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Unusual Strain Dependence of T_c and Related Effects for High-Temperature (A-15-Structure) Superconductors: Elastic, Thermal, and Alloy Behavior

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The specific heats of V_3Ge and V_3Si, and the elastic behavior of V_3Ge are given. These data are used to calculate the strain dependence of T_c in the preceding paper, and to confirm some of the predictions of that calculation. From measurements of specific heat and electrical resistance, it is found that T_c for tetragonal V_3Si is up to 0.4 °K below that for the cubic state. This result, as well as the strain dependence of the specific-heat discontinuity at T_c, are in reasonable agreement with the calculated results obtained in the previous paper. Finally, the dependence of T_c on lattice parameter for V_3Si, V_3Ge, and V_3Ga, predicted in the previous paper, is compared with the results for V_3X alloys. The remarkable agreement obtained in this comparison indicates that the chemical changes on alloying are relatively unimportant in establishing the large changes in T_c.

I. INTRODUCTION

In the preceding paper[1] the strain dependence of T_c of high-temperature (A-15-structure) superconductors was obtained from thermodynamic relations using velocity of sound and specific-heat data at T_c. In this paper we give the details of these data as well as some new results closely bearing on the unusual predicted strain dependence. Some of these data have already appeared in print, but their relevance to the results of the preceding paper are such as to warrant repetition as well as reexamination.

Of all the A-15-structure superconductors lavished with experimental and theoretical attention, the most neglected but interesting component is probably V_3Ge ($T_c = 5.95$ °K). This compound forms a natural link between two high-T_c superconductors (see preceding paper) and may provide the best testing ground for theories of superconductivity in A-15 compounds. The behavior of its sound velocity shows a hint of the V_3Si type instability at high temperatures, but at low temperatures "normalcy" returned.[2,3] This data and the specific-heat results are discussed in the text.

The specific heat of cubic and tetragonal V_3Si, as well as the strain dependence of each, are also given. The change in the specific-heat discontinuity at T_c under strain is in rough but reasonable agreement with the result calculated in the preceding paper.

It has been conjectured that the conditions favorable for high-T_c superconductivity also lead to a lattice instability, and that the structural transformation which results may also lead to a lowering of T_c. In the preceding paper we calculated that this reduction in T_c for V_3Si ~0.38 °K is based on typical transformation parameters. In this paper we show evidence from electrical resistance and specific-heat data of an actual reduction of up to 0.4 °K. Although of minor importance in the case of V_3Si, the reduction in T_c, which is proportional to the square of the distortion (c/a-1), is potentially a serious limitation for T_c's of materials with unstable lattices.

Finally, the predicted dependence of T_c on lattice parameter (previous paper) is compared with analogous results obtained by alloying V_3X. The remarkable agreement obtained in this comparison indicates that the chemical changes on alloying are relatively unimportant in establishing the large changes in T_c.

II. EXPERIMENTAL

All of the experimental details have now been described in published literature. Sample preparation has been described in Refs. 2, 4, and 5. For V_3Si and V_3Ge single crystals were available. For V_3Ga only polycrystalline samples were available.

The basic method used for sound velocity measurements was the McSkimin pulse-superposition technique.[6] For the V_3Ge data near T_c a completely automatic and considerably more precise modification of this technique was used.[7] Other details of the ultrasonic measurements are given in Refs. 2 and 4.

The specific-heat measurements have been described in Ref. 8.

III. RESULTS

Velocity of Sound

In Figs. 1–3 we show the temperature dependence of the velocity of sound for three sound modes in V_3Ge.[9] These modes are (i) $\vec{q}_L \parallel [001]$; (ii) $\vec{q}_T \parallel$

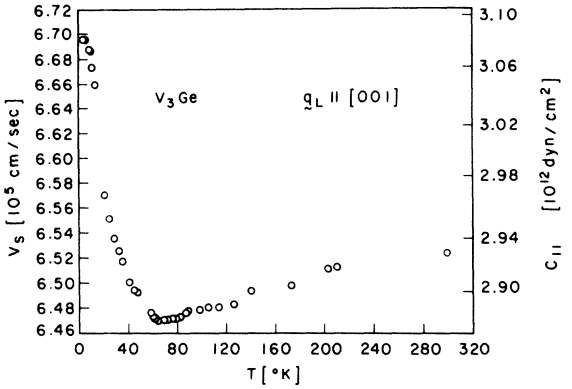

FIG. 1. Velocity of sound for $\vec{q}_L \parallel [001]$ and elastic modulus c_{11} vs temperature for V_3Ge. The right-hand scale is slightly nonlinear.

