# Structural instability and superconductivity in A-15 compounds

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**Structural instabilities are now being found in many high-temperature superconductors. Compounds with the A-15 ($\beta$-W) structure comprise the most important group of these materials, and their properties have been extensively studied for over 15 years. A review is given of some of these results, particularly those relating to the elastic behavior. The empirical relation of the structural instability and the anharmonicity to the high superconducting transition temperature is discussed.**

## CONTENTS



## I. INTRODUCTION

In the ten years or so since its discovery, the structural instability of high-temperature A-15 superconductors has progressed from an unexpected bafflement to an almost inevitable expectation. The "anomalies" we now associate with these materials have become so common that it is a rare and interesting finding when they are absent. These materials have now been studied by a comparatively wide variety of experiments since the late 1950's, and a reasonable picture of their physical behavior is available. Theoretical models have been proposed and have provided good and sometimes exceptional descriptions of these materials. The problems have been sufficiently complex, however, that prior work has at times justifiably restricted itself to dealing with the structural instability or the superconductivity alone. Indeed, the relationship between structural instability and superconductivity is still uncertain. It is true, however, that most high $T_c$ superconductors do exhibit some signs of instability. Whatever that relationship, this fact will continue to confront the researcher who seeks higher $T_c$ superconductors. Ultimately, it may provide better understanding of the broader problem—i.e., what makes solids unstable.

We will present below a summary of some of the experimental findings for A-15 structure superconductors, and a brief mention of the theories relevant to them. A more detailed discussion and references can be found in the two recent review articles on these materials by Weger and Goldberg (1973) and by Testardi (1973a).

Although this paper will be restricted to a discussion of A-15 structure materials, there is evidence for instabilities in other superconducting materials. Experimental results relating structural instability and superconductivity have been given by Luo *et al.* (1965) for In–Te, Hartsough and Hammond (1971) for $V_3Al$, Ho and Collins (1971) for Ti–Mo, Chu *et al.* (1971) for V–Ru, and Lawson (1972a) for ternary molybdenum sulfides (1972). For $HfV_2$, $ZrV_2$, and their alloys considerable work has been reported, including Lawson (1971), Doherty and Gibbons (1971), Lawson and Zachariasen (1972), Smith *et al.* (1973), Takashima and Hayashi (1973, 1974), Inoue and Takashima (1973), and Moncton (1973). Phillips (1971) has given arguments relating structural instability and superconductivity in some rocksalt materials, and some interesting neutron work on several of these has been reported by Smith and Glaser (1970). Matthias *et al.* (1971) and Matthias (1972) have discussed structural instability and superconductivity inferred from the reduction of $T_c$ on grinding several high $T_c$ superconductors. Fisk and Lawson (1973) have observed an interesting characteristic behavior in the temperature dependence of the electrical resistance of some superconductors, which appears related to an instability. This anomalous temperature behavior had been previously observed in $Nb_3Sn$ by Woodard and Cody (1964), and in $V_3Si$ by Kunzler (unpublished).

Finally, Fröhlich (1971) has shown that the interaction that leads to superconductivity may cause anomalies in the phonon spectrum, and Rothwarf (1970) has suggested that the anomalous behavior of many high $T_c$ materials might be due to acoustic plasmons first introduced by Fröhlich (1968).

## II. THE A-15 STRUCTURE

The A-15 (or $\beta$-W) structure (cubic space group Pm3n) is shown in Fig. 1 for the compound formula $A_3B$. For the high $T_c$ superconductors the A atom is a transition-metal atom, usually V or Nb. The B atom is often (but not always) a nontransition-metal atom, e.g., Si, Ge, Sn, Al, or Ga. The B atoms occur at the bcc sites, while the A atoms occur on the cube faces, forming three orthogonal linear chains in the extended structure.

Lattice parameters for the high $T_c$ materials range from 4.72 Å for $V_3Si$ to 5.29 Å for $Nb_3Sn$. Geller (1956) has calculated the lattice parameters of a large number of A-15 compounds from a structural model. An enlarged listing of A-15 materials and their lattice parameters has recently been published by Johnson and Douglas (1974).

It is generally conceded that the unique properties of these materials stem largely from the linear chains of the

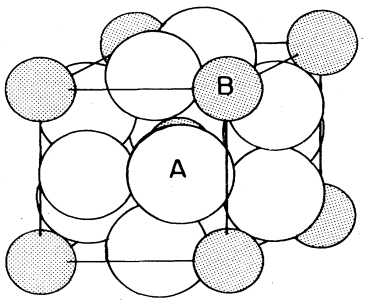



FIG. 1. The A-15 (or $\beta$-W) crystal structure for the compound formula $A_3B$. For the high $T_c$ superconductors, A is a transition metal (usually V or Nb) and B is usually (but not always) a nontransition metal (e.g., Si, Ge, Sn, Al, Ga).

transition metal A atoms (Weger, 1965). Wang (1974) has recently reviewed the phase diagrams and superconducting transition temperatures for about 23 A-15 compounds. He finds a correlation between $T_c$ and the compositional width of the A-15 phase region from which is cited additional evidence of the importance of the A chains in this structure.

One of the major problems imposed on all workers in this field is the preparation and characterization of samples. Only $V_3Si$ and $Nb_3Sn$ have been obtained as single crystals of a size suitable for most experiments. In both cases, fortunately, good crystalline quality has been reported (see, for example, Shirane *et al.*, 1971, and Shirane and Axe, 1971). $V_3Si$ crystals, which can be grown from the melt, were first obtained by Greiner and Mason (1964) and have now been prepared in at least three or four other laboratories. In most respects the physical properties measured on crystals from different sources show reasonable consistency. For $Nb_3Sn$ the preparation of single crystals is more difficult, and Hanak and coworkers at RCA merit credit as the only source of excellent quality (vapor growth) samples today.

Although different crystals of $Nb_3Sn$ and $V_3Si$ show considerable similarities in their anomalous behaviors, exact reproducibility has not been achieved. Workers in this field are, therefore, constantly faced with assessing to what extent the data are sample dependent. Probably the most important nonreproducible behavior is the occurrence of a low-temperature structural transformation in both compounds. Some discussion of this appears in the literature (Mailfert *et al.*, 1967, Testardi *et al.*, 1971a, and King *et al.*, 1967); but the exact metallurgical factors controlling the transformation have not been fully clarified.

The most common criteria for characterizing the samples are chemical composition, crystallographic structure, and lattice parameter (from x rays), and long-range order. The average chemical composition (or average stoichiometry) is seldom known to better than a few percent, and, at least for $V_3Si$, is complicated by the occasional occurrence of several percent of a second phase. The microscopic uniformity of the composition (over $\sim$100 Å, which is roughly the superconducting coherence length) has never been determined. X-ray measurements generally show well-defined diffraction peaks consistent with the A-15 structure (except at low temperatures where a transformation may occur), but the lattice parameter and degree of long-range order (in particular, the amount of antisite defects which put A atoms in B sites and vice versa in the $A_3B$ structure) may depend upon the method of sample preparation. Both the superconducting and some normal-state properties of these materials can depend upon the stoichiometry and the degree of order (see, for example, Blaugher *et al.*, 1969, and Labbe and Van Reuth, 1970). The microscopic defect state of the samples is also generally unknown.

It is unfortunate that materials problems have not received the wide interest their importance warrants. Nevertheless, the unique characteristics of the A-15 superconductors—anomalous temperature dependences, soft modes, possible structural transformations, and high $T_c$'s—are at least qualitatively alike in all samples. It is these similarities, rather than the detailed differences, which much of the theory and experiment have sought to understand.

## III. ANOMALOUS BEHAVIOR AND THE BATTERMAN-BARRETT TRANSFORMATION

Just a few years after their discovery (Hardy and Hulm, 1954) the high $T_c$ superconductors were to start providing a seemingly constant source of unusual physical behavior. Most often, this occurred in the form of "anomalous" temperature dependences of the magnetic susceptibility, Knight shift, and electrical resistivity. (For references to some of this work see the review articles by Weger and Goldberg, 1973, and Testardi, 1973a).

