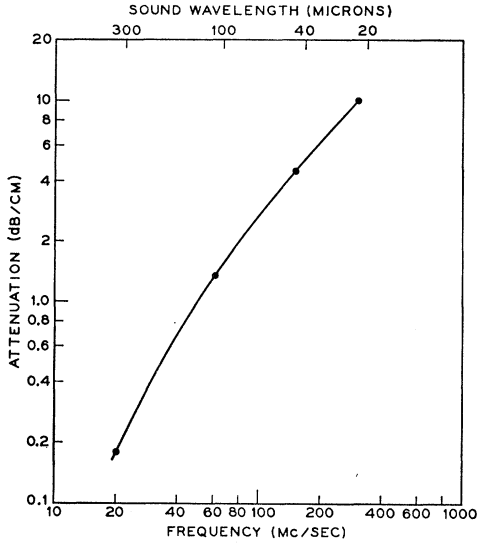

FIG. 2. Frequency dependence of the [110] longitudinal-wave attenuation resulting only from the structural transformation at 4.2°K.

Since the electronic attenuation at low temperatures is small, the arrest of the increasing attenuation at T_c suggests that the structural transformation is arrested with the onset of superconductivity. (Some additional support of this statement comes from the sound-velocity data discussed below.) This conclusion was later confirmed by Batterman and Barrett[13] who found that on cooling through T_c the growing deformation of the transformed lattice is arrested.

For [110] shear waves with [1$\bar{1}$0] polarization the attenuation increases rapidly below 100°K. The temperature dependence of the attenuation at 60 Mc/sec is shown in Fig. 3. The heavy damping which occurs

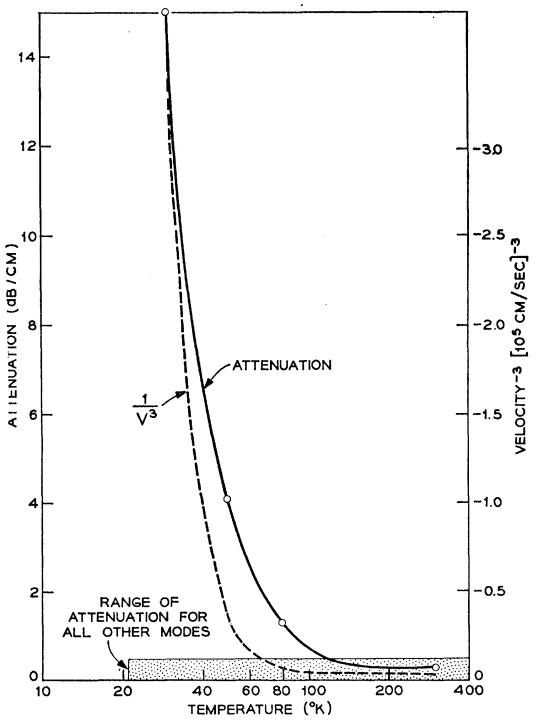

FIG. 3. Temperature dependence of attenuation of 60 Mc/sec [110] shear waves with [1$\bar{1}$0] polarization.

for the shear wave arises from a large reduction in sound velocity of that mode which occurs on cooling (see next section). For losses of a simple viscous nature, the attenuation per unit length will be proportional to $\omega^2\eta/v^3$, where ω, η, and v are the frequency, viscosity, and velocity.[18,19] The loss mechanism, therefore, is no

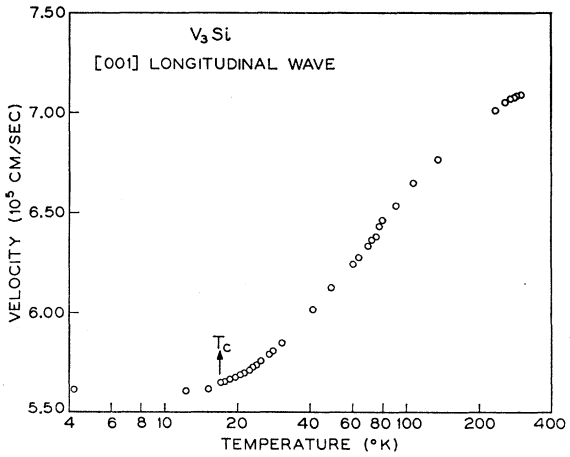

FIG. 4. Temperature dependence of the velocity of [001] longitudinal waves.

