Low-Temperature Structural Transformation in V_3Si

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This paper discusses in detail the experimental observations on the low-temperature martensitic-like transformation of the compound superconductor V_3Si. Evidence is presented showing that the transformation from the high-temperature cubic β-tungsten phase to a tetragonal structure occurs at temperatures above the superconducting transition T_c(17.0°K). The detailed behavior of the transformation can vary between specimens, most probably because of deviations from exact stoichiometry. In high-resistance-ratio specimens, the transformation to tetragonal is complete at $T_m=21.0\pm0.5$°K with a c/a ratio increasing continuously from unity and reaching a maximum value of 1.0024 within 0.1°K of T_c. The volume of the unit cell remains constant to better than one or two parts in 10^4 in both the cubic and tetragonal phases below 30°K. No further change in c/a occurs as the temperature is lowered, and hysteresis effects are never observed. Evidence is presented which leads to the conclusion that the transformation is of second order. Our results together with Testardi's ultrasonic measurements imply that the transformation is a result of a general softening of the lattice as a temperature is lowered, and in particular is triggered at T_m by the near-vanishing of the restoring force for shear in a $[1\bar{1}0]$ direction on a (110) plane. The structural transformation is not necessarily a precursor of superconductivity, but it is most probably the large temperature dependence of the elastic properties that leads to both phenomena.

THE compound superconductor V_3Si ($T_c=17.0$°K) undergoes a martensitic-like transformation in the vicinity of T_c, as we have reported briefly.[1] This paper will present the results of further work and will give some details of the experimental arrangements used to detect the phenomenon. We have investigated the occurrence of the transformation in different single crystals of V_3Si with varying structural and electrical properties. Also, we have attempted to find what relationships exist between this transformation and the superconductivity of V_3Si.

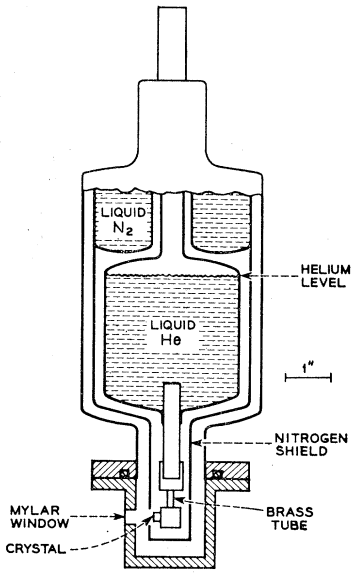

FIG. 1. Schematic of the Dewar arrangement.

The work was initiated when Shull reported[2] some unexpected broadening of neutron diffraction peaks from a sample of V_3Si at helium temperatures. We found that this and various effects described herein resulted from a structural transformation at low temperatures from the cubic form that is stable at ordinary temperatures to a tetragonal structure. The cubic form belongs to space group $Pm3n$ with six V atoms in positions (c) and two Si atoms in positions (a); it is basically an ordered form of the A15 structure, formerly known as the "β-tungsten" structure. The departure from cubicity increases as the temperature is lowered below the temperature, T_m, at which the transformation begins; T_m varies from sample to sample but in general is higher than the superconducting transition temperature T_c by several degrees Kelvin.

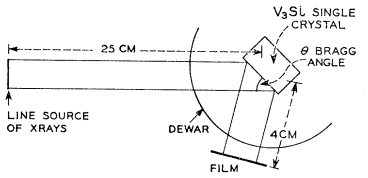

FIG. 2. Geometry for the Berg-Barrett pictures. The film-to-specimen distance is limited by the diameter of the tail section of the Dewar.

EXPERIMENTAL

All x-ray measurements were made with the helium Dewar indicated schematically in Fig. 1. The sample was mounted on a copper block connected by a thin-wall brass tube to a copper bar extending up into the liquid helium. The sample temperature could be raised above the liquid temperature by activating a heating

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† Experiments performed while this author was on temporary leave from the Institute for the Study of Metals, the University of Chicago.

[1] B. W. Batterman and C. S. Barrett, Phys. Rev. Letters 13, 390 (1964).