The first evidence of a structural transformation was obtained by Shull (1963–1964) in neutron diffraction studies of $V_3Si$. Batterman and Barrett (1964, 1966) subsequently carried out detailed x-ray studies and found that this compound undergoes a cubic-to-tetragonal transformation starting at $T_m \sim 21$°K, with distortion progressively increasing (thermodynamic second order) from $c/a = 1$ to $\sim$1.0024 at the lowest temperatures. This is accompanied by the formation of structural domains such that the mono-

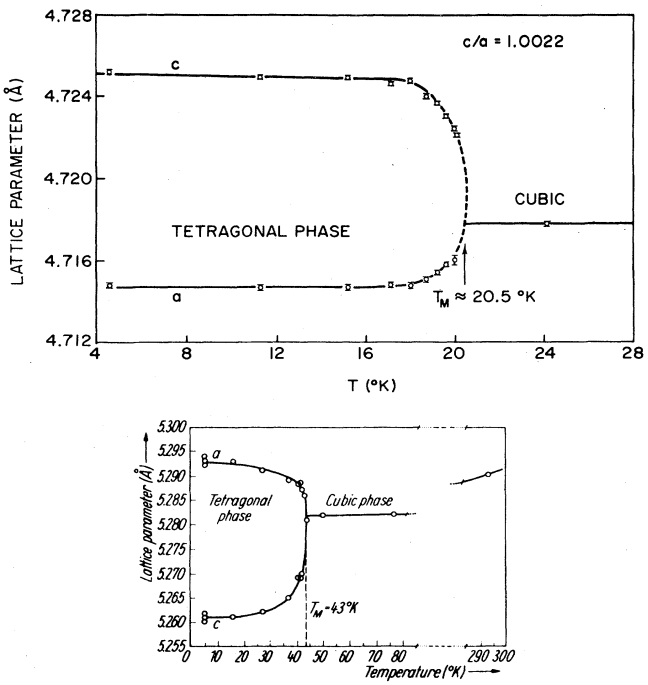



FIG. 2. Upper: The $c$ and $a$ lattice parameters of $V_3Si$ vs. $T$, showing the cubic-to-tetragonal structural transformation at $T_m \sim 20.5$K. (After Batterman and Barrett, 1966.) Lower: Same data for $Nb_3Sn$ showing the structural transformation at 43K. (After Mailfert *et al.*, 1969.)

crystallinity of the sample is, in general (nondestructively), lost. A similar structural transformation (but with $c/a < 1$) was later observed in $Nb_3Sn$ by Mailfert *et al.* (1971), which Vieland *et al.* (1971) subsequently showed to have a first-order transition. These important x-ray results are summarized in Fig. 2.

The structural transformation in $V_3Si$ has been generally found to be second order on the basis of: (i) no discontinuities in the unit cell parameters at $T_m$; (ii) no latent heat; (iii) no hysteresis; and (iv) no coexistence of transformed and untransformed phases below $T_m$. Although they were performed by different experimenters on different samples, these findings may be questioned on the basis of insufficient experimental precision. Dilatometry experiments by Fawcett (1971), however, do provide some test of this criticism for $V_3Si$. No discontinuity in length greater that $\sim 5\%$ of the final transformation strain was found at or near $T_m$ for a sample which showed strong preferred orientation of the structural domains (so that unit-cell changes will lead to sample-length changes). From this it is seen that any discontinutiy in $(c/a - 1)$ in $V_3Si$ is considerably less than the values of $\sim 50\%$ (of the zero K strain) found in $Nb_3Sn$. It should also be noted that for $Nb_3Sn$, which does not show a latent heat at $T_m$ (Vieland and Wicklund, 1968), the x-ray studies have concluded that while the distortion $(c/a - 1)$ undergoes a discontinuity at $T_m$ the volume fraction of tetragonal domains goes continuously to zero as $T_m$ is approached from below.

The importance of the thermodynamic order of the transition stems from the work of Anderson and Blount (1965), who showed that a cubic-to-tetragonal transformation should be first order in the absence of any change in internal symmetry other than mere strain. For $V_3Si$, the first-order character of the transition, if such character exists, has so far escaped detection. Other order parameters may be involved, but none, as yet, has been observed. For both $V_3Si$ and $Nb_3Sn$ it is not known to what extent the results may be dependent upon the sample and its state of strain.

Detailed and informative neutron studies of $Nb_3Sn$ by Shirane and Axe (1971a) have found the sublattice distortion accompanying the Batterman–Barrett transformation. The tetragonal structure was determined to be $D_{4h}^9$–$P4_2/mmc$ (the cubic structure is $O_h^3$–Pm3n). The sublattice motion in this transformation, shown in Fig. 3, involves a pairing of the Nb atoms ($\Gamma_{12}(+)$ symmetry) along a chain similar to what is expected for a Peierls distortion in a one-dimensional system.

It is useful to summarize here some of the similarities and differences between $Nb_3Sn$ and $V_3Si$, the most thoroughly studied A-15 compounds. Both materials have high $T_c$'s (17–18°K); similar anomalous temperature dependences of many properties (see above); very soft acoustic modes (see Sec. IV); can exhibit cubic-to-tetragonal structural transformations; and have large stress dependences for some of their physical properties. The differences are that the structural transformations are reported to be first-order for $Nb_3Sn$ and second-order for $V_3Si$; the low-temperature tetragonal distortions $(c/a - 1)$ are $\sim -6 \times 10^{-3}$ for $Nb_3Sn$ and $\sim +2.5 \times 10^{-3}$ for $V_3Si$; and a considerably larger softening of the acoustic mode $c_{44}$ occurs in $Nb_3Sn$ as compared with $V_3Si$. Other differences are discussed below.

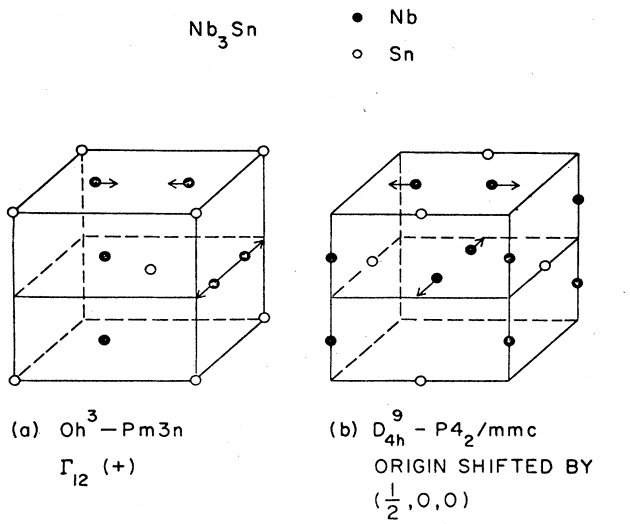



FIG. 3. Model showing the Nb atom sublattice distortion due to the structural transformation in $Nb_3Sn$ (● Nb; ○ Sn). a) $O_h^3$ – Pm3n, $\Gamma_{12}(+)$; b) $D_{4h}^9$ – $P4_2/mmc$, origin shifted by $(\frac{1}{2},0,0)$. (After Shirane and Axe, 1971a).

Much of the interest in the general problem of structural instability and high-temperature superconductivity is derived from the unique physical behavior common to both compounds, particularly the high $T_c$'s, mode softening, and structural transformations. Indeed, other work has now shown that these three characteristics occur in all high $T_c$ A-15 superconductors (see review articles by Weger and Goldberg, 1973, and Testardi, 1973a, and the recent report by Viswanathan, 1974). The differences between $Nb_3Sn$ and $V_3Si$, however, may provide a stringent test for any theory or physical understanding of these important materials.

## IV. ULTRASONIC BEHAVIOR AND SOFT PHONONS IN THE HIGH $T_c$ SUPERCONDUCTORS

Following the discovery of Batterman and Barrett, a study of the sound velocity and attenuation in $V_3Si$ was reported by Testardi *et al.* (1965). Generally similar behavior was later found in $Nb_3Sn$ by Keller and Hanak (1966, 1967), although a few important differences were to be uncovered in subsequent work (Rehwald, 1968 and Rehwald *et al.*, 1972). (The growth of the largest crystals of $Nb_3Sn$ as well as much of the significant experimental and theoretical work for this compound have been carried out at RCA.)