[17] R. E. Love, R. W. Shaw, and W. A. Fate, Phys. Rev. **138**, A1453 (1965); B. R. Tittmann and H. E. Bömmell, Phys. Rev. Letters **14**, 296 (1965).

[18] Reference 15, pp. 28–30.

[19] B. D. Josephson (private communication) has calculated the attenuation anisotropy for a cubic crystal with this model. His findings, which are in qualitative agreement with the experimental results, cannot be applied quantitatively because the observed frequency dependence of the attenuation was not quadratic.

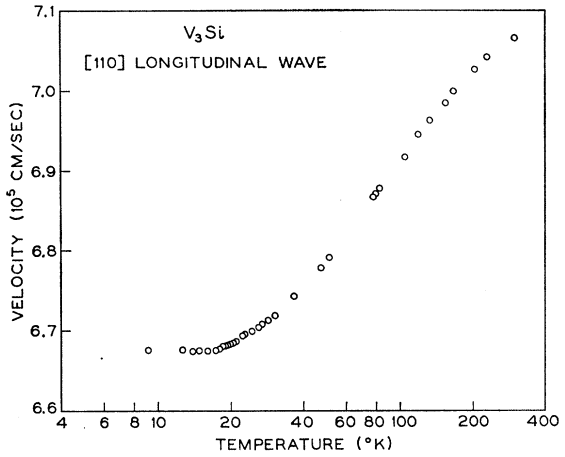

FIG. 5. Temperature dependence of the velocity of [110] longitudinal waves.

doubt an ordinary one which gives a large attenuation because of the elastic softening. The temperature dependence of $1/v^3$ is approximately like that of the attenuation (see Fig. 3). However, since the observed frequency dependence of the attenuation is more nearly linear than quadratic and since η is temperature-dependent, some discrepancy with the simple model is not surprising. Below 25°K the attenuation of the soft shear wave becomes so large that no echoes can be detected even at 20 Mc/sec.

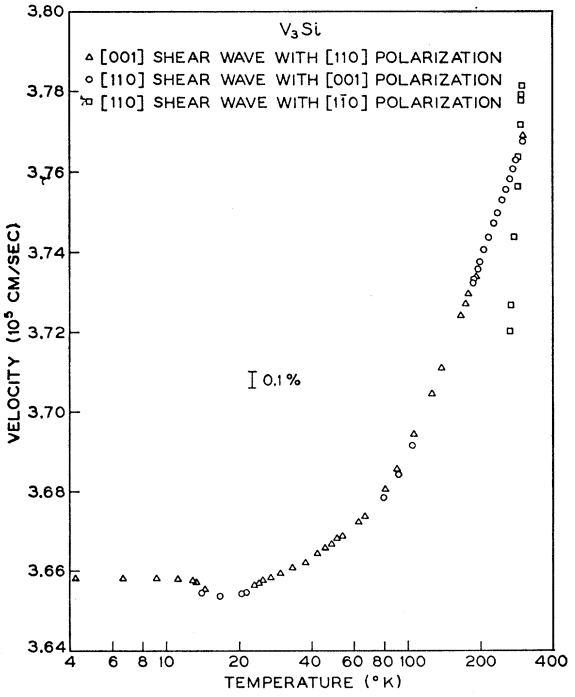

FIG. 6. Temperature dependence of the velocity of shear waves propagating along [001] and [110].

Sound Velocity

In Figs. 4, 5, and 6 the anomalous temperature dependence of the sound velocities in V_3Si is displayed. At room temperature the elastic moduli calculated from the velocity data and expressions in Table I have the following values:

$$C_{11}=2.870\times10^{12}\ \text{dyn/cm}^2,$$
$$C_{12}=1.202\times10^{12}\ \text{dyn/cm}^2,$$
$$C_{44}=0.8096\times10^{12}\ \text{dyn/cm}^2.$$

The temperature dependences of C_{11} and C_{44}, given in Fig. 7, show reductions of 36% and 4%, respectively,