[2] C. G. Shull, MIT Annual Report—Research in Materials Science 1963–1964 (unpublished).

coil located in the copper block on which the sample was mounted. A copper radiation shield with aluminum-foil windows (not shown in Fig. 1) surrounded the specimen and was clamped to the mounting block. This shield was surrounded by another shield at liquid-nitrogen temperature. Carbon resistance thermometers were placed in holes 0.5 cm apart in the sample block.

BERG-BARRETT TOPOGRAPHS

X-ray topographs were made at different temperatures with the arrangement indicated in Fig. 2. Exposures on fine-grained film were made when the specimen was held stationary at an angular setting giving a desired reflection. To maximize resolution in the topographs, the film was placed normal to the reflected beam and as close to the specimen as was possible without inserting it in the cryostat. Topographs such as Fig. 3 were made using Cu $K\alpha$ 200 or 400 reflections on Eastman type M x-ray film with 10-min exposures.

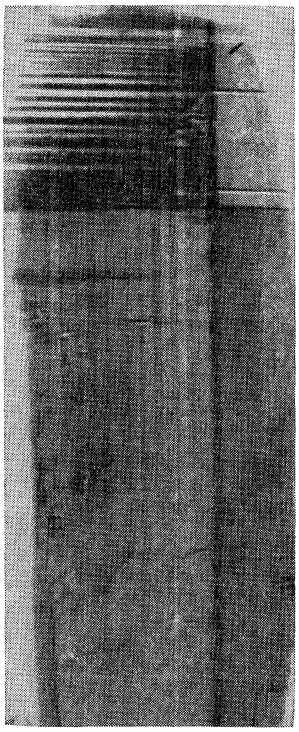


FIG. 3. Example of a Berg-Barrett topograph of V_3Si at 4.7°K. The reflection is 400 with Cu $K\alpha$ radiation. The film plane is normal to the diffracted beam causing a foreshortening in the horizontal direction.

Figure 3 is a 400 reflection from a (100) surface of a V_3Si crystal. The topograph shows the lamellar domains that develop parallel to {110} planes in the crystal on cooling below T_m. Various experiments showed that the lamellar structure in the topographs was caused by reflected beams originating in adjacent domains being tilted slightly from each other; the lattice in each crystal domain was slightly disoriented from the lattice in the adjacent domains when the lattice was distorted from cubic into tetragonal symmetry. The lamellar structure disappeared when the specimen returned to cubicity on heating.

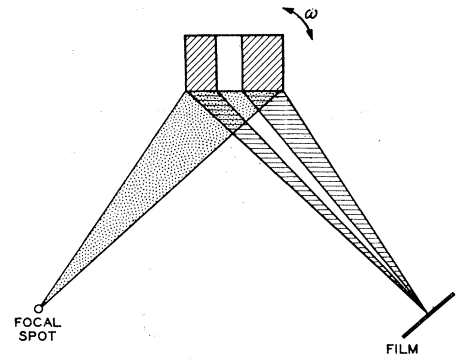


FIG. 4. Schematic showing the focusing condition which eliminates tilts from the d spacing measurement. As the crystal is rotated, domains of the same d spacing will diffract at different times but will image at the same point on the film. This is basically the geometry for a powder diffractometer.

The same arrangement was used for thin crystal transmission topographs, which resolved individual dislocations.

LATTICE-PARAMETER DETERMINATION

In measuring lattice parameters, any errors arising from the lattice tilts from one domain to another must be avoided. We employed two methods to accomplish this. The first is a film technique which is generally useful to measure *relative* changes in lattice spacings. The second,[3] using counter techniques, measures an *absolute* spacing by establishing the differences in crystal angle settings for which diffraction takes place.

The film technique for *relative* spacings uses the focusing condition shown schematically in Fig. 4. The film is kept stationary and the crystal is rotated through its reflecting range. Although different domains will diffract at different crystal positions, all domains of a given d spacing will produce an image at a given point on the film. A convenient and accurate calibration for lattice parameter differences is provided for in the wavelength difference $K\alpha_1-K\alpha_2$, which is accurately known; the doublet separation on the film serves as a unit for measuring differences in lattice spacing.