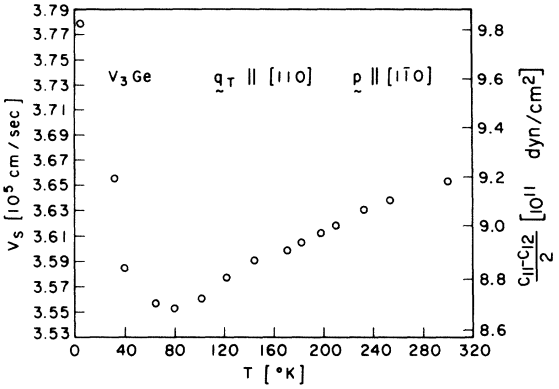

FIG. 3. Velocity of sound for $\vec{q}_T \parallel [110]$, $\vec{p} \parallel [1\bar{1}0]$, and elastic modulus $\frac{1}{2}(c_{11}-c_{12})$ vs temperature for V_3Ge. The right-hand scale is slightly nonlinear.

[001], $\vec{p} \parallel [110]$; and (iii) $\vec{q}_T \parallel [110]$, $\vec{p} \parallel [1\bar{1}0]$, where $\vec{q}$ and $\vec{p}$ are propagation and particle motion directions and L and T are longitudinal and transverse (shear). (The details of the low-temperature behavior for these modes are given in the previous paper.) These three modes permit the determination of the three independent components of the elastic modulus tensor. We have taken these to be (in the usual matrix notation) c_{11}, c_{44}, and $\frac{1}{2}(c_{11}-c_{12})$. The temperature dependences of these moduli are also given in Figs. 1–3.

Specific Heat

The specific heat of V_3Si obtained by Kunzler *et al.*[8] is reproduced in Figs. 4 and 5. These data show the specific heats of cubic (Fig. 4) and tetragonal (Fig. 5) V_3Si both at zero and nonzero stress. The stress was produced by snugly fitting a copper band around the ([001] axis) cylindrical sample at high temperature. On cooling, a cylindrical stress resulted from the larger thermal contraction of the copper relative to V_3Si causing a tetragonal distortion of the sample with $(c/a-1) > 0$. Neither the magnitude nor the homogeneity of the stress is known with any certainty. However, an estimate of the strain can be made by comparing the suppression of the (cubic-tetragonal) structural transformation under stress observed in the specific-heat studies with that found in the x-ray studies of Patel and Batterman.[10] From this work and from a rough estimate of the elastic behavior of the banded sample we obtain the very approximate result $\sigma \sim 5 \times 10^8$ dyn/cm^2(500 atm), and tetragonal strain $(c/a-1) \sim 10^{-3}$ at $T \sim 20\,^\circ$K. Further details of this work are given in Ref. 8.

The specific heat for V_3Ge at zero stress and at several values of magnetic field is shown in Fig. 6.

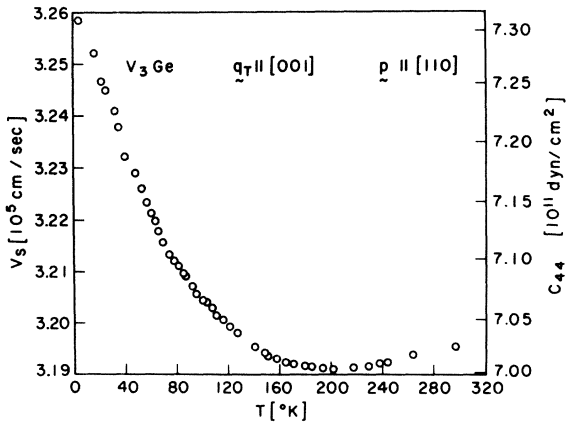

FIG. 2. Velocity of sound for $\vec{q}_T \parallel [001]$ and elastic modulus c_{44} vs temperature for V_3Ge. The right-hand scale is slightly nonlinear.