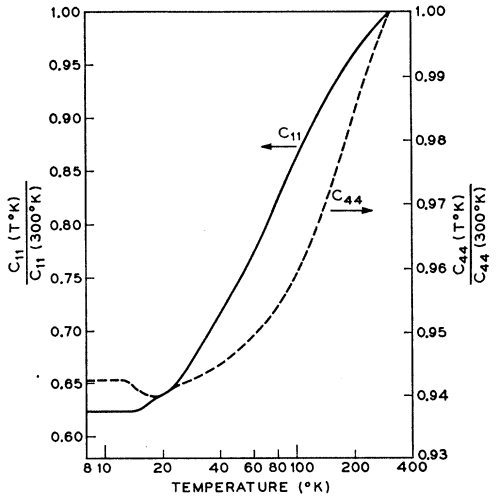

FIG. 7. Temperature dependence of the elastic moduli C_{11} and C_{44}.

between room temperature and 4.2°K. (For most metals an increase of 2% to 10% is observed.) An extraordinary degree of softening occurs for [110] shear waves with [1$\bar{1}$0] polarization. Figure 8 shows the temperature dependence of the modulus for this wave in the dimensionless form $(C_{11}-C_{12})/2C_{44}$.[20] (C_{44} is relatively independent of temperature.) Between 80 and 25°K the decrease in modulus occurs at a rate which would lead to the vanishing of the shear-restoring force at approximately 20°K. The growing shear instability triggers the structural transformation to the tetragonal phase at 21°K. The mode which exhibits the large softening represents a form of deformation consistent with that needed to give rise to the tetragonal form[13] and the domain structure which occur in the transformed state. The increased stability of the transformed state reduces the rate at which the shear modulus falls. In the superconducting state a further drop in the shear stiffness

[20] $(C_{11}-C_{12})/2C_{44}$ is the reciprocal of the elastic anisotropy factor. (See Ref. 15, p. 357.) The value of unity for this factor near room temperature indicates glasslike isotropy.

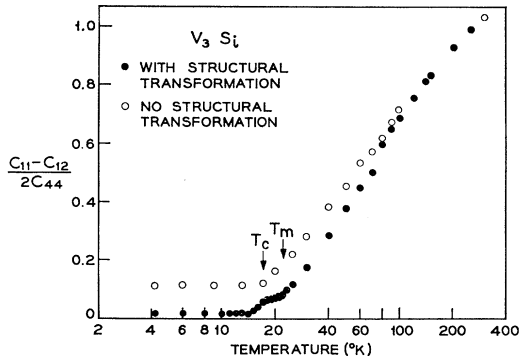

FIG. 8. Temperature dependence of $(C_{11}-C_{12})/2C_{44}$.

occurs leading to some small positive stiffness value which differs from zero only by the magnitude of the experimental error.

In the superconducting state the elastic softening is arrested, although for some modes the transition to lattice stability occurs over several degrees below T_c. This stability is relevant to the arrest of the structural transformation below T_c. The variation of the velocity (which, unlike the attenuation, is not simply related to the amount of transformation) several degrees below T_c probably reflects the temperature variation of a superconducting process in the transformed crystal.

Below 21°K the existence of a tetragonal structure leads to some uncertainty in the interpretation of the elastic moduli on the assumption of cubic symmetry. Since the deviation from the cubic structure is quite small, it is not likely that large errors result from this simplification. This was confirmed by propagation of shear waves along [001] and [110] with [110] and [001] polarizations, respectively. The velocities of these two waves are equal in a cubic crystal, but this is not generally true for the lower symmetries. The difference in the velocities (see Fig. 6) was found to be less than one part in 10^3 from 300 to 4.2°K and showed no irregularity at either T_m or T_c.

Nontransforming V_3Si

Figure 8 shows the stiffness parameter $(C_{11}-C_{12})/2C_{44}$ for a sample of V_3Si for which no structural transformation occurs. Although at higher temperatures the elastic behavior is similar to a transforming sample, the soft-shear-wave modulus for the nontransforming sample is considerably larger at low temperatures. (C_{44} differs by only 0.5% between the two samples.) For the transforming sample $(C_{11}-C_{12})/2C_{44}=0.08$ at T_m.[21] Extrapolating the elastic behavior of the nontransforming sample shows that values of the stiffness parameter between 0 and 0.08, which would probably give rise to the structural transformation, occur below 14°K. However, the onset of superconductivity at 17°K stabilizes the crystal at a higher value of the shear stiffness parameter. Thus, samples which do not exhibit the structural transformation are those for which the transformation probably would occur below T_c. For the (stiffer) nontransforming samples the variation in the soft shear modulus below T_c is much smaller than that found for the transforming sample.