A sequence of parameter determinations near the temperature of the cubic to tetragonal transformation in V_3Si is given in Fig. 5. The absolute temperatures indicated are accurate to about ±0.5°K, whereas differences are accurate to better than 0.1°K. The sequence reveals a rapid onset of tetragonality below T_m. The films show that in the region irradiated, there is no cubic phase present below T_m; in this region the transformation is complete. It is interesting to note that at 18.3°K and below, the pattern is a triplet,

[3] W. L. Bond, Acta Cryst. 13, 814 (1960).

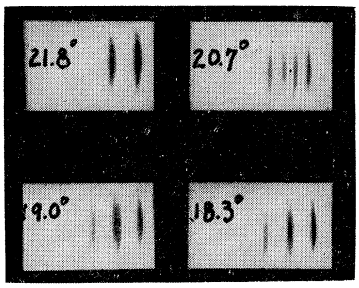


FIG. 5. Example of the film technique of Fig. 4. The crystal is oscillated through the reflection range at 1°/min for the (600) reflection ($\theta=78.4°$) with Cu $K\alpha$ radiation. The doublet at 21.8°K is the normal $\alpha_1-\alpha_2$ separation and would correspond to a $\Delta d/d$ of 0.0025. The triplet at the lowest temperature (18.3°K) shows, by inspection, a ratio of spacings of 1 ± 0.0025.

indicating that the ratio of the two lattice parameters involved is identical to the Cu $K\alpha$ wavelength ratio $K\alpha_2/K\alpha_1$; and hence, simply by inspection it is clear that the ratio of the two parameters (c and a if one assumes tetragonality) must be 1.0025.

The technique for the *absolute* lattice parameter measurements, applicable to good single crystals, has been discussed in detail by Bond.[3] One simply measures the crystal position Φ_1 for diffraction from a high order reflection. The crystal is then rotated to Φ_2 so that the Bragg angle for reflection from the same planes is reached where now the diffracted beam is on the opposite side of the incident beam. The absolute Bragg angle θ for the reflection is given by the relation $\Phi_1-\Phi_2=\pi-2\theta$. This method can be applied to V_3Si not only in the cubic state but also in the tetragonal state, below T_m, because the tetragonality subdivided the crystal into subgrains having only a few accurately defined orientations. Some irradiated areas appear to have effectively only one or two orientations. It is therefore possible to separate the effects of the lattice tilts and the lattice parameters on $\Phi_1-\Phi_2$ and thus determine θ. The results of absolute measurements of this type on one specimen are presented in Fig. 6; these are discussed in a later section.

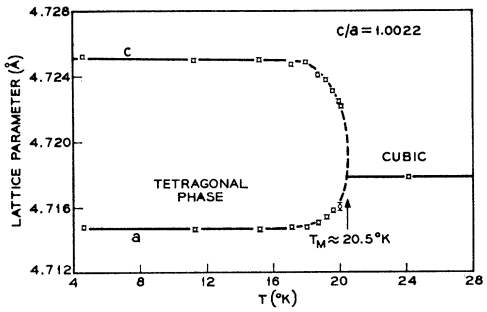


FIG. 6. c and a parameter versus T of a well-behaved specimen. The data in the dashed region were difficult to obtain because of peak overlap and broadening. All evidence indicates that the change is smooth but rapid in this region.

THE STRUCTURE OF THE NONCUBIC PHASE

The obvious similarities between the present transformation and the cubic-tetragonal transformation in indium-thallium alloys[4] immediately suggested that the noncubic phase might be tetragonal. A study of $h00$ and $hh0$ reflections showed that both types split into two components at temperatures below T_m, and that hhh reflections remained unsplit and undisplaced from their positions above T_m. These facts and the fact that the relative d spacings for the pair of split $h00$ reflections differed twice as much as for the pair of split $hh0$ are consistent with tetragonality.

To determine whether the tetragonal c/a ratio is greater or less than unity and to determine with what certainty the axial ratios correspond to those for tetragonal unit cells rather than unit cells of lower symmetry, the following observations were made. On a crystal with face parallel to (100), we observed the domain pattern of Fig. 3 with a Berg-Barrett 400 topograph and established with the film technique using a 600 reflection that two lattice spacings were present; the ratio of these was determined from the separation of the reflection on the film. This established that the (100) face of the crystal in the transformed state was made up of domains which reflected with two different ($h00$) lattice spacings. The crystal was then rotated about the [010] direction [see Fig. 7(a)], in which [010] is perpendicular to the plane of the drawing] and the 404 reflection was photographed. This then became an asymmetric reflection from the same (100) crystal face. With the film method we found that only one {404} spacing was present in the noncubic state. Since the x-ray beam was much wider than the domains, we concluded that both types of domains have the same {101} lattice spacing.