The primary finding of the ultrasonic experiments was the existence of large elastic softening which provides a natural precursor to the structural transformation (and which also suggests how the anomalous behavior may be related to the high-temperature superconductivity). Although a softening with decreasing temperature was found for all of the high-symmetry modes, the largest decrease by far was observed for shear waves propagating in a [110] direction with $[1\bar{1}0)$ polarization. The elastic modulus associated with this type of deformation is $(c_{11} - c_{12})/2$. The temperature dependence of this modulus, found in both a transforming and nontransforming sample of $V_3Si$, is shown

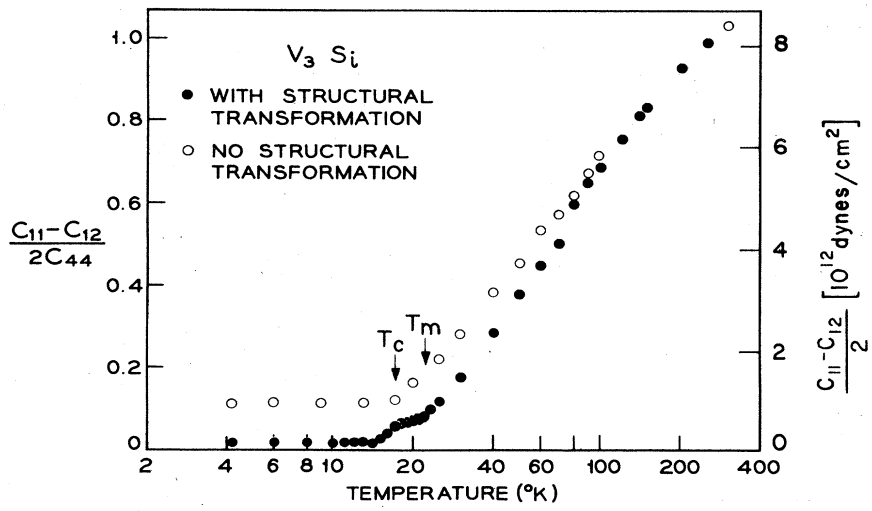



FIG. 4. Temperature dependence of the elastic moduli $(c_{11} - c_{12})/2$, and the inverse anisotropy factor $2c_{44}/(c_{11} - c_{12})$ for transforming (●) and nontransforming (○) $V_3Si$. $T_m$ and $T_c$ are the structural and superconducting transition temperatures. (After Testardi and Bateman, 1967.)

in Fig. 4. Instead of the usual stiffening on cooling (~5–10%) expected for most stable solids, this compound shows elastic softening, even at room temperature, and which, for the transforming crystal, increases on cooling at a rate that would lead to a total instability (vanishing modulus) near 17°K, the superconducting $T_c$. The partial stabilization which occurs near 21°K marks the onset of the Batterman–Barrett transformation. Indeed, the soft shear mode represents a form of deformation consistent with what is needed to drive the cubic-to-tetragonal structural change as well as to establish the domain structure, which is found to accompany the transformed state (Batterman and Barrett, 1966).

For the transforming sample, data below $T_m$ (21°K) cannot be reliably interpreted because of the complicating effects of the domains.

For the nontransforming crystal a similar elastic instability is found (see Fig. 4) but of somewhat reduced magnitude on cooling, so that a vanishing modulus is due to occur at ~12°K. Here, however, we see the surprising result that the onset of superconductivity at 17°K abruptly arrests the growing instability and maintains the modulus at a constant but low value at the lower temperatures. This stabilizing effect of superconductivity has probably prevented the need for a transformation and may explain why structural transformations, which occur from ~17 to 25°K, are generally not observed below $T_c$.

A second effect of superconductivity upon the structural behavior came from the sound-attenuation studies (Testardi *et al.*, 1965). The occurrence of the structural transformation leads to an increased attenuation which is shown in Fig. 5 for a longitudinal wave in $V_3Si$. Since one would correlate the continuous increase in attenuation below 21°K with the continuous structural transformation, the arrest of the attenuation at $T_c$ led to the suggestion that the onset of

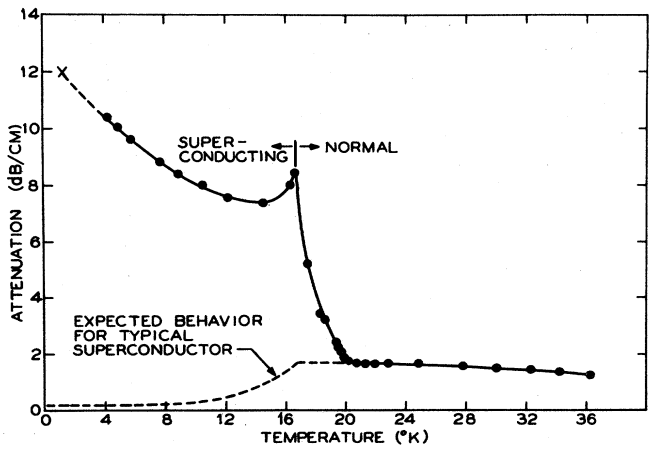



FIG 5. Temperature dependence of the attenuation of 310 MHz longitudinal waves propagating along [110] in $V_3Si$. The structural transformation begins at ~21K. (After Testardi *et al.*, 1965.)

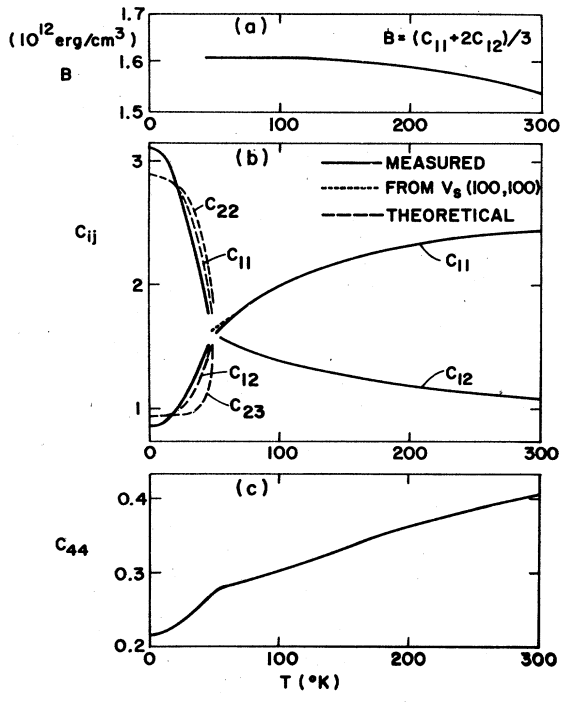



FIG. 6. Elastic moduli of $Nb_3Sn$ vs temperature. The dashed curves have been obtained from theory (Vieland *et al.*, 1971). (After Rehwald *et al.*, 1972.)

superconductivity arrests the structural transformation. Direct x-ray evidence confirming this was later obtained by Batterman and Barrett (1966).

The elastic behavior of transforming $Nb_3Sn$ obtained by Rehwald *et al.*, (1972) is shown in Fig. 6. One sees the same near vanishing of $c_{11} - c_{12}$ as the structural transition is approached from high temperatures. In contrast to $V_3Si$, however, $(c_{11} - c_{12})/2$ recovers to a high (stable) value below $T_m$. Other marked differences are that the magnitude of $c_{44}$ in $Nb_3Sn$ is half or less than that in $V_3Si$, and its decrease on cooling is far greater in $Nb_3Sn$ than in $V_3Si$. These results are puzzling and no explanation has been offered.

The elastic instability, found in both transforming and nontransforming $V_3Si$ and $Nb_3Sn$, was later found by Testardi *et al.*, (1967) to occur in polycrystalline samples of all of the high $T_c$ A-15 superconductors while not occurring in the isostructural compounds with low $T_c$.

## V. BEHAVIOR OF THE SOUND VELOCITY AT $T_c$: RELATING SUPERCONDUCTIVITY AND THE STRUCTURAL INSTABILITY

The two findings in the acoustic studies relating superconductivity and the structural instability were (i) the arrest of the growing elastic instability with the onset of superconductivity in nontransforming $V_3Si$, and (ii) the arrest of the growing structural distortions at $T_c$ for a transforming crystal. Testardi (1971) later developed a simple thermodynamic formalism to relate the sound velocity behavior at $T_c$ to the general strain dependence of $T_c$. When the elastic behavior of $V_3Si$ (and also $V_3Ge$—an A-15 superconductor with $T_c \sim 6°K$) was analyzed some further understanding of the first of these findings emerged. The consequences of the strain dependence of $T_c$ are broader, however, and relate to the strain dependence of the structural instability, a behavior reflected in the unusually large anharmonicity of these materials.

