Structural Instability, Anharmonicity, and High-Temperature Superconductivity in A-15-Structure Compounds

L. R. Testardi
Bell Laboratories, Murray Hill, New Jersey 07974
(Received 28 September 1970; revised manuscript received 17 January 1972)

The strain dependence of T_c, inferred from velocity of sound data, is given for a number of A-15-structure compounds. Arguments relating the high T_c and the structural instability are presented and a correlation of the corresponding strain dependences is proposed. The unusual anharmonicity expected is confirmed by old and new experimental data. A model for the superconducting and anomalous-normal-state properties, based on the anharmonicity rather than singular bare-electron properties, is presented. Several conjectures on structural instability and high-temperature superconductivity are made.

I. INTRODUCTION

In a recent series of publications[1] the strain dependence of T_c for superconductors of the type V_3X was discussed. It was shown that many of the anomalies of the high-T_c superconductors could be quantitatively explained from the full calculated strain dependence of T_c.

In the present paper arguments relating the high T_c and the structural instability are presented and a correlation of the corresponding strain dependences is proposed. Tetragonal (shear) and volume strains are discussed separately. Some new and old data on the anharmonic behavior are presented and show that the high-T_c superconductors are among the most anharmonic solids known. The unusual anharmonicity expected is qualitatively confirmed by the experimental data.

Previous microscopic models of these materials attribute the superconductivity to singular behavior of the bare electronic density of states. An alternative model, based on extraordinary anharmonic-phonon behavior, is presented here. The model assumes that the A-15 structure is extremely weak (or unstable) for tetragonal strains $\lesssim 10^{-3}$. The stable-cubic-state properties occur at high temperatures where the thermal strains exceed this magnitude. It is proposed that the volume dependence of this structural instability determines the volume dependence of T_c and that this is mainly responsible for the large difference in T_c between V_3Si and V_3Ge. The tetragonal-strain dependence of this instability is of greater importance in understanding much of the anomalous behavior of these materials.[1]

Finally, several conjectures on structural instability and high-temperature superconductivity are made. In brief these conjectures hold that structural instabilities lead to rather than inhibit high-temperature superconductivity. It is concluded that very close to solid-state phase boundaries the conditions may exist for superconductivity at temperatures considerably higher than the usual values reported for the phases in question.

II. STRAIN DEPENDENCE OF T_c FOR SUPERCONDUCTING A-15 COMPOUNDS

It was shown in a previous work[1] that one can calculate the strain dependence of T_c if the complete behavior of the elastic moduli (sound velocities) near T_c is known. For A-15-structure superconductors other than V_3Si and V_3Ge, however, only data for polycrystalline samples are available.[2] To estimate the strain dependence of T_c in these cases the polycrystalline-sample data have been scaled relative to polycrystalline V_3Si. The accuracy of these results may be poor—perhaps no better than a factor of 2. However, the strain dependence is sufficiently large that the major features of the results are still important even if the error is as given above.

The relation between T_c and strain for the high-T_c A-15-structure superconductors calculated in the approximate way described above is[3]

$$T_c - T_c(\max) \sim -10^5 \epsilon^2 \,^\circ\mathrm{K}\,, \tag{1}$$

where for tetragonal strains $\epsilon = (c-a)/a$ and for cubic strains $\epsilon = (a-a_p)/a_p$ is the lattice parameter corresponding to the maximum T_c as a function of volume.

The result that T_c is highest for the cubic state and decreases for tetragonal deformations comes from an analysis of the shear-wave sound-velocity data of the superconducting transition.[1] It is expected to apply to all of the high-T_c A-15-structure superconductors; however, for V_3Ge ($T_c \approx 6\,^\circ$K) the opposite behavior is predicted. (No experimental test of this unusual result is available.) The predicted[1] tetragonal-strain dependence of T_c for V_3Si and V_3Ge is shown in Fig. 1. Roughly similar behavior to V_3Si is expected for the other high-T_c materials.

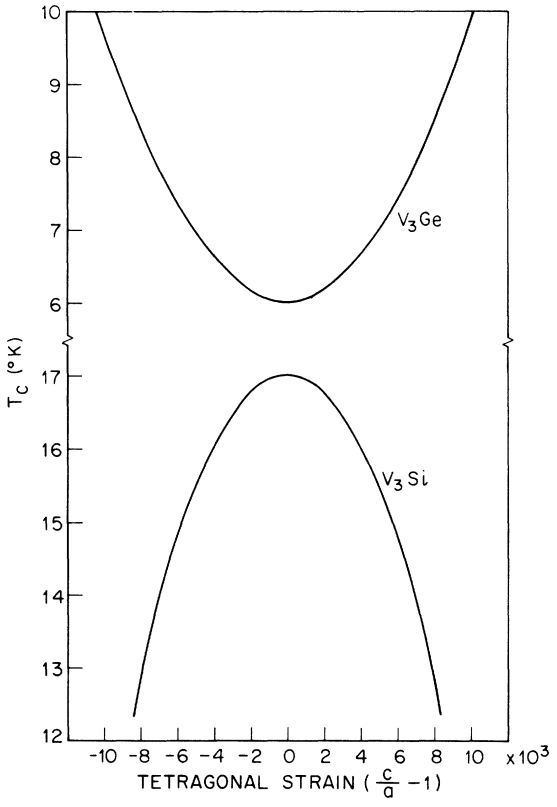

FIG. 1. Dependence of T_c on tetragonal strain at constant volume for V_3Si and V_3Ge. The curves for V_3Si should also be representative for most of the high-T_c A-15-structure compounds.