The configuration was consistent with an orthogonal system, as may be seen from Fig. 7(b). Here are indicated two adjacent domains which present planes with two different lattice spacings (a and c) parallel (very nearly) to the original (100) cube face but which would give a single (404) spacing for diffraction as in Fig. 7(a). This single (404) spacing was measured; and when with the same orientation the crystal was heated to the cubic phase, the relative lattice spacings of the 404 reflections in the two phases could be determined.

We assume the possibility of an orthorhomic crystal and call the third axis b. If the crystal were rotated 90° about the [100] direction, the resulting domain configuration consistent with Fig. 7(b) would be as indicated in Fig. 7(c). With this orientation the 404 cubic reflection should be split into 440 and 044 in the noncubic state because the face diagonals of the two possible domains would no longer be equal. This is indeed what was observed. Using the cubic 404 line

[4] J. S. Bowles, C. S. Barrett, and L. Guttman, Trans. AIME **188**, 1478 (1950); Z. S. Basinski and J. W. Christian, Acta Met. **2**, 148 (1954).

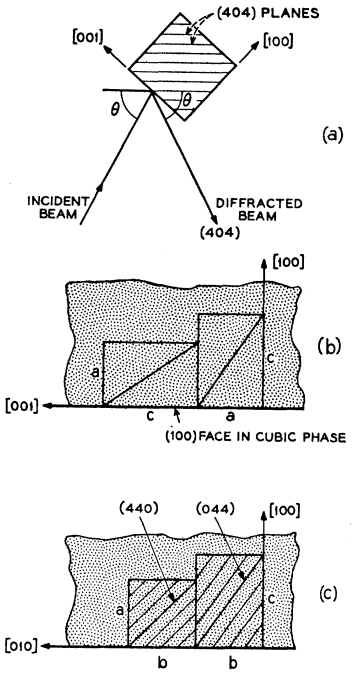


FIG. 7. (a) Rotation about [010] axis (normal to plane of the figure) to record the 404 reflection asymmetrically from the (100) cut face. (b) The two types of domains consistent with observation. Note that the diagonals in both domains are equal and hence the corresponding 404 reflections have the same Bragg angle although they diffract at slightly different crystal angles. (c) Figure (a) rotated 90° about the [100] axis. Now the two face diagonal reflections 440 and 044 will have the same spacing as that in Fig. 4(b) only if $a=b$.

($T>T_m$) as a reference, the relative lattice spacings of the 440 and 044 pair of lines associated with the configuration in Fig. 7(c) was compared with the single 404 spacing corresponding to Fig. 7(b). The distance between the 404 tetragonal and 404 cubic lines was indentical with that between the 044 tetragonal and the same 404 cubic line. This indicates that $a=b$.

The line positions can be measured on the films to a precision of 0.05 mm which corresponds to a $\Delta d/d=\pm 0.00006$. From the relative spacings in the two orientations, it was established that $c>a$ and that $a/b=1.0\pm 0.00006$. The data are consistent with a crystal in the tetragonal system.

RESULTS

The results of measurements of the transformation in V_3Si indicated that the metallurgy of the specimens plays an important role in determining its details. We will discuss so-called "well-behaved" specimens first and then point out the exceptions.

The lattice parameter of a well-behaved specimen was shown in Fig. 6. The transformation temperature T_m (first loss of cubicity upon cooling) was at 21 ± 0.5°K. The c/a ratio increased rapidly from unity upon decreasing temperature to its maximum value at about 17°K and remained constant upon lowering the temperature. The maximum c/a value was in the range 1.0024 ± 0.0002. Hysteresis effects between cooling and reheating were never observed; our limit of detectability was several tenths of a degree K. After a cooling cycle (or several cycles) through T_m the sample always returned to a single cubic crystal of the original orientation without detectable alterations in the cubic state topographs. The volume of the unit cell was constant throughout the cubic and tetragonal phases below 30°K to at least one or two parts in 10^4.