The analysis of the general strain dependence of $T_c$ for *cubic* $V_3Si$ from the sound velocity data yielded the separate behavior for tetragonal as well as volume (hydrostatic) strains. (Similar results have been reported by Fawcett, 1971.) The largest and, for the instability, most significant effects occur for tetragonal strains. Figure 7 shows the predicted dependence of $T_c$ on tetragonal strain (at constant volume) for $V_3Si$ and $V_3Ge$. The quadratic dependence of $T_c$ on strain in this case is a result of symmetry—no linear term (at constant volume) can occur for high-symmetry shear type deformation leading to such tetragonal distortions. The negative strain dependence for $V_3Si$ shows that, for a given volume, the cubic state will always have the highest $T_c$. Four predictions or confirmations can be made on the basis of this calcualted strain dependence.

(1) Arrest of the structural transformation at $T_c$: The results of a free energy calculation using the predicted strain dependence show that tetragonal $V_3Si$ will undergo a discontinuity at $T_c$ in the tetragonal distortion $d(c/a)/dT \sim 2.6 \times 10^{-4}°K^{-1}$. Since at temperatures just above $T_c$, Batterman and Barrett (1966) find $d(c/a)/dT \sim -3 \times 10^{-4}°K^{-1}$, the temperature dependence of $c/a$ is largely

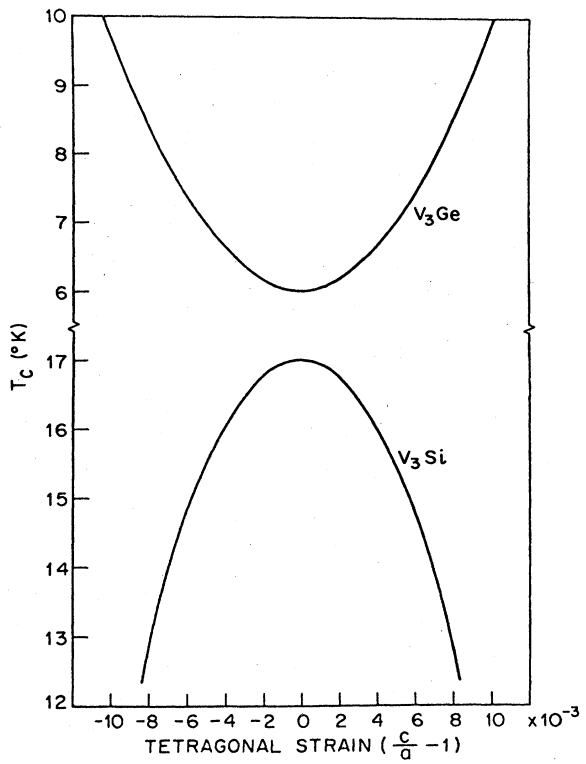



FIG. 7. Predicted dependence of $T_c$ on tetragonal strain (at constant volume) for $V_3Si$ and $V_3Ge$. (After Testardi, 1972.)

reduced below $T_c$. Thus the arrest of the structural transformation at $T_c$ is explained, in this thermodynamic sense, by the large quadratic dependence of $T_c$ on tetragonal strain.

(2) Change in $T_c$ due to the structural transformation: Based on macroscopic strains only, the structural transformation will lead to a reduction in $T_c$ by an amount proportional to $(c/a - 1)^2$. For $V_3Si$, $T_c$ in the tetragonal state is found to be less than that in the cubic state by $\sim 0.4°K$, with some spread expected in view of the variation found in $c/a$. This calculation does not account for any contribution from the sublattice motion. The measured $T_c$'s of a number of transforming and nontransforming $V_3Si$ samples obtained by J. Kunzler (given in Testardi *et al.*, 1971a) confirm these results. Matthias *et al.*, (1971) have concluded from measurements on ground $V_3Si$ powder that the tetragonal phase has $T_c \sim 10°K$. However, measurements on the best existing single crystal samples have always shown the tetragonal phase to have a $T_c$ of $\sim 1°K$ or less below that of the cubic phase. [See also McCarthy and Viswanathan (1971) and Viswanathan and Luo (1971) for another interpretation of the $T_c$ measurements on the $V_3Si$ ground powders.] Measurements by Mailfert *et al.*, (1967) on $Nb_3Sn$ and Vieland and Wicklund (1971) on $Nb_3Sn_{1-x}Al_x$ show that the difference in $T_c$ between the cubic and tetragonal states is also $< 1°K$.

(3) Uniaxial stress dependence of $T_c$: Weger *et al.* (1964) have found that the stress dependence of $T_c$ for $V_3Si$ failed to exhibit the isotropy (i.e., proportional to volume change only) expected for a cubic crystal. By taking into account the large quadratic strain effects as well as the nonlinear

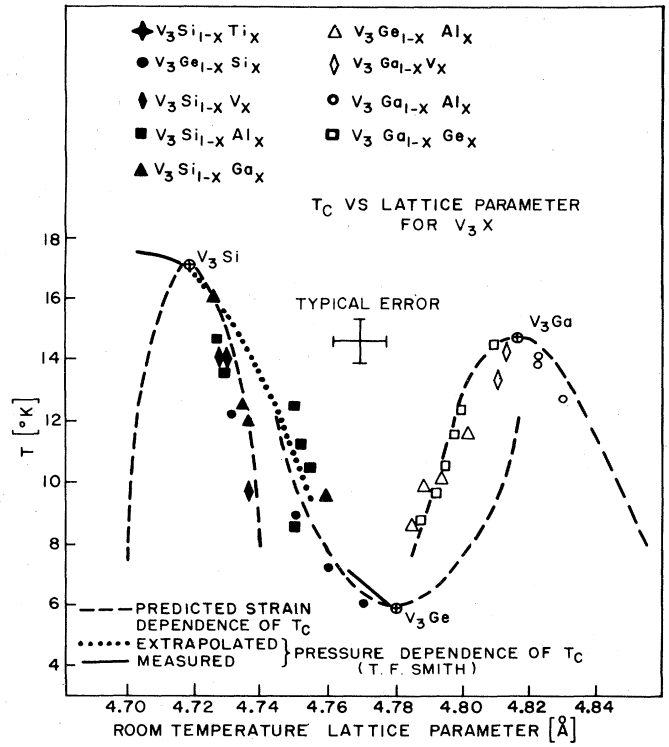



FIG. 8. The predicted dependence (dashed lines) of $T_c$ on lattice parameter for $V_3Si$, $V_3Ge$, and $V_3Ga$ (estimated). The solid lines are the experimental pressure results of Smith (1971). Also given are $T_c$'s for nine alloys of the form $V_3A_{1-x}B_x$. (After Testardi *et al.*, 1971.)

stress–strain relation (found by Patel and Batterman, 1966), a calculated behavior in reasonable agreement with the observed magnitudes and anisotropies was obtained (Testardi, 1971). For uniaxial stresses the largest effects are obtained along ⟨001⟩. The uniaxial stress dependence of $T_c$ for tetragonal $Nb_3Sn$ was measured by McEvoy and found to have a large value similar to that in $V_3Si$. Other effects possibly related to the damain structure were observed.

(4) Strain dependence of specific heat discontinuity at $T_c$: This behavior can be readily related to the strain dependence of $T_c$ and the calculated results are only in rough agreement with experiment. Details are given in Testardi (1971) and Testardi *et al.* (1971a).

The predicted effects for the volume (hydrostatic) deformations were also found to be large, but here the agreement with experiment is not satisfactory. Figure 8 summarizes these results by showing as dashed lines the (extrapolated) predicted dependence of $T_c$ on lattice parameter for cubic $V_3Si$, $V_3Ge$, and $V_3Ga$ (estimated). A large quadratic strain dependence is again expected with the as-grown lattice parameters close to where the $T_c$ extrema of these curves occur. The observed data for nine alloys of the form $V_3A_{1-x}B_x$ are also shown, and indicate that an approximate single-valued relationship exists between $T_c$ and lattice parameter, and that this roughly resembles the extrapolated behavior predicted from the pure compounds. Although some direct measurements of the pressure dependence of $T_c$ in A-15 materials have shown nonlinearity (see Testardi, 1973a for references) recent measurements of Neubauer (1969) and Smith (1970, 1972) indicate that the nonlinearity is much less than predicted. Some of Smith's results are shown in Fig. 8.