For the volume dependence of T_c it is expected that the lattice parameter in the as-grown state is close but not necessarily equal to a_p. (Therefore, both linear- and quadratic-strain dependences are expected for the as-grown state.) Figure 2 shows the dependence of T_c on lattice parameter for a number of A-15 compounds. For Nb_3Sn and Nb_3Al the calculated curves are from Eq. (1) and in all cases it is assumed that $a_p \approx a$, the zero-stress lattice parameter. However, because of the possible error arising from the polycrystalline nature of the sample the following qualification is introduced. The parabolic relationship between T_c and strain is as given by Eq. (1) with an uncertainty of perhaps a factor of 2 in the numerical coefficient. Furthermore, the point of peak T_c for each parabola may be displaced from these shown by as much as several degrees in the vertical direction and about 0.02-Å lattice parameter in either horizontal direction. For V_3Si, where single-crystal data (of greater precision) were available,[1,4] the uncertainty in the position of the peak T_c was less.

The importance of the cubic-strain dependence of T_c in these materials can be seen by a comparison of this effect with the behavior of 14 alloy systems (assumed cubic) of the form[5-8] A_3X-A_3Y (see Fig. 1). (These data have come largely from the compilation by Roberts.[9]) It is seen that the alloy results largely follow the predicted volume dependence of the compounds.

The tetragonal-strain dependences are of greater importance in discussing the structural instability. The interrelation of the tetragonal and volume dependences is best seen with the aid of Fig. 3 which gives the general behavior of T_c as a function of lattice parameter a and tetragonality $(c/a-1)$. The representative point for most high-T_c materials is within roughly[10] 2° of the peak T_c [see Eq. (1) and following] along the line of (assumed) cubic structure. Tetragonal strains (such as occur in the structural transformation) always lower T_c by an amount proportional to the square of the strain. For volume strains of a given sign, T_c may initially increase or decrease this uncertainty (i.e., whether $a >$ or $< a_p$) resulting from the fact that dT_c/da was not obtained in these studies. However, increases in T_c will tend to saturate within several degrees.

It will be argued below that an interpretation of Fig. 3 can be made in terms of structural instability. This interpretation assumes that T_c reflects the degree of shear-mode instability. The tetragonal-strain dependence results because such strains (of either algebraic sign) markedly stiffen (stabilize) the structure. The volume dependence of T_c

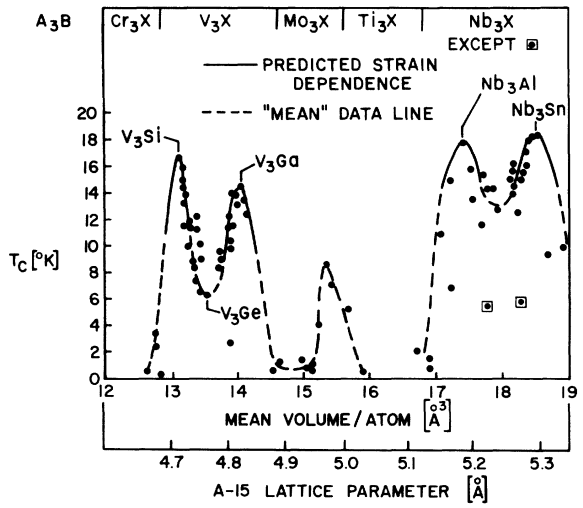

FIG. 2. Predicted dependence of T_c on lattice parameter for a number of compounds in the A-15 system. The experimental points are for compounds and alloys. In this figure the horizontal scale is linear in mean atomic volume. See text for a discussion of the error in the predicted behavior.

reflects the volume dependence of the shear instability. The peak T_c in the figure, then, represents the maximum shear-mode instability which the structure can support and marks a limiting value of the lattice parameter for which the cubic phase can exist. The basic predictions of such a model relating to the anharmonicity are discussed below.

III. DIRECT MEASUREMENTS OF STRAIN DEPENDENCE OF T_c

The tetragonal- and volume-strain dependences of T_c are considered separately. The tetragonal-strain dependence of T_c for V_3Si measured by Weger, Silbergnagel, and Greiner[11] is in agreement with the calculated results,[1] and has successfully explained a number of reported anomalies for this material including (i) the arrest of the structural phase transformation at T_c, (ii) the anisotropic-stress dependence of T_c, and (iii) the strain dependence of the specific-heat discontinuity at T_c. These results also predict, with reasonable success, the reduction in T_c which results from the structural transformation.