Ultrasonic Dispersion

A search was made for the frequency dependence of the sound velocities. Velocities for [001] and [110] longitudinal waves as well as the [001] shear waves were measured between 20 and 60 Mc/sec at 4.2, 20.4, and 77°K. Measurements at 120 Mc/sec were also made at 20.4°K for the [001] longitudinal wave. Although this range of frequencies is a small part of the available phonon spectrum, the high precision (several parts in 10^4) allows the detection of small dispersion. Furthermore, the sound wavelength at these frequencies is comparable to the domain size in the transformed state. Any dispersion effects resulting from (or contributing to) the domain formation should be large at these frequencies. The measurements described above showed no dispersion greater than one part in 5000.

DISCUSSION

The unusual elastic behavior which occurs for V_3Si probably characterizes all of the high-temperature β-tungsten superconductors (see previous paper). Quantitative estimates of the effects of the softening are difficult to make, but some of the immediate consequences, based on simple physical models, are relevant to the anomalous behavior of other properties of these materials.

Thermal Vibrational Amplitudes

By equating the elastic vibrational energy of the unit cell to the thermal energy one can express the mean-square thermal vibrational amplitude $\langle\epsilon^2\rangle_{av}$ in terms of the elastic behavior. The relation is contained in standard expressions for the Debye-Waller factor.[22]

$$\langle\epsilon^2\rangle_{av}=\frac{3kT\Phi(\Theta/T)}{(6\pi^2)^{2/3}Vv_M^2\rho}, \tag{1}$$

where V is the unit cell volume, ρ the density, Θ the Debye temperature (see next section),

$$\Phi(x)=\frac{1}{x}\int_0^x\frac{\epsilon d\epsilon}{e^\epsilon-1},$$

[21] The same value of the elastic anisotropy at T_m has been found in Nb_3Sn. K. R. Keller and J. J. Hanak, Phys. Letters **21**, 263 (1966) and private communication.

[22] R. W. James, *The Optical Principles of the Diffraction of X Rays* (Cornell University Press, Ithaca, New York, 1965), p. 220.

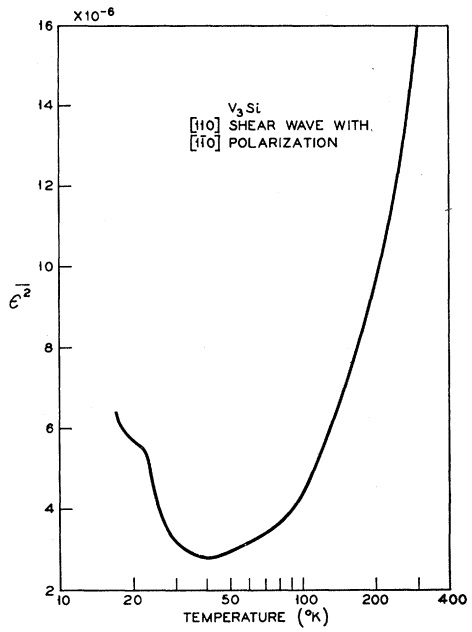

FIG. 9. Temperature dependence of mean-square thermal strain for [110] shear deformations with [1$\bar{1}$0] polarization.

which has been evaluated by Debye,[23] and v_M is an average sound velocity which is approximately equal to the Debye average velocity v_D, where

$$v_D=\frac{kV^{1/3}\Theta}{\hbar(6\pi^2N)^{1/3}}. \tag{2}$$

N is the number of atoms per unit cell. To obtain a rough estimate of the thermal vibrational amplitudes of the [110] soft shear waves we assume $\rho v_M^2=\rho v_D^2=(C_{11}-C_{12})/2$. The temperature dependence of the mean-square strain for the soft mode is shown in Fig. 9. In the vicinity of room temperature $\langle\epsilon^2\rangle_{av}$ is approximately proportional to T. (For a Debye solid $\langle\epsilon^2\rangle_{av}\propto T$ for $T\gg\Theta$.) The rapid decrease of the modulus $(C_{11}-C_{12})/2$ below room temperature causes the vibrational amplitudes to reach a minimum value around 40°K. In the vicinity of T_m the amplitude of the thermal strains is comparable to those distortions which occur spontaneously with the structural transformation. All experimental data presently available indicate that the structural transformation is of second order.[24] (No discontinuities in the unit-cell size and no latent heat have been detected at T_m.) Since the structural transformation probably takes place by means of the soft-shear deformation, the behavior represented in Fig. 9 indicates that in the vicinity of T_m the new lowest energy state (tetragonal) may be reached from the cubic state by ordinary thermal motion.