The time to reach equilibrium lattice spacings at a given temperature appeared to be substantially the same as the time for the sample and its mounting to equilibrate thermally, which was the order of tens of seconds. The unit-cell volume remained unchanged to within about two parts in 10 000 when the cubic transformed to the tetragonal and remained unchanged throughout the temperature range of the c/a variation. A comparison of the position of the 600 peaks as a function of temperature from 4.3°K through T_m showed a smooth variation in the c/a ratio to within a few tenths of a degree of T_m. The transformation was in general complete. That is, the specimen became completely tetragonal or completely cubic, there was no mixture of the two phases at a given temperature.

In one experiment a 10 mh coil was placed around the specimen and the superconducting transition (which had a width of the order of 0.3°K) could be detected with a standard ac bridge. At the same time, the effective c or a parameter of the tetragonal phase could be observed as the temperature was lowered. Precisely at T_c, as determined by the coil inductance, the increase in c/a ratio was arrested and the cell parameters remained unchanged between 16.9°K(T_c) and 4.5°K. This is strong evidence of a relationship between the phase transformation and the superconductivity of the compound.

The above results are what we feel may be characteristic of a pure stoichiometric specimen and represent the behavior of most of the several specimens investigated. There were notable exceptions to this behavior, however, the most extreme being a single crystal which remained cubic down to 1.9°K and yet became superconducting below 17°K.

As Greiner and Mason[5] have already pointed out, single-crystal specimens grown as these were can contain visible second-phase precipitates which can comprise up to several percent of the sample. In general, even with large amounts of second phase inclusions, the V_3Si matrix is usually quite perfect, having few if any high-angle grain boundaries. The seed end of the crystals has the least visible second phase; whereas as growth progresses, more second phase comes out. The part to be grown last tends to contain an interconnected network of the impurity, which can be seen metallographically. The crystals can have an appreciable composition change along the growth direction which becomes evident in the resistance ratio being variable and in the characteristics of the transformation.

Figure 6 gives the c and a parameters of a well-behaved crystal. Figure 8 gives the c parameter of a

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

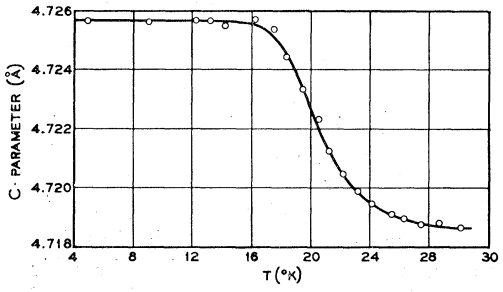


FIG. 8. C parameter versus temperature. The initial drop in the curve extrapolates to about 23°K. There is, however, an inflection point and the cubic parameter is reached at approximately 27°K.

more complicated behavior. As temperature was increased from 4.5°K, no change occurred in this latter crystal until $T=T_c$; c then decreased rapidly along a curve which extrapolates to $T_m=23$°K. There is an inflection point in the curve at 21°K and the crystal remained tetragonal up to approximately 27°K. Another specimen which transformed over its entire face and yielded good Berg-Barrett pictures had a value of $(c/a-1)$ half as large as the value 0.0024 of the well-behaved crystals.

The one specimen which did not transform was from the seed end of a high-quality crystal. Berg-Barrett pictures showed that only small regions on one face of the crystal, which was one cm in diameter and 0.2 cm thick, underwent the transformation. When the lattice parameters of these small regions were measured, it was found that tetragonal cell size varied continuously from the lowest temperature (4.5°K) to the beginning of cubicity at approximately 25°K. The integrated intensities of low order reflections measured with neutrons by Shull and Wedgewood[6] on the same crystal had a similar behavior with temperature.

The depth of penetration of the Cu $K\alpha$ x rays in these measurements was of the order of microns. To determine whether the transformation took place in the *bulk* of the specimen we thinned a single crystal by grinding and polishing to a thickness of 0.01 cm (0.004 in.) and measured a high order reflection in *transmission* with Mo $K\alpha$ radiation.[7] The crystal was one which had some regions which transformed and some which remained cubic. We could establish unequivocally that in some of the tetragonal regions no trace of the cubic lines existed below T_m, thus proving that the entire thickness was tetragonal and that the martensitic transformation was not in general confined to surfaces.