For the volume-strain dependence the agreement is less satisfactory. Itskevich, Il'ina, and Sukhoparov[12] have found that T_c of Nb_3Sn is reduced quadratically with hydrostatic pressure in measurements up to 10 kbar. This result is in agreement with Eq. (1) with $a_p \approx a$ and the numerical coefficient about 30% smaller. Measurements of V_3Si and Nb_3Sn up to 18 kbar by Neubauer[13] show a linear relation between T_c and pressure. Smith[14] has reported the pressure dependence of T_c in V_3Si, V_3Ge, and V_3Ga. Although Smith reports a linear pressure dependence of T_c the data show a smooth negative curvature whose magnitude is about half that given by Eq. (1) and with saturation occurring at $a_p \approx a - 0.02$ Å. This curvature cannot be reliably estimated, however, because of experimental uncertainties.[15]

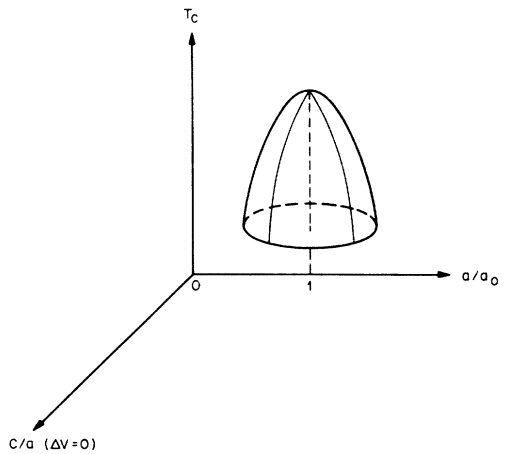

FIG. 3. Schematic dependence of T_c upon lattice parameter and tetragonal strain for high-T_c A-15 superconductors.

Although this curvature is comparable to that given by Eq. (1) for the "typical" behavior of these materials, it is considerably less (by an order of magnitude) than that predicted for the case of V_3Si. Several possible sources of this discrepancy can be noted. The first is experimental error in the sound-velocity measurement resulting, most likely, from a small amount of structural transformation in the sample which was assumed to be cubic. Fawcett (private communication) has found from thermal-expansion measurements that about 1% of the sample did transform, but this as well as other likely possibilities would not appear the source of sufficient error. A second possibility is that the predicted volume dependence occurs for the small strains of the ultrasonic experiments ($\sim 10^{-6}$) but not those of the high-pressure ($\sim 10^{-3}$) experiments. This appears unlikely since the predicted tetragonal-strain dependences are largely confirmed at strains $\sim 10^{-3}$. Finally, the effects of high pressure on the elastic behavior and structural transformation are not known and may complicate the interpretation of the pressure work. Although the source of the discrepancy is not known at this time it should be noted that the observed curvature for V_3Si, though less than predicted, will still largely maintain the correlation of T_c and lattice parameter between V_3Si, V_3Ge, and their alloys shown in Fig. 2.

Other measurements of the stress dependence of T_c for the A-15 superconductors have been published by Muller and Saur[16] and Buchel, Gey and Wittig.[16] These workers find T_c of Nb_3Sn, V_3Si, and V_3Ga to decrease with compression. Muller and Saur have also found a decrease in T_c for tension, bending, and torsion. Both linear- and quadratic-T_c-stress relationships have been observed. [For the quadratic-stress dependences the numerical coefficient is roughly half that given by Eq. (1).] These results are consistent with Eq. (1) but there is uncertainty as to which strain dependence is measured. Furthermore, the predicted behavior refers to the cubic structure and assumes no change in this structure under stress. This assumption may not be justified in some experiments.

IV. MICROSCOPIC MODELS OF HIGH-T_c SUPERCONDUCTORS

Current theoretical models[17] of the high-T_c A-15 materials are based on assumed "singular" features of the electronic band structure.[18] In these models the elastic softening is calculated or assumed to

occur for the very long-wavelength phonons only. The anomalous properties and the high T_c result only from a peak in the bare density of states.

Recent neutron-scattering experiments in V_3Si and Nb_3Sn by Shirane, Axe, and Birgeneau[19] have now shown that an appreciable phonon softening occurs at high frequencies, extending out at least halfway to the Brillouin-zone boundary. A reexamination of the role of mode softening in these materials is required.

One result of the neutron work is that the phonon spectrum differs from the Debye model used to interpret the specific heat. (The large specific-heat term linear[20] T is taken as evidence of a large density of states.) An approximate low-energy-phonon density of states of V_3Si, based on the neutron data, has been used to calculate[21] the (harmonic-mode) specific heat. It is found that the phonon softening gives rise to an additional specific heat which is approximately linear in T in the temperature range (20–30 °K) where specific-heat analyses are made. The magnitude is 10–20% of the observed linear term in V_3Si. A significant contribution to the specific heat may also result from the large low-temperature anharmonicity. Using the Grüneisen γ's and thermal-expansion coefficient α presented below, and a method similar to that of Estabrook,[22] one estimates an anharmonic correction (linear in T) for the V_3Si soft-shear mode which may also be comparable to the above correction. Although such calculations are only approximate they do indicate that the electronic density of states obtained from specific-heat data has probably been overestimated,[23] and that the anharmonicity can play a major role in the unusual behavior of these materials.

V. ANHARMONICITY

The microscopic source of the strain dependence of T_c and other anomalies, it is postulated, is an unusually large anharmonic-phonon behavior.[24] The anharmonic behavior is discussed for tetragonal and volume strains separately.