Omitted from Fig. 9 is the contribution from zero-point motion. For a Debye solid this is temperature-independent and comparable in amplitude with the thermal motion at $T\approx\frac{1}{2}\Theta$.[22] In V_3Si the calculated amplitude for the zero-point motion increases as the temperature is lowered, reaching, at T_m, a magnitude about four times larger than that found for the thermal motion.

Lattice Specific Heat and Debye Temperature

Equation (1) is based on a Debye model which assumes no anharmonic effects and no dispersion for the phonons up to the Debye frequency. By performing a prescribed average of the sound velocities the Debye model, with these assumptions, can be used to calculate the lattice specific heat. We have used the tables provided by de Launay[25] to calculate Θ from the elastic moduli. Figure 10 shows the variation of Θ with T obtained in this manner. The lattice softening causes Θ to fall from 530°K at room temperature to 300°K at T_m. In the range of 21–40°K the lattice specific heat calculated with these Θ's exceeds the total (lattice and electronic) observed specific heat reported by Kunzler, Maita, Levinstein, and Ryder.[26] At 21°K the discrepancy is about a factor of 2 in magnitude. Below 21°K the comparison is complicated by the specific-heat anomalies due to the structural and superconducting transitions. At comparable values of Θ/T most solids

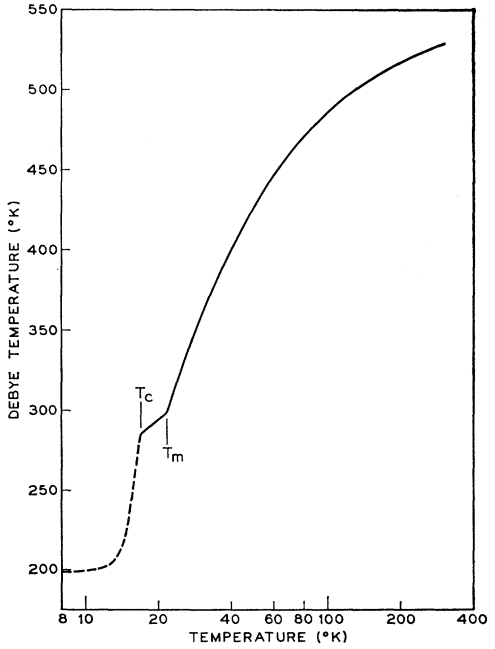

FIG. 10. Temperature dependence of the Debye temperature calculated from the elastic moduli.

[23] P. Debye, Ann. Physik **43**, 49 (1914).
[24] For further discussion see P. W. Anderson and E. I. Blount, Phys. Rev. Letters **14**, 217 (1965).
[25] J. de Launay, Solid State Phys. **2**, 285 (1956).
[26] J. E. Kunzler, J. P. Maita, H. J. Levinstein, and E. J. Ryder, Phys. Rev. **143**, 390 (1966).

exhibit more lattice specific heat than is calculated from the Debye model, because the high-frequency phonons have smaller velocities (normal dispersion) than the long-wavelength sound waves on which the Debye model is based. For V_3Si the deficiency in the observed specific heat would imply that the high-frequency phonons are stiffer than the low-frequency phonons measured in our experiments. This conclusion rests on the assumption that at $\Theta/T\sim15$ anharmonic effects will not reduce the specific heat to one-half of its Debye model value. But there is, furthermore, the expectation of a large contribution to the specific heat from the temperature-dependent zero-point motion if the softening in the phonon structure occurs out to Debye frequencies. Thus, the general magnitude of the discrepancy in the specific heat suggests that the very large softening may be mainly confined to the longer wavelength phonons.

Electrical Resistivity

The elastic softening of the phonon structure may appear in those transport properties determined by the phonon velocities (vibrational amplitudes). The thermal-phonon contribution to the electrical resistivity is determined (in part) by the atomic vibrational amplitudes. For comparison with the electrical resistivity the mean-square vibrational amplitude for all modes has been calculated using Eqs. (1) and (2) and the Debye temperatures given in Fig. 10. In this average the large selective-mode softening is appreciably diluted; however, the thermal vibrational amplitudes and, presumably, the electrical resistivity do decrease on cooling at a rate which is slower than that expected for a normal solid.