The discrepancy between the predicted and observed volume dependence of $T_c$ probably results from experimental error rather than from incorrect assumptions on which the thermodynamic treatment is based. A likely source of this error in the ultrasonic measurements is that the sample may not have had the cubic symmetry assumed in the analysis. This could result from small (undetected) amounts of transformed material in the crystal. Furthermore, recent studies (Testardi, 1973b) have shown that even at relatively high temperatures (~70°K) the crystals may not exhibit, for acoustics, the cubic symmetry inferred from x-ray data. Finally, the extrapolation of the acoustic measurement predictions (for small strains) to the strains indicated in Fig. 8 must be questioned. Although some attempt to justify this has been made (Testardi *et al.*, 1971a) it remains an unproved and possibly erroneous assertion.

For the hydrostatic pressure dependence of $T_c$ in $V_3Si$ good measurements have been made. However, Blaugher *et al.* (1974) have recently reported that the application of ~15 kbar pressure to $V_3Si$ at room temperature (similar to that in the $T_c$ measurement) may lead to a structural transformation. Varma *et al.* (1974) subsequently interpreted this by suggesting that hydrostatic pressure (at 300°K) alters the defect state of the crystal as well as the lattice parameter. The former is expected to increase the structural instability (and possible alter $T_c$) in addition to the volume effects. It is not yet known whether this observation or the proposed behavior could complicate measurements where pressure is applied at room temperature (Neubauer, 1969; Smith, 1970, 1972; and Chu and Testardi, 1974). The experiments of Blaugher *et al.* are even more important in showing an unexpected behavior of this material at room temperature. This, if Varma *et al.* are correct, may indicate the great importance of an aspect not considered by many workers—the defect state of the crystal.

The results of Fig. 8 give the behavior expected for cubic samples. For transformed samples the application of hydrostatic pressure can cause a change in $c/a$ as well as volume. The pressure dependences of $T_c$ and $T_m$ have recently been measured (Chu and Testardi, 1974) and will be discussed in Sec. VII.

One of the results of the volume strain work which deserves note is that the difference in $T_c$ between $V_3Si$ and $V_3Ge$ (as grown) arises in significant part from the difference in lattice parameters (see Fig. 8). We shall show shortly that a similar argument can be made for the structural instability.

## VI. STRAIN DEPENDENCE OF THE ELASTIC BEHAVIOR: ANHARMONICITY

One of the strongest correlations between high $T_c$'s and structural instability is that both exhibit large strain effects so coupled that an increase or decrease in the latter is accompanied by a similar change in the former. Again we discuss separately the results for tetragonal and volume type strains.

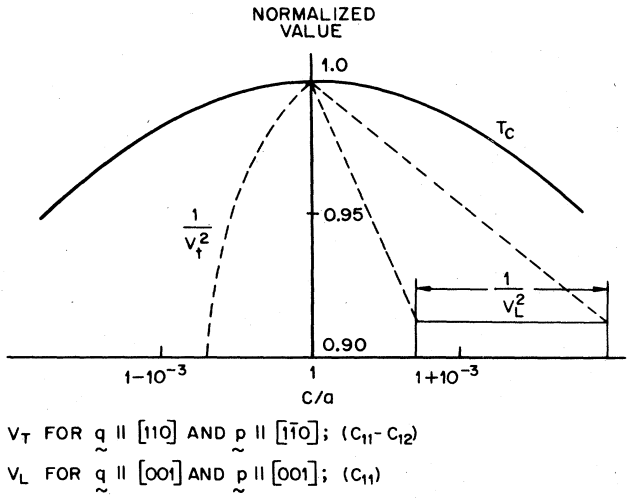



FIG. 9. Dependence of observed elastic softening $1/V^2$ {where $V_T$ and $V_L$ are longitudinal and transverse sound velocities: $V_T$ for $q$ [110] and $p$ [110] ($c_{11} - c_{12}$); $V_L$ for $q$ [001] and $p$ [001], ($c_{11}$)} and calculated $T_c$ as a function of tetragonal strain $c/a$ (with no volume change). The behavior shows the correlation between the strain dependence of $T_c$ and the strain dependence of the structural instability. (After Testardi, 1972.)

(A) Tetragonal strain effects: The first measurements of anharmonicity came in the work of Patel and Batterman (1966) on $V_3Si$. They reported that static strains which produced a tetragonal structure with $1 - c/a \sim 10^{-3}$ at 25°K caused a change in the modulus $(c_{11} - c_{12})/2$ by roughly a factor of two. This is perhaps two orders of magnitude larger than one expects for a normal solid. The strains of this experiment are comparable to those which occur in the structural transformation, and to the amplitude of the thermal phonons at that temperature.

Other experiments using ultrasonics have been discussed by Testardi (1973a). These results are summarized in Fig. 9, which shows how the elastic softness (proportional to the reciprocal sound velocity squared) and the $T_c$ (from Fig. 7) depend on tetragonal distortion. Note that for tetragonal distortions of either sign the elastic softness and the $T_c$ are reduced.

Barsch (1974) has recently calculated some third- and fourth-order elastic moduli using data from pressure measurements of the sound velocity. He finds the third- and fourth-order moduli to be one and five orders of magnitude larger, respectively, than those for typical solids. Semiquantitative agreement with the uniaxial stress–strain relation is obtained.

Testardi (1973b) has observed efficient harmonic shear wave generation in $V_3Si$. This result again indicates the strong anharmonicity in the high $T_c$ superconductors, particularly for shear (tetragonal) type deformations. However, the observation of a strong even ordered shear wave harmonic, which is contrary to symmetry predictions for this cubic material, indicates the existence of some mechanism which lowers the symmetry of this crystal even at temperatures well above that of the structural transformation. Noolandi (1974) has proposed an effect based on the anharmonic coupling of the shear wave to a dynamic strain induced by the low-temperature structural transition, and obtains reasonable agreeement with experiment. Chui (1974) has recently calculated some possible effects of defects in a soft lattice, and finds these may include the harmonic sound generation observed in $V_3Si$.

(B) Volume strain effects: The volume dependence of the $V_3Si$ elastic moduli has been studied by Carcia *et al.* (1971), Larsen and Ruoff (1973), and Carcia and Barsch (1973). The results show that at room temperature the bulk modulus and the shear moduli $c_{44}$ and $(c_{11} - c_{12})/2$ all increase with hydrostatic pressure. However, below ~80°K the modulus $c_2 = (c_{11} - c_{12})/2$, which drives the instability, decreases under pressure. For a nontransforming sample, the negative pressure dependence continually increases on cooling until reaching the value $dc_s/dp = -5$ at 15–20°K ($\sim T_c$), below which it appears to remain roughly constant. A transforming sample, however, shows $dc_s/dp$ becoming positive again below 50°K, with no measurements reported below 37°K. Microscopic and macroscopic Gruneisen parameters have been calculated by Carcia *et al.*, (1971). The correlation of the pressure dependence of $c_s$ and $T_c$ will be discussed in Sec. VI.