The internal energy is usually assumed to be a parabolic function of strain (as in the Debye model) and the curvature at zero strain $d^2U/d\epsilon^2 = c = \rho V_s^2$. c is an elastic modulus and ρ is the mass density. At temperature T the system is thermally excited out to an average strain $\epsilon_{\text{thermal}}^{\text{rms}}$ which can be calculated for the Debye model. A test for anharmonicity is to apply, at T, a static strain equal to $\epsilon_{\text{thermal}}^{\text{rms}}$ and observe the change in velocity of sound (or $d^2U/d\epsilon^2$). This change, of course, should be zero in the harmonic approximation.

The values of $\epsilon_{\text{thermal}}^{\text{rms}}$ for V_3Si, calculated in several ways, have been given elsewhere.[4] In the vicinity of 25 °K, $\epsilon_{\text{thermal}}^{\text{rms}} \sim 10^{-3}$. For most solids $d\ln c/d\epsilon \sim -1$ to -5. Therefore, at these temperatures the change in $d^2U/d\epsilon^2$ covered in the thermal motion is less than 1%. This small amount of anharmonicity is often adequately treated in the quasiharmonic treatment of the Debye model.

For V_3Si, and presumably for all high-T_c A-15 superconductors, the result is quite different. In Fig. 3 are sketched the results of two experiments which have measured the strain dependence of the elastic moduli in V_3Si. In both cases the strains have been those which produce a tetragonal distortion $c/a \neq 1$ with little change in volume.

In one experiment a tetragonal strain with $c/a > 1$ was produced by shrink fitting a coaxial copper band onto a cylindrical [001] sample of V_3Si. The strain, as discussed elsewhere,[1] was estimated to be roughly $(c/a - 1) \sim 10^{-3}$. The velocity of [100] longitudinal waves (giving c_{11}) in this sample did not differ by more that $\frac{1}{2}$% from that in the unstrained sample from 300 to 50 °K. Below 50 °K the velocity in the strained sample increased relative to the unstrained-sample value. At 30 °K, $c_{11}(\text{strained}) > c_{11}(\text{unstrained})$ by about 5%. Experimental difficulties prevented measurements below 30 °K but the extrapolated behavior indicated a 10% increase in c_{11} at 20 °K for strains $\sim 10^{-3}$. This difference is more than an order of magnitude larger than what occurs in typical solids. Furthermore, since at $T \approx 20$ °K c_{12} is only about 10% less than[4] c_{11} an increase of c_{11} alone by 10% would lead to a factor of 2 increase in $\frac{1}{2}(c_{11} - c_{12})$ which is the modulus for the soft-shear wave.

In a second experiment on anharmonicity Patel and Batterman[25] found that for strains $(1 - c/a) \sim 10^{-3}$ at $T \sim 25$ °K the modulus $\frac{1}{2}(c_{11} - c_{12})$ increases by roughly a factor of 2. This degree of anharmonicity can be judged by noting that at 25 °K the thermal strains are $\sim 10^{-3}$. Therefore the lattice thermal motion would lead to fractional variations in the shear-mode velocity of order roughly unity. The concept of low-frequency phonons, therefore, may be a limited one in some A-15 materials. [In the recent neutron work[19] on V_3Si the $\frac{1}{2}(c_{11} - c_{12})$ phonon peaks broadened with decreasing temperature and disappeared below about 50 °K.]

Studies of the anharmonic behavior of V_3Si and V_3Ge under hydrostatic strains[26] show an interesting behavior by comparison. All modes at room temperature stiffen under pressure by amounts typical for stable solids. On cooling, the pressure dependence of $\frac{1}{2}(c_{11} - c_{12})$ changes sign and the results extrapolated to 20 °K (80 °K was the lowest measurement temperature) give[27] $\gamma \approx -\frac{1}{2}(d\ln c_s/d\ln V) \sim -5$ to -10 and -1 to -2 for V_3Si and V_3Ge, respectively. γ is the Grüneisen constant, $c_s = \frac{1}{2} \times (c_{11} - c_{12})$, and V is the volume. This can be compared to an average $\gamma = -\frac{1}{2}(\Delta c_s/c_s \Delta\epsilon) \sim +500$ for tetragonal (shear) strains of $\sim 10^{-3}$. Thus, unlike uniaxial stress, hydrostatic pressure will increase

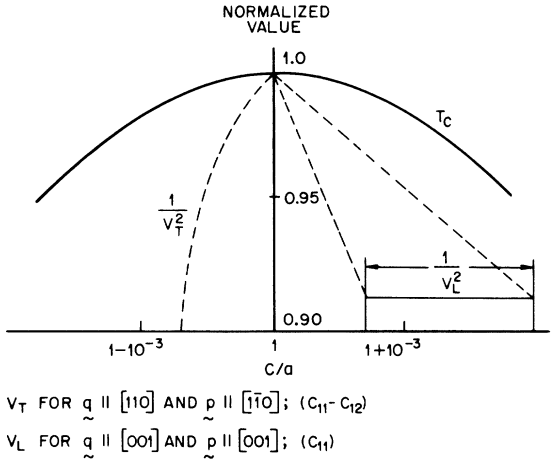

FIG. 4. Dependence of observed $1/V_T^2$ and calculated T_c as a function of tetragonal strain (with approximately no volume change). V_T is the soft shear-wave velocity.

the structural instability and, therefore, T_c.

