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Pressure-Induced Phase Transformation in Nontransforming V_3Si

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(Received 7 April 1978)

The dependence on hydrostatic pressure of the superconducting transition temperature T_c of a nontransforming V_3Si single crystal is determined to 45 kbar with use of a newly developed pressure cell. A clear break in the slope dT_c/dP at 32 kbar supports the existence of the pressure-induced structural phase transition predicted by Larsen and Ruoff.

High-temperature superconductivity, occurring, for example, in A-15 compounds like Nb_3Ge, Nb_3Sn, or V_3Si, is coupled with structural phase instabilities and other anomalous normal–solid-state properties.[1,2] In recent years considerable theoretical and experimental effort has been directed towards a better understanding of this interrelation. High-pressure techniques are especially well suited for testing theory because it allows a well-defined continuous variation of parameters using only a single sample.

One of the most interesting of such anomalous normal-state properties is the drastic reduction of the elastic shear modulus $c_s = \frac{1}{2}(c_{11} - c_{12})$ with decreasing temperature observed, for example, in V_3Si.[3] In so-called "transforming" crystals the lattice softening is sufficient to lead to a cubic-to-tetragonal phase transformation[4] at a temperature $T_L \approx 21$ K only slightly higher than that for the onset of superconductivity $T_c \approx 17$ K; in "nontransforming" crystals, on the other hand, the reduction in c_s is less dramatic and no phase transformation occurs. Pressure studies on "nontransforming" V_3Si crystals are of interest for the following reasons: (1) In "transforming" V_3Si T_L and T_c approach each other under pressure[5] and meet, allowing a study of superconductivity in both tetragonal and cubic phases, consecutively. To investigate accurately the interference of this structural transformation with superconductivity, knowledge of the behavior of superconductivity in a "nontransforming" crystal is essential. (2) Larsen and Ruoff[6] have shown that in "nontransforming" V_3Si c_s decreases with pressure at low temperatures; they predict the onset of a lattice transformation at pressures near 30 kbar. Previous investigations[7] to 20 kbar have found no evidence for a phase transition.

Using a newly developed hydrostatic pressure cell for electrical resistivity measurements, we have determined the pressure dependence of T_c to 45 kbar for two V_3Si single crystals. These crystals are of the "nontransforming" type as evidenced by low-temperature x-ray diffraction studies[8]; in addition, there is no sign from 18 to 30 K of the slight kink in the temperature dependence of the resistivity which is believed to mark the cubic-to-tetragonal transition.[9] The two V_3Si single crystals are cut from the same host crystal and have residual resistance ratios (RRR) of ~14 and $T_c = 16.6$ K with 10%-90% transitions widths $\Delta T_c = 0.015$K.

The results of the present experiments are shown in Fig. 1, where the superconducting transition temperature T_c is plotted versus pressure. The most important feature of the data is the clear break in slope dT_c/dP at a pressure of about 32 kbar. This is strong evidence for the existence of the pressure-induced phase transition predicted by Larsen and Ruoff.[6] Breaks in slope or even discontinuities in $T_c(P)$ are well known to occur at phase boundaries, the most pertinent example in our case being the sharp decrease in slope dT_c/dP observed at about 20 kbar in transforming V_3Si, which defines the tetragonal-to-cubic phase boundary.[11] A slope change at the cubic-to-tetragonal phase boundary is also expected by the theory of Bilbro and McMillan.[12] The nature of the present pressure-induced transformation at 32 kbar is presumably cubic-to-tetragonal, in analogy with the temperature-induced Batterman-Barrett transformation seen in "transforming" crystals, since they are both driven by a softening of the same elastic constant c_s.