[6] C. Shull and A. Wedgewood (private communication).

[7] This experiment was performed with J. R. Patel as part of a general study of the properties of the V_3Si transformation. The results of this study will be published shortly.

DISCUSSION

Concerning the nature of the transformation *per se* (i.e., without considering the relationship to superconductivity) the following can be said. The transformation is martensitic in the sense that there is no diffusion, and a crystal shape change is involved. The banded tetragonal structure is understood as a mechanism permitting the shape change to occur without large accompanying strain energies or boundary energies. Presumably, the mechanism involves very little atomic rearrangements and is similar to the well-known martensitic transformation of indium-thallium.[4] In the In-Tl transformation the banded structure was shown to be the result of a double $\{110\}$ $[1\bar{1}0]$ shear on two $\{110\}$ planes at 60° to one another.

To be consistent with the morphology of that transformation, the main bands in Fig. 3 should contain sub-bands within the main bands. That these were not recognized in the V_3Si topographs can be ascribed to a lack of sufficient resolving power. Our observations would be consistent with each band in Fig. 3 containing both c and a poles nearly normal to the surface of the crystal. The electron diffraction observations of Goringe and Valdrè[8] showing bands with spacings the order of 250 Å probably correspond to the sub-bands mentioned above.

All the measurements made thus far are consistent with the transformation being of second order. No discontinuities in c/a ratio or hysteresis effects were observed as temperature was varied. Additional measurements[7] tend to support the contention of a second order transition.

The variability of the transformation from specimen to specimen is curious. The amount of second-phase material (i.e., other than V_3Si) does not correlate with the varying tendency to transform, but the resistance ratio $R_{300°K}/R_{20.5°K}$ does correlate: those crystals which did not transform had low resistance ratios. In one single crystal, for instance, the seed end which had a resistance ratio of 14 did not transform, while transformation did occur in regions farther away from the seed, where the resistance ratio increased to about 20; there was no large difference in the amount of second phase material in these two regions. Farther away from the seed, where the amount of second phase reached the order of several percent, the ratio remained high and the transformation took place. Low resistance ratios presumably indicate a departure from exact stoichiometry that inhibits the transformation.

We can relate this transformation to superconductivity through the following observations. The strongest link is the arrest of the c/a increase on cooling at precisely the superconducting transition T_c in which vicinity there is a discontinuous behavior in sound

[8] M. J. Goringe and V. Valdrè, Phys. Rev. Letters 14, 823 (1965).

attenuation[9] and a specific heat anomaly.[10] On the other hand, as the specific heat measurements show,[10] a sample which has little or no transformation still can become a superconductor throughout its volume.

The elastic constants determined by Testardi *et al.*[9] show a phonon instability leading to a vanishingly small restoring force for $\{110\}\ \langle 1\bar{1}0\rangle$ shear and this implies a strong temperature dependence for portions of the phonon spectrum. Since superconductivity is a result of a phonon-electron interaction, the link between the structural transformation and superconductivity is no doubt via the phonon spectrum. As temperature is lowered from room temperatures, the phonon spectrum changes. This produces relatively large reductions of the elastic constants C_{11} and C_{12} and a value of $C_{11}-C_{12}$ approaching zero, leading to the very low restoring force for $\{110\}\ \langle 1\bar{1}0\rangle$ shear and the triggering of the tetragonal transformation. In the Appendix we show for completeness how such a shear can lead to a tetragonal structure consistent with experimental observations. Further reduction in temperature brings further changes in the phonons and results in the transformation to the superconducting state. In this picture, the structural transformation is not a precursor of superconductivity but results from a common cause namely, the variation of the phonon spectrum with temperature.

The only other A15-type compound for which there is evidence of a transformation is Nb_3Sn. This statement is based on powder diffraction patterns that lack sufficient resolution of the broadened lines to allow one to draw unequivocal conclusions. However, the trend of broadening of certain Nb_3Sn lines on cooling to low temperatures was so nearly identical in type to that of V_3Si powder patterns as to imply a similar distortion from cubic symmetry and a similar transformation.