The major relevance of this anharmonic behavior to superconductivity is that it probably establishes the microscopic source of the strain dependence of T_c. The basic correlation appears in Figs. 4 and 5. In Fig. 4 is shown the dependence upon tetragonal strain of the calculated T_c and the reciprocal elastic moduli for which the strain dependence is known. Figure 5 shows T_c and the shear modulus versus lattice parameter. The curvature in the T_c results for V_3Si is estimated from Smith's[14] data.

In the microscopic theory of strong-coupled superconductivity[28] T_c increases with increasing electron-phonon interaction parameter λ which is proportional to $1/V_h^2$, the inverse square of some average phonon velocity or frequency. For the high-T_c superconductors,[28]

$$\frac{d\ln T_c}{d\ln V_h^{-2}} \sim 1 \quad \text{and} \quad \frac{d\ln T_c}{d\epsilon} \sim 2\gamma_h\,, \tag{2}$$

where γ_h is the Gruneisen γ for the average high-frequency modes important for superconductivity. Figure 4 shows that the shift in V_s^{-2} with strain for several of the low-frequency modes has the proper sign and is larger in magnitude than that necessary to account for the tetragonal strain dependence of T_c. Figure 5 shows that the anomalous volume dependence of the soft-shear mode[29] correlates at least in sign with the unusual positive pressure dependence of T_c in V_3Si and V_3Ge.

This correlation is important in that the volume dependence of Tc and the soft-phonon velocity V_s are both anomolous in sign. It should also be noted that the correlation is present both for V_3Si which has a high T_c (17 °K) and a very pronounced lattice softening on cooling, and for V_3Ge which has a moderate T_c (6 °K) and essentially no lattice softening.

For both tetragonal and volume strains the low-frequency anharmonicity overestimates the strain dependence of T_c using Eq. (2). For hydrostatic pressure, Smith[14] finds $d\ln T_c/d\ln V \approx -0.037$ and -0.23 for V_3Si and V_3Ge, respectively, which are considerably less than twice the low-frequency γ's for c_s. For the high-frequency modes, however, the anharmonicity, like the softening[19] for V_3Si, is probably smaller. The contribution from other modes will also reduce that expected for c_s alone. Thermal expansion provides some measure of high-frequency anharmonicity but the effects due to shear (volume-conserving) modes may be small for this quantity. The thermal expansion[30] of V_3Si and V_3Ge are shown in Figs. 6 and 7. The most unusual feature is that the thermal expansion, on cooling, decreases more slowly than expected and follows approximately a $\ln T$ dependence. This temperature dependence also approximately describes[4] the fall of the soft-shear modulus $\frac{1}{2}(c_{11}-c_{12})$, and suggests some evidence

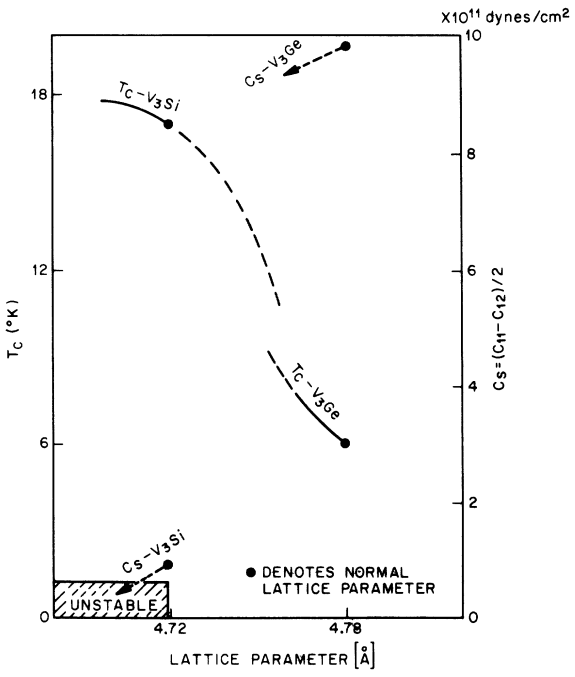

FIG. 5. T_c and shear modulus $\frac{1}{2}(c_{11}-c_{12})$ vs lattic parameter for V_3Si and V_3Ge. Solid and dashed lines give observed and extrapolated behaviors. T_c data are from Smith (Ref. 14). "Unstable" region for V_3Si shear mode is bounded by critical shear modulus (at normal volume) at which the structural transformation occurs.

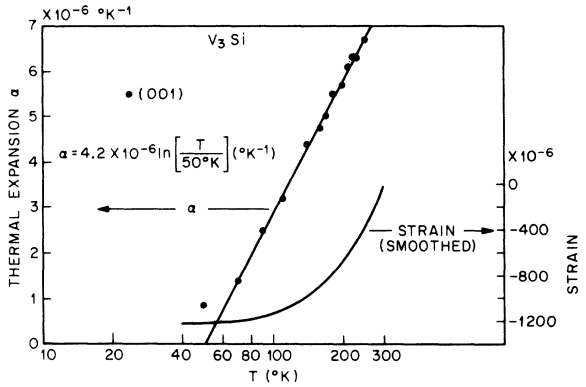

FIG. 6. Thermal expansion of V_3Si vs temperature.

of high-frequency anharmonicity. Another indication of the high-frequency anharmonicity comes from measurements of the strain dependence of the specific heat of V_3Si by Kungler *et al.*[31] These data show a significant increase in specific heat under compressive stress for $T > 25$ °K indicating some mode softening for the high-frequency phonons.