The temperature dependence of $\langle\epsilon^2\rangle_{av}$ in the vicinity of T_m is shown in Fig. 11. (Zero-point motion, which does not scatter electrons, is again excluded.) The

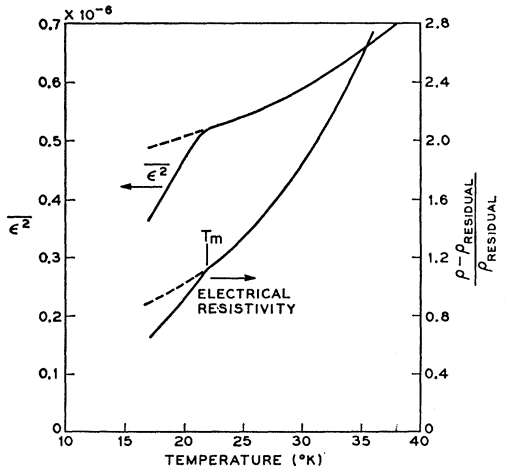

FIG. 11. Temperature dependences of the mean-square thermal strain (calculated) for all modes and the thermal part of the observed electrical resistivity.

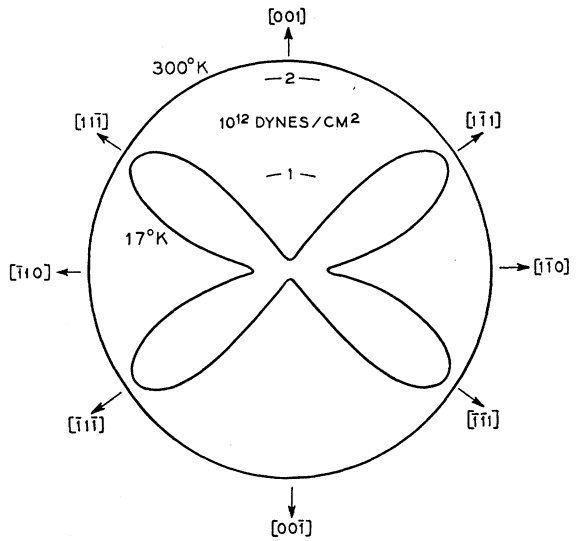

FIG. 12. Anisotropy of Young's modulus in the (110) plane at 17 and 300°K.

arrest of the lattice softening which accompanies the structural transformation causes the vibrational amplitudes to decrease more rapidly. A similar behavior in the electrical resistivity, shown in Fig. 11, has been observed by Kunzler *et al.*[27] It should be noted that in this case the anomaly probably results from high-frequency phonons since long-wavelength transverse phonons do not scatter electrons.[28]

Bulk Modulus

Although the shear modulus $(C_{11}-C_{12})/2$ decreases on cooling to almost zero magnitude, the bulk modulus, $(C_{11}+2C_{12})/3$, is independent of temperature to within 0.5% between 4.2 and 300°K and shows no irregularity at either T_c or T_m. The magnitude of the bulk modulus, 1.76×10^{12} dyn/cm^2, is similar to that of iron. Since both the magnitude and temperature dependence of the bulk modulus are normal, the simple thermodynamic expressions which contain these quantities cannot be used to extend the consequences of the softening to other variables. The instability lies basically in the elastic anisotropy.

Young's Modulus and the Stress Dependence of T_c

Weger, Silbernagel, and Greiner[6] have found for V_3Si that a stress of 1000 atm applied hydrostatically or uniaxially along [111] produced no detectable change in T_c while an equal stress along [001] lowered T_c by 0.5°K. These results can be understood with a knowledge of the Young's-modulus behavior. The anisotropy of the Young's modulus in a (110) plane calculated

[27] J. E. Kunzler, J. P. Maita, E. J. Ryder, H. J. Levinstein, and F. S. L. Hsu, Bull. Am. Phys. Soc. **10**, 319 (1965).
[28] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, England, 1958), p. 256.

from the elastic moduli is shown in Fig. 12. At 300°K the modulus exhibits almost complete isotropy (see footnote 20). At 17°K a very small modulus exists along ⟨001⟩. A secondary minimum occurs along ⟨110⟩, but along ⟨111⟩ the modulus is only slightly less than its room-temperature value. The small modulus along ⟨001⟩ occurs because the applied stress can be resolved into the ⟨110⟩ soft-shear stresses. This does not occur along ⟨111⟩. It is the large tetragonal distortions (with no volume change) due to shear deformations from ⟨001⟩ stress which cause the lowering of T_c. For stresses in other directions the distortions and changes in T_c are much smaller.