Mössbauer studies of $Nb_3Sn$ by Shier and Taylor (1967, 1968) were among the first experiments to indicate the large anharmonicity in these high $T_c$ superconductors. These authors found evidence of a highly anharmonic potential well (for the Sn atoms), and a temperature dependent $s$ electron density at the tin nucleus. These interesting ex-

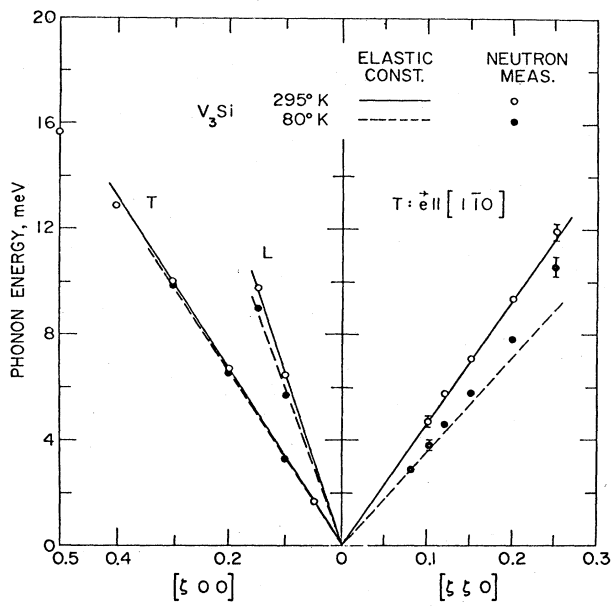



FIG. 10. Acoustic phonon dispersion curve for several acoustic modes in $V_3Si$. $L$ and $T$ denote longitudinal and transverse modes propagating along [001]. The remaining mode is [110] transverse with [1$\bar{1}$0] polarization. Elastic moduli data (extrapolated) are shown as solid and dashed lines. Solid (○) 295°K; dashed (●) 80°K. The wave vector $q$ is given in units of $\zeta$; $q = (\zeta,\zeta,0) \times 2\pi/a$. $\zeta = 0.5$ corresponds to the zone boundary. (After Shirane *et al.*, 1971.)

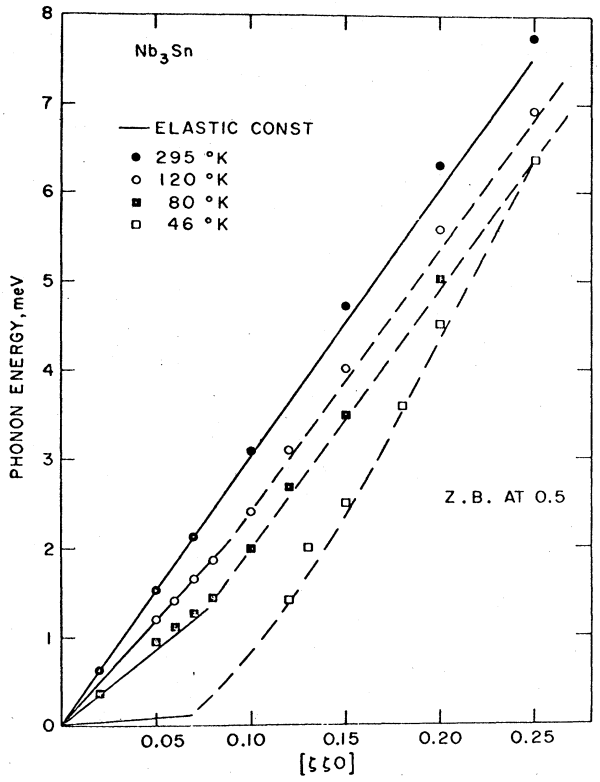



FIG. 11. Acoustic phonon dispersion curves for $q$ [110] waves with [1$\bar{1}$0] polarization in $Nb_3Sn$. $q = (\zeta,\zeta,0) \times 2\pi/a = 1.19$Å. ● 295°K; ○ 120°K; ■ 80°K; □ 46°K. Elastic moduli (solid curve) from Rehwald (1968). (After Shirane and Axe, 1971b.)

periments probably provide the only direct indication at present of the anharmonicity of the high-frequency phonons. Such anharmonicity may contribute significantly to the specific heat but it is difficult to calculate the effects of anharmonicity—or the temperature-dependent moduli—for this property. Kunzler *et al.* (1966) have observed a large strain dependence to the specific heat for $V_3Si$. An x-ray study of $Nb_3Sn$ by Vieland (1971) did not reveal the large Debye-Waller factor found in the Mössbauer experiments.

Thermal expansion can provide some measure of high-frequency anharmonicity, but the effects due to shear (volume conserving) modes may be small. Measurements on $V_3Si$ and $V_3Ge$ (Testardi, 1972) show that the thermal expansion approximately follows a $\ln T$ temperature dependence. This is the same temperature dependence found for $c_s$ and for $dc_s/dp$ in nontransforming crystals (Larsen and Ruoff, 1973). A theoretical explanation of this temperature dependence for $c_s$ has been offered by Weger (private communication) and by Gorkov (1973a, b).

## VII. ANHARMONICITY, STRUCTURAL INSTABILITY, AND HIGH $T_c$'s

The theoretical basis for relating structural instability and superconductivity comes from the work of McMillan (1968) who showed that $T_c$ increases with increasing electron–phonon interaction

$$\lambda = c/M\langle\omega^2\rangle, \tag{1}$$

where $M$ is an ion mass, $c$ is a number which is expected to be roughly constant for similar transition metals (see also Hopfield, 1969) and

$$\langle\omega^2\rangle = \int\omega\alpha^2F d\omega / \int\omega^{-1}\alpha^2F d\omega. \tag{2}$$

Here $\alpha$ is an electron phonon parameter and $F$ is the phonon density of states. Since mode softening precedes (and presumably drives) the structural transformation, an enchancement of $\lambda$ (from the increase in phonons of low $\omega$) can accompany the conditions which lead to structural transformations. The importance of this, however, can only be estimated when the high-frequency phonon behavior (where $F$ is large) is known. Shirane *et al.* (1971) and Shirane and Axe (1971) have, in fact, shown from neutron experiments that a considerable softening of the high-frequency phonons occurs in both $V_3Si$ and $Nb_3Sn$, although this is still appreciably less than for the long-wavelength sound waves discussed previously. These results are shown in Figs. 10 and 11. Testardi and Mattheiss (unpublished) have shown from an approximate calculation of the acoustic mode density of states that the phonon softening might be responsible for an increase of ~6–8°K in $T_c$ (see Testardi, 1973a for details). However, an accurate calculation cannot be made because of insufficient data on the phonon behavior. Furthermore, it is not known whether the soft modes involved in the instability could, in addition, be particularly effective in enhancing $T_c$.

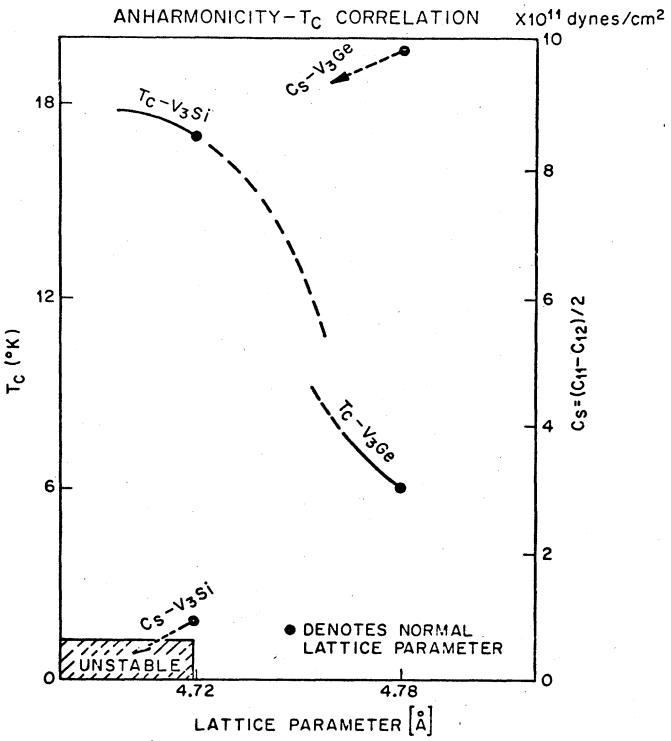



FIG. 12. Dependence of $T_c$ and shear modulus $(c_{11} - c_{12})/2$ on lattice parameter (volume) for $V_3Si$ and $V_3Ge$. Solid and dashed lines give observed and extrapolated behaviors. $T_c$ data are from Smith (1970). "Unstable" region for $V_3Si$ shear mode is bounded by critical shear modulus (at normal volume) at which the structural transformation occurs. (Elastic moduli data from Carcia *et al.*, 1971.) Note that the volume dependence of the shear mode softness correlates with that of $T_c$ for both $V_3Si$ and $V_3Ge$. A maximum in $T_c$ for $V_3Si$ is expected at the critical lattice parameter where the stability of the cubic structure vanishes. ● denotes normal lattice parameter. (After Testardi, 1972.)