Figure 5 also shows the possible existence of a state of maximum instability (and, by inference, maximum T_c) for V_3Si. Since the "unstable"-shear-mode modulus decreases with pressure, cubic V_3Si should no longer exist with lattice parameters much less than 4.72 Å. The value of the shear modulus at which the structural transformation has been found to begin[4] is the upper bound of the region marked "unstable" in Fig. 4. For cubic V_3Si the shear modulus is typically only somewhat larger than this as shown by the circle. With smaller volumes a transformation should occur (possibly at a new critical value of the shear modulus) leading to a tetragonal structure with a lower T_c and a stiffer shear modulus.

A simple physical picture to account for much

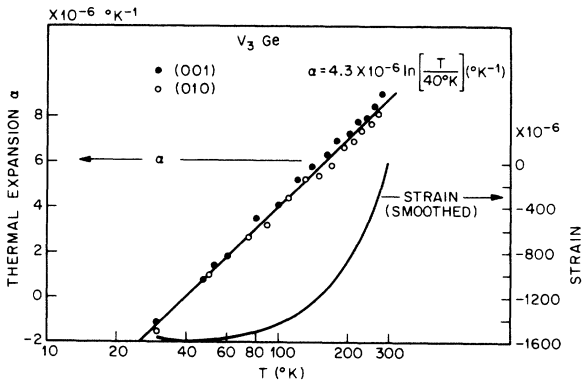

FIG. 7. Thermal expansion of V_3Ge vs temperature. The difference for the two directions may be due to a systematic error.

of the unusual behavior of the high-T_c superconductors is given in Fig. 8. In this picture, the source of the A-15 behavior lies in the phonon spectrum rather than the bare electronic density of states. The potential well $U(\epsilon)$ for an individual shear mode of the type $\vec{q}_T \parallel [110]$, $\vec{p} \parallel [1\bar{1}0]$ ($c_{11} - c_{12}$ type) is shallow for low strains and becomes steep for strains beyond roughly 10^{-3}. At temperatures above several hundred degrees Kelvin the mean thermal amplitude is considerably larger than 10^{-3} and the system spends most of its time "on the walls." The large curvature here reflects normal elastic stiffness. At lower temperatures and thermal motion amplitudes more time is spent in the flat regions and the average restoring force (or phonon velocity) for this shear deformation with decreasing T tends to zero. The structural transformation would then occur according to details of the shape of U at small ϵ which I cannot specify.

From the extent of the flat part of the well one accounts for the temperature (from the corresponding vibrational amplitudes) at which the mode softening is greatest. Roughly equivalent in effect, then, are the tetragonal static strains of $\sim 10^{-3}$ beyond which the normal crystal stability (steep walls) at low temperatures is also made to return. These strains, when applied to the material, will thus lead to a more stable lattice and, consequently, a lower T_c.

The volume effects are accounted for by noting that with increasing volume the bottom of the well

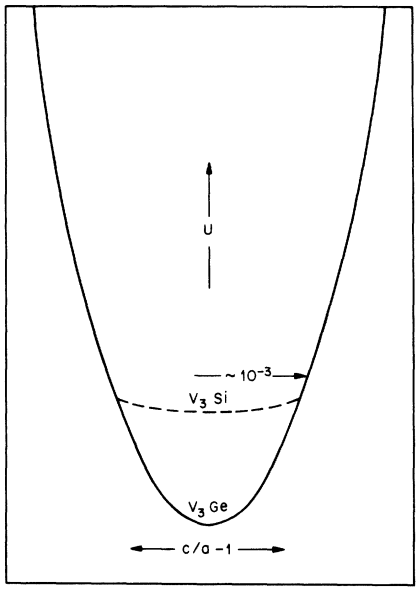

FIG. 8. Potential well proposed for $\vec{q}_t \parallel [110]$, $\vec{p} \parallel [110]$ shear mode in A-15 high-T_c superconductors.

acquires a normal curvature. This volume strain behavior is exemplified in the difference between V_3Si and V_3Ge which has a ~1.3% larger lattice parameter. As previously concluded[2] much of the difference between these compounds is due to the different volumes. Figure 5 shows that V_3Ge extrapolated to the V_3Si lattice parameter would have a high T_c and a soft-shear mode.

Other results of the anharmonicity discussed above are that (a) the Debye model is inappropriate for calculating lattice properties (e.g., corrections to the specific-heat behavior may be large); (b) a strong temperature dependence of the phonon enhancement of the electronic properties may occur; and (c) detailed calculations of the anomolous temperature dependences of these materials based on (rigid) energy-band fine structure must account for the anharmonic motion of the lattice. It is possible that fine structure exists in the electronic bands at energies below the Fermi level, and that this contributes a strong temperature dependence to crystal properties because the smearing of these levels due to lattice motion is reduced on cooling. (See Ref. 18.)