The Stress Dependence of the Structural Transformation

In the structural transformation a cubic to tetragonal conversion occurs with no change in volume larger than one part in 10^4 and with a maximum distortion of $c/a \approx 1.0024$. (This figure varies somewhat among different samples.) It can be shown from the elastic moduli at 21°K that a uniaxial tension along [001] of approximately 300 atm will give rise to a tetragonal distortion which is structurally identical to the spontaneous distortion described above. Experimentally it is roughly at these [001] stress values that the transformation anomalies (multiple-domain structure and specific-heat anomaly) disappear.[26,29]

The Source of the Lattice Instability

Clogston and Jaccarino[2] have postulated that the Fermi level in V_3Si lies at or near a narrow peak in the density of states. Such an occurrence, while providing a high value for T_c, may result in a lattice instability. Since the peak in the density of states will generally be strain sensitive, the structure may become unstable under those deformations which act to lower the total free energy. In view of the elastic behavior, it is clear that the critical deformation for such a peak would be the [110] shear with [1$\bar{1}$0] polarization.

The β-tungsten (A-15) crystal structure is shown in Fig. 13. The silicon atoms occur on the bcc sites while the vanadium atoms occur pairwise on each of the cube faces. The two vanadium atoms on a given face are separated by half the unit-cell length. Labbé and Friedel[30] have recently obtained, theoretically, the major features of the structural transformation. Their calculations apply a tight-binding approximation to the linear chains of vanadium atoms which are parallel to ⟨001⟩. They show that under a tetragonal deformation the relative separations of the vanadium atoms along the three orthogonal chains lead to large changes in the density of states at the Fermi level. In the vicinity of 10–20°K a tetragonal structure with distortions of the order of several parts per thousand is found to have a lower energy. The modulus $(C_{11}-C_{12})/2$ is also shown to decrease as the temperature is lowered to T_m. These results are in good agreement with the experimental findings so far reported. The calculations also show the existence of appreciable fine structure of width 10^{-3} eV in the density of states.

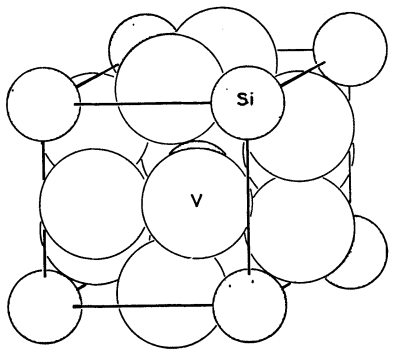

FIG. 13. The β-tungsten (A-15) crystal structure of V_3Si.

CONCLUSIONS

If the cause of the lattice instability lies in the existence of unusual fine structure in the density of states $n(\epsilon)$, the temperature at which a resulting structural transformation occurs may be a rough measure of the width of such fine structure. Thus, the observed $T_m \approx 20$°K would indicate that the widths in $n(\epsilon)$ of $\sim 10^{-3}$ eV calculated by Labbé and Friedel are present in V_3Si.[31] The variation, among different samples, of the low-temperature shear modulus as well as T_m would indicate the critical nature of this structure. With a structure in $n(\epsilon)$ of width $\sim kT_c$, it is not clear to what extent the variations in T_m brought about by sample differences should be accompanied by variations in T_c, since T_m and T_c would probably depend differently on the details of such structure. Furthermore, the width of the fine structure is considerably less than the width of the superconducting gap which occurs at low temperature. One may expect, therefore, that the onset of superconductivity will affect any property determined by the critical structure in $n(\epsilon)$. The lattice stability which attends the superconducting state may result from such occurrences, but it is surprising that the physical consequences of the critical $n(\epsilon)$ structure (c/a distortions and low shear modulus) remain in the superconducting state well below T_c and, in some cases, without exhibiting any change below T_c.

[29] J. R. Patel and B. W. Batterman, J. Appl. Phys. **37**, 3447 (1966).

[30] J. Labbé and J. Friedel, J. Phys. Radium **27**, 153 (1966); **27**, 303 (1966). A. C. Gossard [Phys. Rev. **149**, 246 (1966)] has found qualitative agreement between the NMR behavior of transforming V_3Si and the predictions of the Labbé-Friedel model.