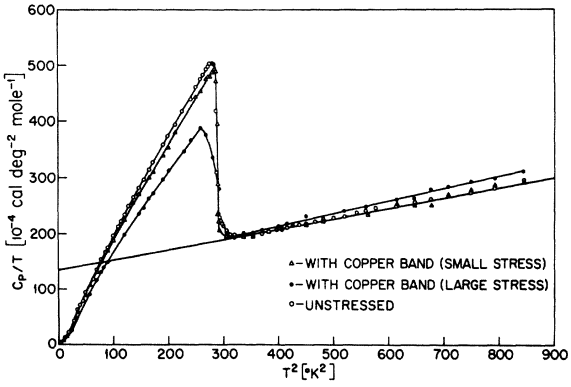

FIG. 4. Temperature dependence of the specific heat of stressed and unstressed V_3Si. Stress in the cylindrical sample was produced by shrink fitting a coaxial copper band (see text and Ref. 8 for details). This sample exhibits just the onset of a cubic-to-tetragonal transformation at several tenths of a degree above T_c.

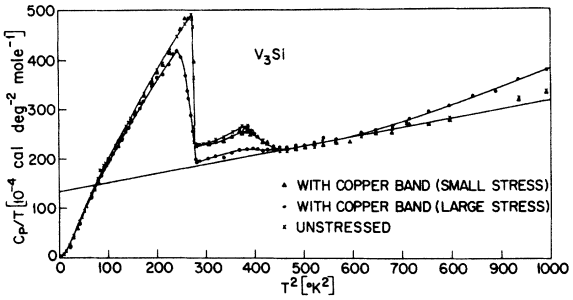

FIG. 5. Temperature dependence of the specific heat of stressed and unstressed V_3Si. Stress in the cylindrical sample was produced by shrink fitting a coaxial copper band (see text and Ref. 8 for details). This sample exhibited a cubic-to-tetragonal transformation at $T = 21$ °K.

T_c Measurements of Several V_3Si Samples

Not all samples of V_3Si exhibit the structural transformation, and, among those that do, there occurs a range in both the temperature of transformation as well as the degree of tetragonality $(c/a\text{-}1)$. From numerous studies, largely carried out by Kunzler *et al.*,[11] a simple but general correlation has emerged. The first to freeze (from a stoichiometric melt) has the lowest resistance ratio (~15), little or no second phase, and exhibits no structural transformation.[12] The subsequent regions to freeze show increasing resistance ratio, increasing amount of second phase, and, with increasing likelihood, a cubic-to-tetragonal transformation at $T_m \gtrsim T_c \approx 17$ °K. The last to freeze portion shows the largest resistance ratio (up to ~60), the greatest amount of second phase (~5%),

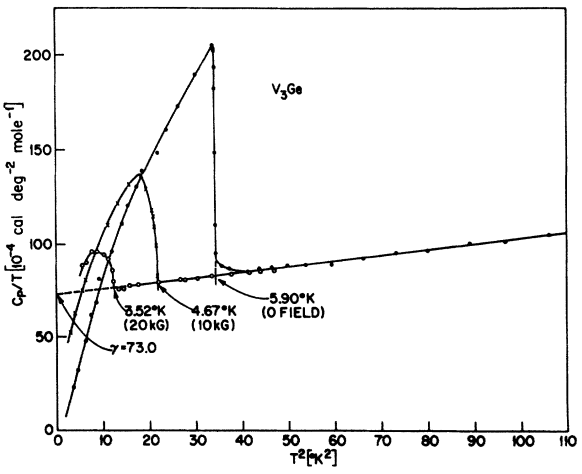

FIG. 6. Temperature dependence of the specific heat of V_3Ge.

and, with great certainty now, a cubic-to-tetragonal transformation at $T_m \sim 20$–22 °K and tetragonality $(c/a\text{-}1) \approx 1.0025$ at 4.2 °K.

The occurrence of the cubic-to-tetragonal transformation can be detected by x-ray measurements,[10] and by anomalies in the temperature dependence of the specific heat and the electrical resistance.[11] The T_c's of a number of transforming and nontransforming V_3Si samples, obtained by the latter two methods, are given in Table I. These results show that to the correlations given above another can be added – that between T_c and the occurrence of the structural transformation.