VI. STRUCTURAL INSTABILITY AND HIGH-TEMPERATURE SUPERCONDUCTIVITY

From the physical picture of A-15 superconductors given above some conclusions emerge on the occurrence of high-temperature superconductivity and structural instability.[32]

The conditions for high-T_c superconductivity are just those which occur because the high-T_c compounds are headed toward structural instability at low temperatures. Any mechanism which relieves that instability at low temperatures will lead to a serious reduction in the superconducting transition temperature. The structural transformation does provide relief from this instability and, phenomenologically at least, it is the large strain dependence of T_c which tells us how much T_c is lowered. The strain which the crystal requires for stability can, in amounts of only 1%, cause a reduction of T_c by ~10 °K. In terms of the parameters of the microscopic theory it is the phonons which show the extraordinary strain dependence (anharmonicity) responsible for the T_c behavior.

To extend these ideas I am led to the following conjectures. The A-15 compounds are, chemically, not unique for high-temperature superconductivity. Nor, in fact, is the Batterman-Barrett[33] transformation which occurs at low temperatures. What is unique (accidental) to these compounds is that the structural transformation is incipient at low temperatures. It makes little difference for superconductivity whether or not the structural transformation actually takes place. The reason is that the strains attendant to such transformations are so small that the reduction of T_c (proportional to ϵ^2) never becomes appreciable. In this sense the high-T_c A-15 compounds achieve the maximum enhancement of T_c which can result from the structural instability.

If, however, the physical conditions lead to a structural transformation at higher temperature then the resulting strains, which continually grow below the transformation temperature, may have become large enough to remove the instability at low T and this will lower T_c.

It can be questioned whether there are materials whose T_c, potentially as good as the A-15's, have been reduced by a Batterman-Barrett–like transformation at higher temperatures. The materials which best suit this description are the σ-phase alloys.[34] (The cubic α-Mn phase also appears to be closely related to the A-15 structure.) The σ phase has chemical constituents similar to the A-15's, and is tetragonal (like Batterman-Barrett–transformed V_3Si) but with $2c/a \sim 1.02$–1.04. These T_c's are about what one would expect for high-T_c A-15 compounds with tetragonal strains of ~1% from Eq. (1) (which probably should be restricted to smaller strains). With regard to atomic volume these alloys form a rather tight group located at the central peak in Fig. 1. One would expect large changes in T_c for certain strains. Indirect evidence of this has been given by Blaugher and Hulm.[35]

The conjectures put forth above suggest that one may, quite often, raise the superconducting transition temperature in many systems by encouraging a structural instability at low temperatures. Obvious occurrences of such instabilities are at the solid-state phase boundaries of many metals. For transition-metal alloys forming σ or α-Mn phases these transformations are quite numerous at high temperatures. In analogy to V_3Si the structural instability will exist only over a narrow range in temperature, usually, so that the conditions for its occurrence will be critical. The problem is to maintain or induce this instability, usually occurring above 1000 °C, at low temperatures without triggering a structural transformation of appreciable strain. Methods other than applied stress are suggested. The proof of these conjectures will depend upon the success of these.[36]

---

[1] L. R. Testardi, J. E. Kunzler, H. J. Levinstein, and J. H. Wernick, Solid State Commun. 8, 907 (1970); also, L. R. Testardi, Phys. Rev. B 3, 95 (1971); and L. R. Testardi, J. E. Kunzler, H. J. Levinstein, J. P. Maita, and J. H. Wernick, *ibid.* 3, 107 (1971).

In the right-hand side of Eq. (A2) (Appendix) of the first

article (L. R. Testardi *et al.*) the coefficients of the 2nd and 5th terms should be 1 and $\frac{1}{4}$, respectively [J. Trivisonno (private communication)]. This alters some numerical factors in this Appendix but not the conclusion.

[2]L. R. Testardi, R. R. Soden, E. S. Greiner, J. H. Wernick, and V. G. Chirba, Phys. Rev. 154, 399 (1967). Single-crystal data for Nb_3Sn were obtained by K. R. Keller and J. J. Hanak [Phys. Rev. 154, 628 (1967)]. However, all three moduli were not obtained at T_c.

[3]It is clear that this formula cannot be used for strains much larger than 1%. Some evidence is available, however, to show that the large strain dependence of T_c extends out to $\sim\frac{1}{2}$% strains.

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

[5]Only alloys where A = vanadium or niobium are shown in the region of the predicted volume dependence. Also, it is found that for alloys where the V or Nb chains are disordered (these are not shown in Fig. 1) the T_c's are lower than what would be inferred by Fig. 1.

[6]Unlike an earlier treatment of the V-based alloys (Ref. 1), Fig. 1 includes, besides alloys containing one of the studied compounds, other materials (Nb_3Pt, Nb_3Au, $Nb_3Pt_{0.5}Au_{0.5}$, and Nb_3Ga) for which the velocity of sound was not measured. These points, which are grouped under the parabola marked Nb_3Al, must be taken as illustrative.

[7]The compounds between the V and Nb wings on this plot quite often have a transition metal for the B atom. There are two Ta compound exceptions in the group marked Nb_3X.

[8]The predicted strain dependence for V_3Ge with increasing lattice parameter has been omitted in the figure. The fit, poorer than that for decreasing lattice parameter, can be seen in Ref. 1. Also, T. F. Smith (unpublished) has found the sign of the pressure coefficient of T_c for one alloy system here ($V_3Ge_{1-x}Al_x$) to be opposite from that predicted.