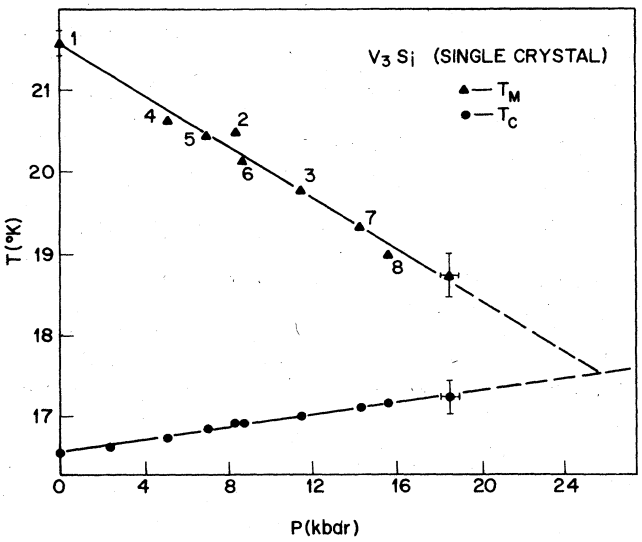



FIG. 13. Pressure dependence of the structural transformation temperature $T_m$ and the superconducting transition temperature $T_c$ of $V_3Si$ (Chu and Testardi, 1974).

Shen (1972) and Vedeneev *et al.* (1972) have observed some of the phonon peaks in $Nb_3Sn$ by tunnelling. Strong low-frequency peaks in the range 6–9 meV have been found.

We have previously discussed the evidence which shows that both the $T_c$ and the structural instability are maximum for the cubic state in $V_3Si$ and that these are reduced in the tetragonal state. For volume-type deformations a correlation between $T_c$ and the shear modulus $c_s$ can also be found. This is shown in Fig. 12 for cubic $V_3Si$ and $V_3Ge$. For $V_3Si$ (lattice parameter 4.72 Å) reducing the atomic volume causes the unstable modulus $c_s$ to decrease further while $T_c$ increases. Since $c_s$ must remain positive the extrapolated behavior indicates some minimum lattice parameter for which the cubic phase is possible. At this point of maximum instability one would expect the highest $T_c$.

It has previously been suggested that much of the difference between $V_3Si$ and $V_3Ge$ may be accounted for from the atomic volume. Figure 12 indicates that if $V_3Ge$ were given the lattice parameter of $V_3Si$ it would probably have a high $T_c$ and a soft $c_s$. (For $V_3Ge$ a negative $d^2c_s/dp^2$ has also been observed at 300°K but is not included in Fig. 12.)

For transforming $V_3Si$ the problem is complicated by the fact that hydrostatic pressure may cause a change in $c/a$ as well as volume. Since the maximum structural instability occurs at the transformation temperature $T_m$, one would expect $T_c$ to increase (or decrease) if $T_m$ moves closer to (or farther from) $T_c$ with pressure. The recent results of Chu and Testardi (1974), shown in Fig. 13, support this expectation. Hydrostatic pressure causes $T_m$ to decrease while $T_c$ increases. The data show that at about 25 kbar $T_m$ would be approximately equal to $T_c$. If $T_m$ continues to decrease with increasing pressure, one would further expect $T_c$ to pass through a maximum (as conjectured above from Fig. 12). However, this behavior could put $T_m$ below $T_c$, a situation not observed in $V_3Si$ samples where $T_m$, which varies among different samples, has always been observed above $T_c$. This leads to an interesting situation where the effect of superconductivity on the structural instability suggested in Sec. IV may be further studied. It is possible that the pressure dependence of $T_m$ at pressure >25 kbar may be altered to avoid $T_m < T_c$. Data at higher pressures would provide useful information. Finally, the expectation of a maximum $T_c$ when $T_m = T_c$ assumes that superconductivity and structural transformations are driven to a nearly exact degree by the same soft modes and that all other pressure effects are negligible. This is, of course, a simplification.

Chu (to be published) has now obtained similar data for $Nb_3Sn$. In this case $T_c$ decreases with pressure. Consistent with the above correlation, however, $T_m$ was found to increase with pressure. These results are shown in Fig. 14.

A model for lattice harmonicity suggested by the anomalous behavior of these materials is shown in Fig. 15 (Testardi, 1972). The model assumes that the A-15 structure is very weak or unstable for tetragonal strains $\lesssim 10^{-3}$. The stable cubic state properties occur at high temperatures where the thermal motion is sufficiently large that the system spends most of its time on the normally steep walls of the potential. For decreasing $T$ and thermal motion, more of the flat portion of the well is experienced leading to the elastic softening. For $T \sim 20$°K where thermal strains are $\sim 10^{-3}$, and largely within the unstable region, a structural transformation occurs. At low temperatures, in addition, static tetragonal strains of $10^{-3}$ would also restore considerable stiffness to the lattice as has been experimentally observed. One may assume from the behavior of $V_3Si$ and $V_3Ge$ given above that the critical flat portion of this curve may also show a strong volume dependence for these compounds. Although the source of the instability must ultimately be predictable from the electronic energy levels of the solid this model would place more emphasis on the phonon behavior than is normally given.

In addition to the effect of phonon softening on the superconductivity, other problems still not quantitatively treated include the contribution of high-frequency soft phonons and the anharmonicity to the specific heat as well as some of the

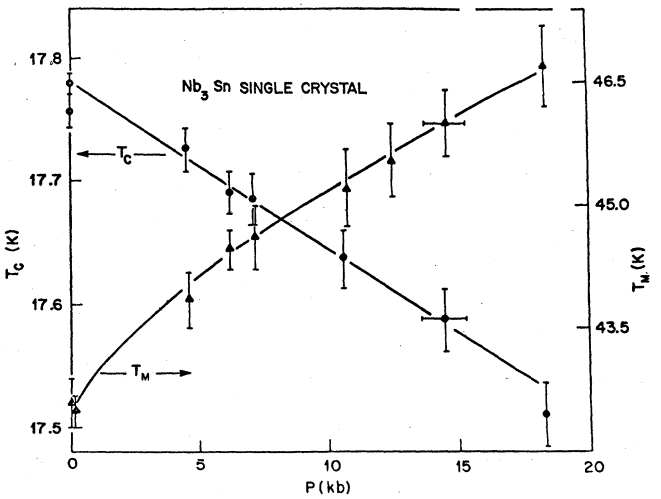
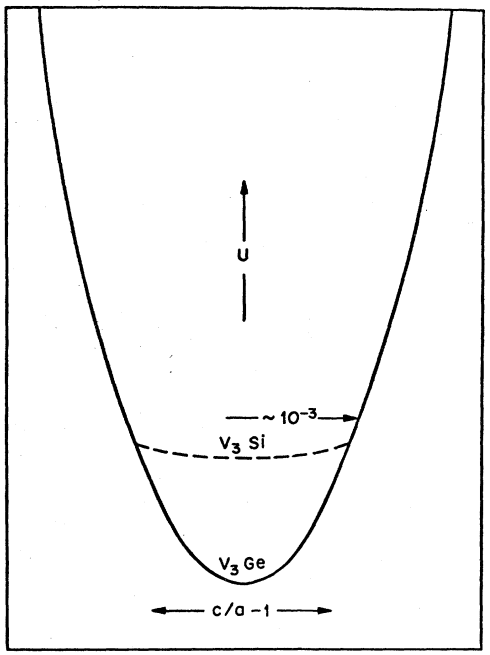



FIG. 14. Pressure dependence of the structural transformation $T_m$ and the superconducting transition $T_c$ for $Nb_3Sn$. (Chu, 1974.)




POTENTIAL WELL FOR INDIVIDUAL SHEAR MODE IN A-15 SUPERCONDUCTORS

FIG. 15. Potential well proposed for tetragonal (shear-type) strains in A-15 high $T_c$ superconductors. (After Testardi, 1972.)

transport properties (e.g., the electrical resistivity, but c.f. Taub and Williamson, 1974, and Cohen and Cody, 1969, who conclude that soft phonon effects are unimportant for the resitivity).

Finally, it should be noted that the structural transformation in these compounds appears to be driven by a $q = 0$ mode while one certainly expects the superconductivity to be determined primarily by the high-frequency modes. Thus acoustic measurements yield relevant data for the former. For superconductivity, however, quantitative estimates require a complete knowledge of the high frequency phonon behavior and the electron–phonon matrix elements. This information is not available. Thus the case for relating structural instability to superconductivity is circumstantial. The proof or disproof of this conjecture must lie in future work.