IV. DISCUSSION

The high-transition temperature for superconductivity as well as much of the anomalous behavior of A-15-structure superconductors have been explained by postulating that the Fermi level lies at or near a peak in the electronic density of states.[13,14] In the Labbé-Friedel model this peak has width ~20 °K ~ T_m ~ T_c. We shall, on occasion, refer to this model; however, a reexamination of its validity[15] cautions against a detailed application.

Elastic Behavior of V_3Ge

At room temperature the sound velocity in V_3Ge shows a behavior which is qualitatively similar to V_3Si. The "anomaly" of elastic softening on cooling occurs for both compounds (except c_{44} in V_3Ge). In both cases the strongest anomaly is found for the transverse mode $\vec{q}_T \parallel [110]$, $\vec{p} \parallel [1\bar{1}0]$. However, the magnitude of this effect in V_3Ge is far smaller than that in V_3Si. Below room temperature the softening first increases in magnitude, but in the vicinity of 150 °K (c_{11}) and 70 °K ($c_{11} - c_{12}$) the sound velocities achieve a minimum value.[16] At lower temperatures a rapid increase in stiffness occurs with cooling, and the rate of stiffening ($-dc/dT$) remains large down to T_c. The disappearance of the anomalous softening at the low temperatures

TABLE I. T_c's of transforming and nontransforming V_3Si samples.

T_c(°K)	Transformation
17.16	No
17.12	No
17.07	No
17.07	Slight
17.06	No
17.02	No
17.00	No
17.00	Slight
16.98	Yes
16.87	Yes
16.70	Yes
16.70	Yes

should not be considered the result of a "normal" background elastic behavior which has come to dominate the low-temperature behavior. Between T_c and 60 °K, $-dc/dT$ is one to two orders of magnitude larger than that found in typical solids.

Within the Labbé-Friedel (density-of-states peak) model the microscopic source of this behavior would not be difficult to find. V_3Ge, like V_3Si, has (presumably) fine structure in its density of states but the Fermi level is displaced from it by (say) ~70 °K. For $T > 70$ °K, $dc/dT > 0$ because the reduction of kT broadening on cooling "uncovers" the fine structure. (The fine structure leads to a reduction of crystal stiffness.[14]) For $T < 70$°K, the fine structure is no longer seen resulting in normal elastic behavior ($dc/dT < 0$), a low T_c, and a small electronic density of states (linear specific-heat term).

Qualitatively, at least some of these results are not at variance with the Labbé-Friedel model. But a definitive experimental test is preferable and possibly available. This test is to move the Fermi level E_F in V_3Ge or V_3Si by ~70 ° K(~ 6 mV) or 20 °K, respectively, holding all other independent parameters constant. The expected shift $|\Delta T_c/\Delta E_F|$ ~1–5 deg/mV [17] is far larger than what is obtained in typical superconductors. Electric (or polarization) charging experiments in thin films, while possibly not achieving such large Fermi level shifts, should still show effects of a very large (relative) magnitude. Further tests of the theory are suggested in Ref. 15.

The major differences in the elastic properties of V_3Si ($T_c = 17$ °K) and V_3Ge ($T_c = 5.95$°K) are in the temperature dependences of the c_{ij} and in the magnitude[18] of the shear modulus $\frac{1}{2}(c_{11} - c_{12})$. For V_3Si this shear modulus decreases on cooling to a very small value before being stabilized by the onset of superconductivity (or the structural transformation). However, the shear moduli c_{44} of V_3Si and V_3Ge are comparable and the bulk moduli $\frac{1}{3}(c_{11} + 2c_{12})$ are remarkably similar – within 1% for the samples measured. An interpretation of these differences and their relations to the superconducting transition is made elsewhere.[15]

The Debye temperature Θ_e of V_3Ge calculated from the low-temperature elastic moduli is (480 ± 5)°K. The value obtained from specific-heat measurements is $\Theta_c = 395$ °K. Although one often finds $\Theta_c < \Theta_e$,[19] the difference in this case is considerably larger than the value of several percent typical of cubic materials when $T/\Theta \sim 100$. This discrepancy may be of major importance in establishing the difference between low- and high-T_c A-15-type superconductors. We know of no reasonably certain explanation for this behavior. Anharmonic effects, which are of great consequence in these superconductors, are discussed in relation to this behavior in another paper.[15]