[31] The difficulty of confirming this result experimentally (e.g., the Seebeck coefficient) is that at temperatures where the thermal broadening is small compared to the fine structure the material is superconducting with a critical field ~200 kG.

The importance of the lattice softening to superconductivity (via the electron-phonon interaction) will depend on how much of the phonon spectrum experiences the softening which we have detected in the megacycle range. A consideration of transport and equilibrium properties has indicated that for the high-frequency phonons some softening may occur, but it is probably of smaller magnitude than that found for the ultrasonic waves. However, an appreciable influence on superconductivity of the unusual phonon behavior may not require that the softening extend out to Debye frequencies. Morin and Maita[5] have found from specific-heat data that for the high-T_c superconductors the important phonon frequencies involved in the superconductivity are at least an order of magnitude smaller than the Debye frequency.

Finally, there is little evidence from existing data that the structural transformation has led to an appreciable reduction in the transition temperature for superconductivity. For materials which do transform, the cubic state at 21°K clearly cannot possess any properties sufficiently superior for superconductivity to raise T_c by more than 4°K. Stress experiments[6,26] which have produced tetragonal strains comparable to what occur in the structural transformation do not alter T_c by more than 0.5°K. Since the difference in T_c between transforming and nontransforming samples is generally less than 0.5°K and apparently not consistent in sign, the effect of the structural transformation on T_c is small. However, the proposed fine structure in $n(\epsilon)$ is of the order $\sim kT_c$, and it is not evident what value (or average) of $n(\epsilon)$ determines T_c. A degradation of the superconducting behavior could be present if such fine structure should limit T_c because of the width of the peak.

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Virial Theorem for the Homogeneous Electron Gas

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A proof is presented of the virial theorem for the interacting electron gas in a uniform positive background with the boundary conditions used in actual calculations of the total energy.

INTRODUCTION

THE virial theorem for an interacting electron gas in a uniform background of positive charge, a simple model useful in the theory of solids, was written some time ago by March[1] in the form

$$2\bar{T}+\bar{V}=-r_s d\bar{E}/dr_s. \tag{1}$$

Here $\bar{T}$, $\bar{V}$, and $\bar{E}$ are, respectively, the average kinetic, potential, and total energies per particle for the system in its ground state and r_s is the radius of a sphere containing one electron, in units of the Bohr radius $a_0=\hbar^2/me^2$, i.e., $(4\pi/3)r_s^3a_0^3=\Omega/N$, where Ω is the volume and N the number of electrons. In conjunction with $\bar{E}=\bar{T}+\bar{V}$, this relationship can give the average kinetic and potential energies separately, once $\bar{E}$ is known as a function of r_s. Explicitly we have

$$\bar{T}=-\bar{E}-r_s\frac{d}{dr_s}\bar{E}=-\frac{d}{dr_s}(r_s\bar{E}), \tag{2}$$

$$\bar{V}=2\bar{E}+r_s\frac{d}{dr_s}\bar{E}=\frac{1}{r_s}\frac{d}{dr_s}(r_s^2\bar{E}). \tag{3}$$

These relations have been quite useful.[2]

However, no proof of (1) has been reported in the literature.

A relation similar to Eq. (1) was proved long ago by Slater[3] for the electronic energies of a diatomic molecule with the nuclei fixed away from their equilibrium positions. Different proofs of the Slater relation have since been given by various authors.[4] Also for the system of interacting particles in a box, a relation analogous to (1) was used by de Boer[5] and proved later with the method of scaling by Cottrell and Paterson,[6] who paid particular

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[1] N. H. March, Phys. Rev. **110**, 604 (1958).
[2] See, e.g., W. J. Carr, Jr., R. A. Caldwell-Horsfall, and A. E. Fein, Phys. Rev. **124**, 747 (1961); W. J. Carr, Jr., and A. A. Maradudin, *ibid.* **133**, A371 (1964); L. Hedin, *ibid.* **139**, A796 (1965).
[3] J. C. Slater, J. Chem. Phys. **1**, 687 (1933).
[4] See, e.g., Per-Olov Löwdin, J. Mol. Spectry. **3**, 46 (1959).
[5] J. de Boer, Physica **15**, 843 (1949).
[6] T. L. Cottrell and S. Paterson, Phil. Mag. **42**, 391 (1951).