## VIII. THEORETICAL MODELS

Many of the theoretical models which have been proposed for these materials have been summarized in the review articles by Weger and Goldberg (1973) and Testardi (1973a). Clogston and Jaccarino (1961) first suggested the existence of a peak in the electronic density-of-states in the high $T_c$ compounds to explain their anomalous behavior. Weger (1964) later suggested that the unusual properties of these materials might stem from the linear chains of transition-metal atoms. Most recent calculations employ either the Labbé-Friedel (1966a, b) model or the Cohen, Cody, and Halloran (1967) model. In both cases a density-of-states peak or step is assumed (in the LF model the peak follows from the assumed one-dimensional nature of the A atoms), and the Fermi level is taken to be roughly of order $kT_m$ from this singularity. At very high temperatures thermal broadening prevents the peak from causing unusual behavior of the properties, while at low temperatures a lower free energy is obtained if the crystal distorts and removes the 3-fold (orthogonal-chain) degeneracy in the density-of-states.

Considerable success has been achieved with this model although 3–4 adjustable parameters must be used. A recent more detailed application of this model, which takes into account the sublattice distortion, has been given by Noolandi and Sham (1973). References to part of the extensive literature on these theoretical calculations, including the extensive work of Barisic, can be found in the review articles.

Another model has recently been proposed by Gorkov (1973a, b), in which the particular symmetry properties of the $X$ point in the reciprocal lattice establish the source of the structural instability. This theory shows that the elastic modulus $c_s$ will vary as $\ln T$, in agreement with experiment, and provides some correlations with the superconducting behavior.

APW-band-structure calculations have been made by Mattheiss (1965). However, the density-of-states fine structure assumed in the models discussed above is probably too small to be obtained in any detailed and reliable band-structure calculation of this type. In more recent calculations (Mattheiss, to be published), although the accuracy is insufficient to predict the precise shape of the density of states near the Fermi level, Mattheiss finds that (i) corrections to the Labbé–Friedel and Weger models are sufficient to wash out fine structure in the density of states on an meV energy scale, and (ii) there is no evidence for describing the electronic structure of the A-15 compounds as one dimensional.

The basic shortcoming of the models is that they start from several assumptions of an unusual electronic density-of-states which appear more a restatement of the known unusual behavior than a reasonable (or verifiable) assertion from which unique predictions follow. The models proceed by deriving a free energy which, necessarily, will have fine structure on the scale of $T_m$, and which contains 3–4 adjustable parameters. At this point the models do not differ greatly from each other (though somewhat in detail) and, probably, not greatly from the truth. The calculations which have been made show that, with the adjustable parameters, good consistency in explaining a number of experiments (though not all) can be achieved. This success is nontrivial and quite informative. What is lacking, however, is the physical or theoretical justification for the fine structure or whatever the mechanism for the instability. We do not know how to show, from atomic or chemical information, why such properties occur in these materials. The theory of Gorkov, which exploits a symmetry property of the A-15 structure, may be a start in this direction. In any case, however, a model free energy which ignores the phonon contribution (in particular, from the observed high-frequency softening) may not yield either a self consistent or physically informative description of the behavior of these materials.

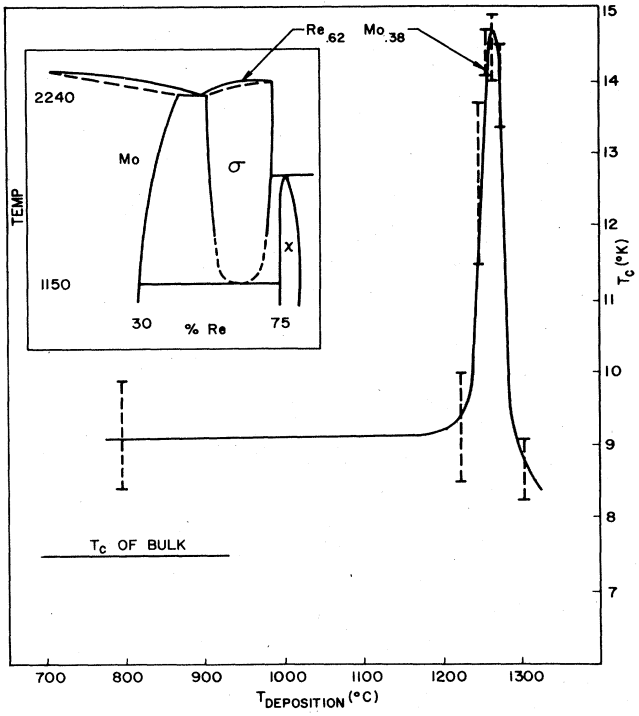



FIG. 16. $T_c$ vs film deposition temperature for $Mo_{0.38}Re_{0.62}$. Insert shows part of the phase diagram after Knapton (1958). Note the large enhancement of $T_c$ for films prepared at temperatures close to the structural transformation temperature. Later measurements showed the true film-surface temperature to be ~100–150°C below that given in the figure. (After Testardi *et al.*, 1971b.)

## IX. HIGHER $T_c$'s

The experimental results discussed above can suggest that the phonon softening which accompanies structural instabilities may lead to enhanced $T_c$'s, but if the softening is sufficiently large to trigger a structural transformation a reduction in $T_c$ will occur (Testardi, 1972). The unique feature of the A-15 superconductors may lie in that their phonon softening could make an appreciable contribution to $T_c$ while the structural transformation, if it occurs, lowers $T_c$ by amounts only ~1°K.

One task for the experimentalist in this field is to determine what types of structural instabilities (leading to transformations) can be good for superconductivity. Based on the A-15 behavior, three conditions which may possibly give enhanced $T_c$'s are: (i) the parent and transformed phases should be chemically similar so that gross diffusion is not required; (ii) the (incipient) structural transformation should be a displacive rather than a reconstructive one (no rebuilding of the unit cell should be required); and (iii) there exist a small energy barrier, $\sim c\epsilon_v^2$ (where $c$ is an elastic modulus and $\epsilon_v$ is the amplitude of atomic motion), between the phases at low temperature. Whether the structural transformation (if it occurs) has a first- or second-order character is not as important as having large precursor effects (hopefully, mode softening) which extend over a wide range in temperature above $T_m$.

Enhanced $T_c$'s may be associated with structural instabilities in other materials, these conditions possibly occurring near solid-state phase transformations which are numerous at high temperatures. One attempt to detect this has employed sputtered films deposited at high temperatures where phase transformations are known to occur (Testardi *et al.*, 1971b). The reasoning is that sputtering may freeze in the unstable atomic structure and this may contribute to enhanced $T_c$'s. The results of experiments on Mo–Re alloys are shown in Fig. 16 along with a portion of the phase diagram showing the section of interest. Films sputtered in a narrow temperature interval at approximately the eutectoidal decomposition temperature of the $\sigma$ phase do show a significant increase in $T_c$. A similar though less dramatic effect has now been found in a large number of sputtered alloy films (Testardi *et al.*, 1974).

The history of high $T_c$ A-15 superconductors began in 1954 when Hardy and Hulm found $V_3Si$ to be superconducting at ~17°K. Matthias *et al.* (1954) subsequently reported a $T_c \sim 18$°K in $Nb_3Sn$. Alekseevskii *et al.* (1966) were first to show that the A-15 ternary $Nb_3Al_{0.8}Ge_{0.2}$ had a higher $T_c$ than the constituent compounds. Later, Matthias *et al.* (1967) obtained $T_c \sim 21$°K with this alloy. Webb *et al.* (1971) have achieved $T_c$'s above 20°K in $Nb_3Ga$. Recently Gavaler (1973) provided an important advance in obtaining $T_c = 22.3$°K in $Nb_3Ge$ sputtered onto hot substrates in high argon pressures. This was later increased to $T_c$ onsets ~23°K (Testardi *et al.*, 1974; Gavaler *et al.*, 1974).

Whether structural instability is the promise or the pitfall of superconductivity is yet to be decided. In the pursuit of higher $T_c$'s, however, an important question for research—what makes structures unstable—will hopefully receive some answers.

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