Specific Heat

Close examination of the V_3Si specific-heat data of Fig. 4 shows that a small but steep increase in C_p occurs at temperatures of several tenths of a degree above T_c. A similar increase occurs at temperatures between T_c and 21 °K in the data of Fig. 5 where a cubic-to-tetragonal transformation occurs. From this similarity, we propose that for the sample of Fig. 4 just the onset of the structural transformation has occurred at T_c. This contributes an appreciable (~ 15%) amount to the "jump" in C_p occurring near T_c. This contribution has been removed from the data to obtain the discontinuity in C_p due to the superconducting transition (which is used in the analysis of the preceding paper).

When this correction is made it is found that the discontinuity in (unstressed) C_p in Fig. 4 is only ~10% larger than that for the unstressed sample in Fig. 5 and only ~10–15% larger than the stressed samples in Figs. 4 and 5. The difference in specific heats between transforming and (almost) nontransforming V_3Si samples is not large, except for the anomaly due to the transformation.

The data of Figs. 4–6 show that above T_c one can approximate the temperature dependence of the specific heat in the usual way,

$$C_p/T = \gamma + \beta T^2. \tag{1}$$

The values of γ and β for V_3Ge and V_3Si are given in Table II. For V_3Si the values refer to the specific-heat behavior above the structural-transformation temperature. In the usual interpretation γ is proportional to the density of states (averaged over kT) at the Fermi level, and β to the inverse cube of the Debye temperature. The large value of γ for V_3Si is typical of most of the high-temperature (A-15-structure) superconductors. The very large densities of states calculated from these γ's are felt to be primarily responsible for the high T_c's and, indeed, constitute an important part of the experimental basis for the "density-of-states peak" models used to explain the anomalous behaviors of these superconductors. However, the relation between γ and the density of states is

TABLE II. Specific-heat results.

$C = \gamma T + \beta T^3$	V_3Si	V_3Ge
γ (10^{-4} cal deg^{-2} mole^{-1})	140	73
β (10^{-4} cal deg^{-4} mole^{-1})	0.18	0.30
N [states of one spin (eV)$^{-1}$ (vanadium atom^{-1})]	4.15	2.14
Θ_D(°K)	470	395
Θ_e(°K)	~300	480

greatly complicated[15] by the temperature dependence of the elastic behavior and by anharmonicity. It appears that, because of these factors, both the density of states and the Debye temperature obtained in the usual way [from Eq. (1)] are probably in error, and both have probably been overestimated.

For V_3Si the specific-heat discontinuity in the strained state is smaller than that in the unstrained state. For the data of Fig. 4, a small part of the jump in C_p is due to the onset of the structural transformation at temperatures just above T_c. Under stress, this contribution to C_p is largely diminished (see Fig. 5). Removing this contribution from the data and, ignoring the usually small difference between C_p and C_v, one finds for the discontinuity in C_v due to superconductivity

$$\frac{\Delta C_v(\text{unstressed}) - \Delta C_v(\text{stressed})}{\Delta C_v(\text{unstressed})} \sim 15\%. \qquad (2)$$

In the previous paper it is shown that this quantity should approximately equal $[T_c(0) - T_c(\epsilon)]/T_c(0)$, that is the fractional change in T_c produced by the same strain. From Fig. 4, the fractional shift in T_c when stressed is roughly about 5–7%. Considering that the strain in the sample is nonuniform, and that the quantity in Eq. (2) can only be obtained very approximately (because of the slight amount of transformation) this agreement is satisfactory.

T_c of Cubic and Tetragonal V_3Si

For the specific-heat samples whose data are given in Figs. 4 and 5, it is found that the transforming crystal has a T_c about 0.3 °K lower than the (almost) nontransforming one. From the data of Table I it is seen that the T_c for the tetragonal state is less than that for the cubic state by ~0–0.4 °K.