ACKNOWLEDGMENTS

The experimental assistance of L. D. Fullerton and P. E. Freeland is gratefully acknowledged. To list all our colleagues at Bell Telephone Laboratories who have contributed in some way to the understanding of the properties of V_3Si as discussed in this paper would require a substantial expansion of this paper. We, therefore, acknowledge and thank them collectively. Outside of this group we are indebted to Professor C. Shull and Dr. A. Wedgewood of Massachusetts Institute of Technology for invaluable discussions of their neutron-diffraction experiments.

[9] L. R. Testardi, T. B. Bateman, W. A. Reed, and V. G. Chirba, Phys. Rev. Letters **15**, 250 (1965).

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

APPENDIX

The results of Testardi *et al.*[9] showing the low restoring force for $\{110\}\ \langle 1\bar{1}0\rangle$ shear give the basis for the following speculation on the mechanism of the transformation from cubic to tetragonal. Bowles *et al.*[4] have shown that two $\{110\}\ \langle 1\bar{1}0\rangle$ successive shears of ϵ and 2ϵ on two $\{110\}$ 60° apart will change a cube to a tetragonal prism. For completeness we show this graphically in Fig. (9). In Fig. 9(a) a small shear of magnitude

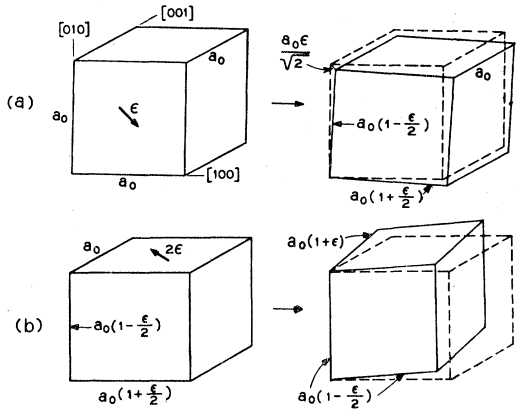
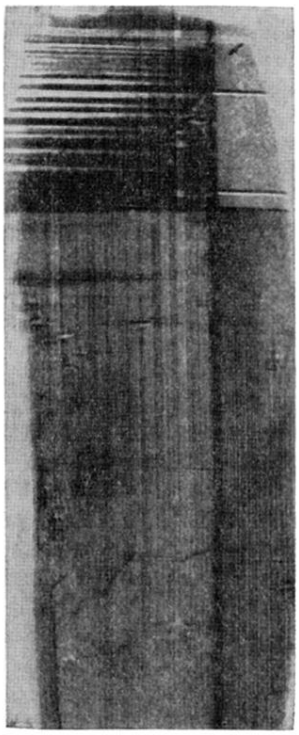


FIG. 9. Application of two successive shears of the $\{110\}\langle 1\bar{1}0\rangle$ type to transform from cubic to tetragonal.

ϵ acting on the (110) plane in the $[1\bar{1}0]$ direction produces a rectangular parallelepiped of sides $a(1-\frac{1}{2}\epsilon)$, $a(1+\frac{1}{2}\epsilon)$, a_0. In Fig. 9(b) a second shear of magnitude 2ϵ acting on the (101) in the $[\bar{1}01]$ direction changes this to a tetragonal form of sides $a(1-\frac{1}{2}\epsilon)$, $a(1-\frac{1}{2}\epsilon)$, $a(1+\epsilon)$. Since only shears are involved, the volume remains constant. If the second shear acted, in the opposite sense the necessary shear would be of magnitude ϵ. Thus, application of the same type of soft shear two times in the ways described can lead to a tetragonal structure with same volume as the initial cube. This is consistent with the experimental observations.



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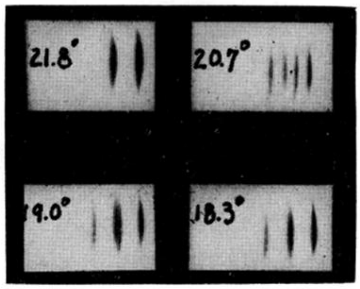

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