[9]See, for example, B. W. Roberts, *Intermetallic Compounds* (Wiley, New York, 1967).

[10]For V_3Si the estimate was considerably less but see the discussion of T. F. Smith's work (Ref. 14).

[11]M. Weger, B. G. Silbernagel, and E. S. Greiner, Phys. Rev. Letters 13, 521 (1964). A large tetragonal-stress dependence of T_c in Nb_3Sn has been reported by J. P. McEvoy [Physica (to be published)].

[12]E. S. Itskevich, M. A. Il'ina, and V. A. Sukhoparov, Zh. Eksperim. i Teor. Fiz. 45, 1378 (1963) [Sov. Phys. JETP 18, 949 (1964)].

[13]H. Neubauer, Z. Physik 226, 211 (1969).

[14]T. F. Smith, Phys. Rev. Letters 25, 1483 (1970). Smith also finds the T_c of V_3Ge to increase with pressure, as predicted (Ref. 1), but at a rate which is linear with pressure. The pressure dependence of the bulk modulus will give a positive curvature to the volume dependence, as predicted, but smaller than expected (see Fig. 4).

[15]T. F. Smith (private communication).

[16]C. B. Müller and E. J. Saur, Advan. Cryogenic Eng. 8, 574 (1963); Rev. Mod. Phys. 36, 103 (1964); W. Buckel, W. Gey, and J. Wittig, Phys. Letters 11, 98 (1964).

[17]J. Labbé and J. Friedel, J. Phys. (Paris) 27, 153 (1966); 27, 303 (1966); see also R. W. Cohen, G. D. Cody, and J. J. Halloran, Phys. Rev. Letters 19, 840 (1967); and E. Pytte, *ibid.* 25, 1176 (1970).

[18]In many of the existing models the source of the A-15 behavior is a postulated extraordinary fine structure — of the order of 20 °K ($\sim$ 2 meV) — in the bare electronic band structure. The anomalous temperature dependences come from the significant role played by kT thermal broadening in such a picture. Other reasons aside, there is some doubt that such fine structure will exist in a compressible lattice. The thermal motion of the lattice should give rise to an energy-level broadening $(dV/d\epsilon) \times \epsilon_{\text{thermal}}^{\text{rms}}$, where $dV/d\epsilon$ is a deformation potential. Since the phonon velocity $V_p \ll V_e$ (for electrons), and for $\lambda_p \ll \lambda_e$, the phonon deformations are static compared to the electron motions. This should lead to an estimated level broadening in V_3Si at $\sim$ 25 °K which is greater than the kT (rigid-lattice) broadening.

[19]G. Shirane, J. Axe, and R. Birgeneau (unpublished).

[20]See Ref. 1 for the specific-heat data of V_3Si.

[21]This work was done in collaboration with L. Mattheiss.

[22]J. N. Eastabrook, Phil. Mag. 2, 1415 (1957).

[23]Similar conclusions were reached by L. J. Vieland and A. W. Wicklund, Phys. Rev. 166, 424 (1968).

[24]J. S. Shier and R. D. Taylor [Solid State Commun. 5, 147 (1967)] have obtained evidence of anharmonicity in Nb_3Sn from Mössbauer-effect studies.

[25]J. R. Patel and B. W. Batterman, Phys. Rev. 148, 662 (1966).

[26]P. F. Carcia, G. R. Barsch, and L. R. Testardi, Phys. Rev. Letters 27, 944 (1971).

[27]The large uncertainties in the quoted γ's arise from the temperature extrapolation and the fact that the samples showed deviation from elastic cubic symmetry under pressure. For V_3Ge further work is necessary to justify the extrapolation.

[28]W. L. McMillan, Phys. Rev. 167, 331 (1968).

[29]Among the high-symmetry modes only the soft-shear mode $\frac{1}{2}(c_{11}-c_{12})$ has the anomalous-volume dependence.

[30]Low-temperature thermal-expansion data for V_3Si, supporting the predicted tetragonal-strain dependence of T_c, have been obtained by E. Fawcett [Phys. Rev. Letters 26, 829 (1971)].

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

[32]Twenty years ago G. Wentzel [Phys. Rev. 83, 168 (1951)] showed, using a perturbation theory of Bardeen and Fröhlich, that the conditions for superconductivity would also lead to negative sound velocities. However, Wentzel concluded from this "absurd" behavior that the theoretical treatment was wrong. In superconducting materials the behavior of the sound velocity is, except for high-T_c materials, not anomalous.

[33]B. W. Batterman and C. S. Barrett, Phys. Rev. 145, 296 (1966).

[34]See J. H. Wernick, *Intermetallic Compounds* (Wiley, New York, 1967), Chap. 12.

[35]R. D. Blaugher and J. K. Hulm, J. Phys. Chem. Solids 19, 134 (1961).

[36]Recent work in the Mo-Re system has shown large increases in T_c ($\sim$ 5–7 °K) for materials prepared "close" to a phase-boundary line [L. R. Testardi, J. J. Hauser, and M. H. Read, Solid State Commun. 9, 1829 (1971)].