From the theory given in the preceding paper it is found that the reduction in T_c due to the transformation is proportional to the square of the tetragonality $(c/a - 1) = \delta$. A typical value of δ for a sample showing extensive transformation is $\sim 2.5 \times 10^{-3}$. This gives a calculated reduction in T_c of 0.38 °K (see previous paper). This is in reasonable agreement with the observed values for the specific-heat samples and with the data of Table I.[20]

Strain Effects on Alloying

No adequate experimental confirmation exists of the large quadratic strain dependence of T_c predicted in the previous paper. It is true that the stress dependence of T_c measured by Weger, Silbernagel, and Greiner,[21] which cannot be explained by the usual theory for cubic crystals, is in quite satisfactory accord with the proposed strain dependence (see preceding paper). Of equal importance, however, is the prediction of a comparable dependence of T_c on hydrostatic strain. Such large effects with unbroken cubic symmetry would appear unexpected from either the theoretical (density-of-states) models or the experimental behavior.[22] The confirmation of this, as well as establishing how large a strain is adequately described by the results of the preceding paper[23] require an experimental determination. Such data are not known to us. The magnitude (and uniformity) of the strains required are such as to offer certain experimental difficulties.

With a view to approximating this test, but mainly to show the relative importance of these large strain effects, we consider alloy behavior in the A-15 system. We show in Fig. 7 the predicted strain dependence for V_3Si, V_3Ge, and V_3Ga (see previous paper for discussion) and the results for some nine binary compound alloys containing at least one of these compounds. For this comparison we have chosen alloys of the form $V_3A - V_3B$, where the vanadium sublattice is not substitutionally disordered.[24,25]

There are several sources of error in this plot which must be recognized. Low-temperature lattice parameters should be used, but only the room-temperature values are generally available. All points must be moved to the left because of thermal contraction but the relative displacements may vary by ~0.01 Å (0.2%). Because of differences in sample condition, and because of experimental errors, the reported room-temperature lattice parameters may vary by ~0.1% (for V_3Ge the reported values are 4.77 and 4.78 Å). Variations in T_c are caused by differences in sample conditions, different cri-

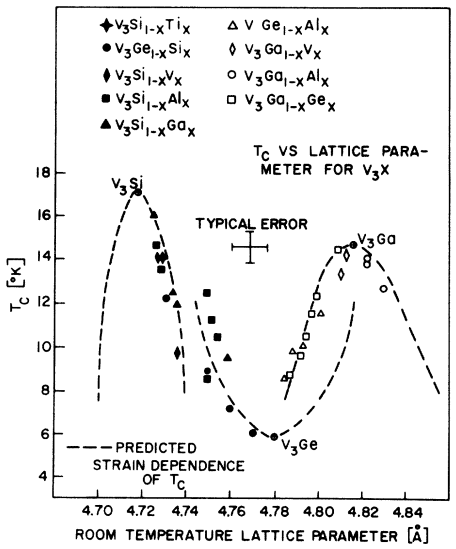

FIG. 7. T_c versus lattice parameter for $V_3A - V_3B$ alloys. The predicted strain dependence for three compounds are shown by the dashed lines.

teria for the choice of T_c with broad transitions, and experimental error. The error bars shown in the figure are a rough estimate of all of these uncertainties.

One expects the variation of T_c with alloy composition to arise from changes in lattice parameter, chemical composition, and crystalline order. The results, given in Fig. 7, show that for the nine alloy systems, T_c is grossly a single-valued function of the lattice parameter. Much of the large changes in T_c is found to agree with the strain effects predicted for the compounds V_3Si, V_3Ge, and V_3Ga. The changes in chemical composition and order (at constant strain) are relatively unimportant for superconductivity of the alloy systems indicated in the figure.

The correlation established in Fig. 7 is not an implicit restatement of valency – T_c correlations.[26] For example, the substitution of Si for Ge in V_3Ge does not change the valency, but causes T_c to increase by 11 °K in rather good agreement with the predicted strain dependences of V_3Ge and V_3Si.

Although the principal approach to understanding these high-temperature superconductors has been, heretofore, through the electronic band structure, a reexamination of the A-15-structure properties[15] suggests that the (passive) role of the lattice has been erroneously miscast. The source of this remarkable strain dependence will be discussed in another paper.[15]

ACKNOWLEDGMENTS

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[1]L. R. Testardi, preceding paper, Phys. Rev. B 3, 95 (1971).

[2]L. R. Testardi, R. R. Soden, E. S. Greiner, J. H. Wernick, and V. G. Chirba, Phys. Rev. 154, 399 (1967).

[3]M. Rosen, H. Klimker, and M. Weger, Phys. Rev. 184, 466 (1969).