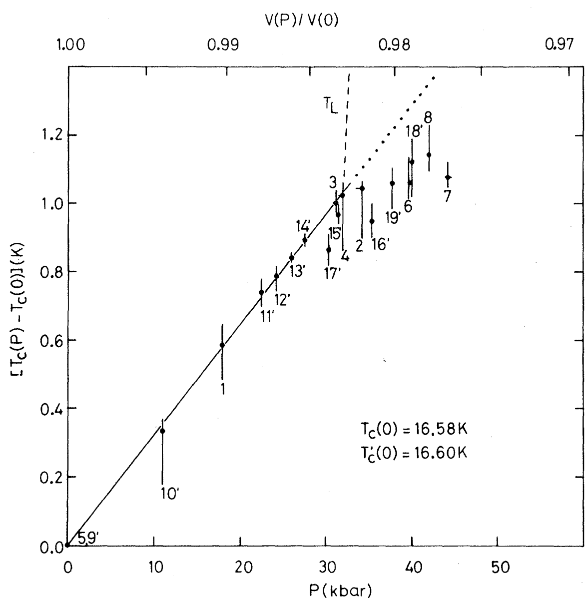

FIG. 1. Superconducting transition temperature versus hydrostatic pressure or relative volume (see Ref. 10) for "nontransforming" V_3Si single crystals. Two crystals were measured (numbers primed and unprimed), numbers giving order of measurements. Note break in slope at about 32 kbar. Solid line extended with dots is drawn for clarity and reveals linear dependence of T_c on P to 32 kbar. Dashed line indicates cubic-tetragonal phase boundary (see text). Error bars for P are smaller than points except for measurements 6, 7, and 8 where contacting problems caused artificial width. Vertical bars give 10%-90% widths for V_3Si.

As is evident in Fig. 1, the superconducting transition temperature T_c has an accurately *linear* reversible pressure dependence with $dT_c/dP = +(32.2\pm 0.5)$ mK kbar^{-1} for pressures below the critical pressure for the phase transition. This linear dependence thus extends previous results to considerably higher pressures. In addition, T_c does not appear to go through a maximum to 45 kbar. According to a calculation by Labbé, Barišić, and Friedel,[13] such a maximum in $T_c(P)$ would be expected at sufficiently high pressures. In addition these findings appear inconsistent with the lattice model of Testardi[14] where T_c versus pressure should show a marked negative curvature and reach a maximum at the critical pressure where the stability of the cubic structure vanishes. It is felt that the present results can be properly accounted for by an "electronic" model such as that of Bilbro and McMillan[12] and/or Lee, Birman, and Williamson.[15]

For the present work a new type of pressure cell for electrical resistivity measurements was developed.[16] This cell, shown in Fig. 2, is based on the miniature diamond anvil cell.[17] The samples and pressure fluid are located in a small bore in a metal gasket. Two opposing WC anvils press into the metal gasket generating hydrostatic pressure in the pressure fluid. The six electrical leads which are brought into the pressure chamber allow accurate four-probe resistivity measurements on the two samples, a lead manometer,[18] and the V_3Si single crystal. The samples are mounted on either side of a small plastic disk which provides electrical insulation. The pres-

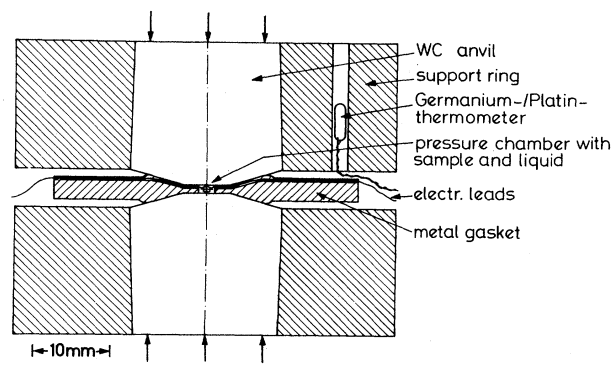

FIG. 2. New hydrostatic pressure cell for four-point electrical resistivity measurements. Opposing WC anvils press into metal disk with pressure chamber containing pressure fluid and samples.

sure-transmitting fluid consists of a 1:4 mixture of ethanol-methanol which remains liquid to 100 kbar at room temperature.[19] With this cell it has to date been possible to reach ~ 55 kbar at room temperature (monitored by a Manganin coil) and ~ 45 kbar at liquid-helium temperatures. The pressure change on cooling from 300 to 10 K is estimated from the temperature dependence of the resistivity of the Pb sample to be less than +10% at all pressures. This result was confirmed by comparing the pressure at room temperature, inferred from the known pressure dependence of the resistivity of Pb,[20] to the pressure at low temperatures from $T_c(P)$ of Pb.[17]

The scatter in the data in Fig. 1 above 30 kbar is presumably due to pressure hysteretic effects in the phase transition or to the detailed past pressure or thermal history of the two samples. The superconducting transition width of the Pb sample decreases by a factor of 2 up to 40 kbar and the transition width of the V_3Si sample decreases up to the pressure (~ 32 kbar) where the phase transitions believed to occur. Significant shear stresses or pressure inhomogeneities, if present at low temperatures, should cause these widths to increase. In addition, the pressure dependence of the residual resistance ratio has the opposite sign to that expected for uniaxial stress[21] and shows no irregularities near 32 kbar. Indeed, a buildup of shear stress would seem unlikely in this cell where the pressure is only changed at room temperature and the pressure increase upon cooling has been shown to be quite small.[22]

We now discuss in detail the pressure-induced phase transition and its relationship to the elastic properties of V_3Si. As shown in Fig. 3 the shear modulus $c_s = \frac{1}{2}(c_{11} - c_{12})$ is reduced drastically with decreasing temperature. Below $T_c \approx 17$ K, the softening of the lattice is arrested.[3,4] Whether or not a crystal is of the "transforming" or "nontransforming" variety thus depends on whether or not the reduction of c_s for $T > T_c$ is sufficient to precipitate the cubic-to-tetragonal Batterman-Barrett transformation. The presence of defects and/or internal strains stiffens the crystal and reduces the falloff of $c_s(T)$, preventing the transition. As indicated by the arrows in Fig. 3, the pressure dependence of c_s is strikingly different for the two types of crystals. A "transforming" crystal is found to stiffen with pressure ($dc_s/dP > 0$) at low temperatures,[23] which is consistent with the decrease of T_L with increasing pressure observed by Chu and Testardi.[5] For a "nontransforming" crystal, however, Larsen and Ruoff[6] find a softening under pressure to 2 kbar. Recent thermal expansion measurements[24] support this result. Extrapolating $c_s(P)$ to higher pressures and assuming that dc_s/dP is independent of pressure and only a function of temperature, they find that for any temperature between the superconducting transition temperature T_c and 80 K there should exist a pressure P_L such that c_s vanishes leading to a phase transition. Larsen and Ruoff estimate the critical pressure to be $P_L \approx 28$ kbar for $T = 17$ K. Since superconductivity stabilizes the crystal, $P_L \approx 28$ kbar would thus be the lowest pressure where this transformation could occur. The temperature T_L of this pressure-induced transformation should increase with pressure, in contrast to the Batterman-Barrett transition where $dT_L/dP < 0$.[5] The rate of increase of T_L is given by $dT_L/dP = -(\partial c_s/\partial P)_T/(\partial c_s/\partial T)_P$.[25] Using the data from Fig. 3 for a "nontransforming" sample, one obtains $dT_L/dP \approx +0.7$ kbar^{-1}, which defines the cubic-to-tetragonal phase boundary drawn in Fig. 1.[26] It is seen that for "nontransforming" V_3Si, therefore, T_c and T_L recede from each other with increasing pressure; this is opposite to what is found in "transforming" crystals.[5] However, the sign of the slope change of $T_c(P)$ at the phase boundary is in both cases consistent with the model of Bilbro and McMillan[12]: i.e., the *farther* T_L is located above T_c, the *greater* is both the tetragonal distortion and the

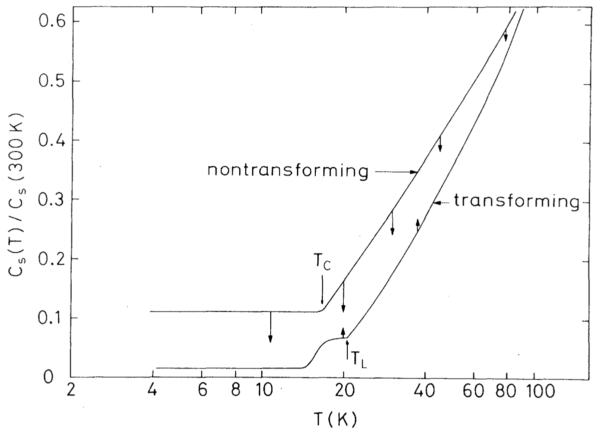

FIG. 3. Relative shear modulus vs temperature for both "transforming" and "nontransforming" V_3Si single crystals (see Ref. 3). T_c is superconducting transition temperature and T_L is temperature of Batterman-Barrett transformation in "transforming" crystal. Arrows indicate magnitude and direction of change of shear modulus for about 10 kbar hydrostatic pressure (see Refs. 6 and 22).

resulting suppression of T_c. Because the sign of dT_L/dP is determined by the sign of the tetragonal distortion,[27] c/a should be less than unity for the present pressure-induced transformation. The contrasting behavior of the phase transition in nominally "transforming" and "nontransforming" crystals stems from the opposite signs of dc_s/dP. The reason for this sign difference may have to do with lifetime-broadening effects[28] in "nontransforming" crystals which usually have higher levels of defect scattering.

The authors would like to express our special gratitude to Professor S. Methfessel for his support of this work and for many helpful discussions. Many thanks are due Dr. Hess, Zentralinstitut für Tieftemperaturforschung der Bayrischen Akademie der Wissenschaften, Garching, for the x-ray diffraction studies at low temperatures on V_3Si samples used in this investigation.

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