[4]L. R. Testardi and T. B. Bateman, Phys. Rev. 154, 402 (1967).

[5]E. S. Greiner and H. Mason, Jr., J. Appl. Phys. 35, 3058 (1964).

[6]H. J. McSkimin, J. Acoust. Soc. Am. 33, 12 (1961).

[7]For the details of this modification see L. R. Testardi and J. H. Condon, Phys. Rev. B 1, 3928 (1970).

[8]J. E. Kunzler, J. P. Maita, H. J. Levinstein, and E. J. Ryder, Phys. Rev. 143, 390 (1966).

[9]The results for single crystal V_3Ge were published in part by one of the authors (L. R. T.) previously (see Ref. 2). Similar results have been recently obtained by others (see Ref. 3).

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

[11]J. E. Kunzler, J. P. Maita, E. J. Ryder, H. J. Levinstein, and F. S. L. Hsu, Bull. Am. Phys. Soc. 10, 319 (1965).

[12]The occurrence of the structural transformation was determined by anomalies in the specific heat (see Fig. 5), electrical resistance (see Ref. 4), and sometimes directly from x-ray studies [B. W. Batterman and C. S. Barrett, Phys. Rev. Letters 13, 390 (1964); Phys. Rev. 145, 296 (1966)].

[13]A. M. Clogston and V. Jaccarino, Phys. Rev. 121, 1357 (1961).

[14]J. Labbé and J. Friedel, J. Phys. Radium 27, 153 (1966); 27, 303 (1966). See also R. W. Cohen, G. D. Cody, and J. J. Halloran, Phys. Rev. Letters 19, 840 (1967).

[15]L. R. Testardi (unpublished).

[16]The Seebeck coefficient of V_3Ge exhibits a maximum at ~60 °K [M. P. Sarachik, G. E. Smith, and J. H. Wernick, Can. J. Phys. 41, 1542 (1963)]. The relevance of this to the velocity of sound behavior is momentarily intriguing to speculate upon, but difficult to prove.

[17]Finite differences are used because $dT_c/dE_F \approx 0$ in V_3Si at normal equilibrium but should increase to ~ (– deg)/mV for shifts of ± several mV in the Fermi level. This is not expected for V_3Ge.

[18]See previous paper (Ref. 1) for the values of c_{ij} at T_c.

[19]For reasons such as normal dispersion (which affect Θ_c at finite temperature) and impurity contributions to the specific heat (which usually lower Θ_c).

[20]The calculated value is based only on the tetragonal strain and does not consider the effect of possible atomic displacements within the unit cell. A search for some of the displacements which are possible in the transformation yielded essentially negative results. See, J. Perel, B. W. Batterman, and E. I. Blount, Phys. Rev. 166, 616 (1968).

[21]M. Weger, B. G. Silbernagel, and E. S. Greiner, Phys. Rev. Letters 13, 521 (1964).

[22]The large elastic softening for V_3Si occurs for a shear (not bulk) modulus which is associated with a cubic-to-tetragonal deformation with no volume change.

[23]Although the strong anharmonic behavior of these crystals (see Ref. 15) may suggest that the predicted strain dependence is valid only for very small strains, there are two factors which indicate otherwise. The first is that the linear as well as quadratic strain dependences have been obtained accounting, thereby, for at least some of the anharmonic behavior. The second is that it is the strain, not the stress, dependence which is obtained. Those effects of anharmonicity which greatly complicate the stress-strain behavior (at finite strain) are (at least partly) removed in a description of the strain dependence.

[24]For the alloys formed with excess vanadium this point is debatable. The data are included primarily for completeness.

[25]Data for Fig. 7 were obtained by us and by E. M. Savitskii, V. V. Baron, Yu. V. Efimov, V. R. Karasik, T. V. Vylegzhanina, and E. I. Gladyshevskii, Russ. J. Inorg. Chem. 9, 1106 (1964); T. Asada, T. Horivchi, M. Uchida, J. Appl. Phys. Japan 8, 958 (1969); H. Bruning, Phillips Res. Rep. 22, 349 (1967).

[26]B. T. Matthias, in *Progress in Low-Temperature Physics*, edited by C. J. Gorter (North-Holland, Amsterdam, 1957), Vol. 2, p. 138.