

X-ray diffraction study of V_3Si and V_3Ge

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A double superconducting transition in a single crystal of V_3Si was reported by Dayan and co-workers. We have measured lattice parameters of a sample of this material down to about 8 K with the use of x rays. The crystal is found to contain two kinds of regions having room-temperature lattice parameters differing by about 300 ppm, and we believe the regions have different Si concentration. One kind of region undergoes the martensitic transformation, while the other does not. The nontransforming region shows a negative thermal expansivity below about 40 K, in contrast to the transforming region. We have also measured the lattice parameter of V_3Ge (which does not undergo a martensitic transformation) and it shows a negative thermal expansivity below about 35 K. We discuss how these and other reported differences between transforming and nontransforming samples could be explained.

I. INTRODUCTION

There has been a great deal of interest in the $A15$ compounds because of their high superconducting transition temperatures. A martensitic transformation from the cubic $A15$ structure to a tetrahedral structure [with (c/a) close to unity] has been observed in "good" samples (characterized by a high resistivity ratio $[\rho(300\text{ K})/\rho(25\text{ K})]$) of V_3Si (Ref. 1) and Nb_3Sn ,² and these two compounds have been extensively studied. There has been evidence from specific heat and susceptibility data of their electronic density of states having a sharp peak near the Fermi level. Most theoretical models view the martensitic transformation as electronically driven, although other models^{3,4} have also been put forth. The various electronic models⁵⁻⁷ differ on the location in the Brillouin zone, of the electronic states driving the transformation, and on to which phonons the electrons couple strongly. The electronic model of Bhatt and McMillan⁷ succeeds very well in relating the sign of the pressure dependences of the superconducting and the martensitic transformation temperatures $\partial T_c/\partial P$ and $\partial T_m/\partial P$, respectively, and also in relating these to the sign of the tetragonality $(c/a - 1)$. They place the Fermi levels of V_3Si and Nb_3Sn above and below, respectively, a sharp peak in the density of states.

The general behavior of V_3Si appears to be well understood but some details, which may be classified as sample-dependent behavior, remain unexplained. The foremost among these is the difference between the samples which show the martensitic

transformation (hereafter referred to as T- V_3Si) and the ones which do not (NT- V_3Si). Correlations between (i) Si concentration, and (ii) residual resistivity ratio and whether or not the sample transforms, have been established.⁸ Disorder induced by neutron irradiation has been shown⁹ to reduce T_c but its effect on T_m has not been studied and so it is not clear which one of the above two is the more important correlation. The pressure dependence of the "soft" elastic constant $(\partial C_s/\partial P)$ was found to be positive¹⁰ for T- V_3Si but negative¹¹ for NT- V_3Si at low temperatures. At high pressures the martensitic transformation in T- V_3Si is suppressed, and Chu and Diatschenko¹² found positive and approximately equal $\partial T_c/\partial P$ for T- V_3Si and NT- V_3Si at pressures such that both remain in the cubic phase. The most puzzling observation was of Dayan and co-workers¹³ who observed a double superconducting transition in a V_3Si sample. We decided on a high-resolution x-ray diffraction study of the same sample, which was kindly provided by A. M. Goldman, in order to study its structure below 20 K.

The $A15$ compound V_3Ge has a lower T_c (~ 6 K) than V_3Si and does not show a martensitic transformation. It has a negative¹⁴ $\partial C_s/\partial P$ similar to that of NT- V_3Si and has a positive $\partial T_c/\partial P$. Prompted by these similarities we also did an x-ray diffraction study on a single crystal of V_3Ge , the crystal being provided by T. H. Geballe and M. V. Klein.

In the next section we present the details of our measurements and the results. We then compare them with some previous measurements of the thermal expansivity. We finally discuss how one could

relate our results to other measured differences between transforming and nontransforming samples of V_3Si .

II. EXPERIMENTAL DETAILS AND RESULTS

The measurements were made using an oscillating back-reflection x-ray camera.¹⁵ The temperature was measured using a platinum thermometer (a germanium thermometer was used below 13 K) and the estimated uncertainty in measurements was less than 20 mdeg. The data were obtained using $Cu K\alpha$ radiation. The $K\alpha_1$ line was used with the $K\alpha_2$ line being used at some temperatures as a check. The wavelengths of these two lines were taken from Bearden.¹⁶ The (600) reflection was used for V_3Si and the (610) reflection for V_3Ge . The estimated accuracy of the absolute lattice-parameter measurement was better than 20 ppm for V_3Si (it deteriorated to 30 ppm below T_m) and better than 15 ppm for V_3Ge , the difference being caused by the quality of the crystal. Errors in the relative measurement of the lattice parameter (LP) were only 6 ppm for V_3Si and 4 ppm for V_3Ge .

The results of our measurements are shown in Figs. 1 and 2. The V_3Si sample shows two spots corresponding to two regions having LP differing by about 300 ppm. As the temperature is lowered the region with a lower LP undergoes a martensitic transformation at about 21 K and, as shown in Fig. 3, the transition gets arrested at about 15 K. The LP of the other region reaches a minimum near 40 K and increases on further cooling. The measurements on V_3Ge also show a minimum in the LP, al-

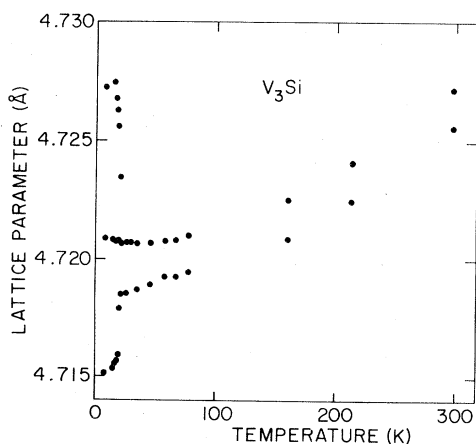


FIG. 1. Lattice parameter of V_3Si as a function of temperature. Two sets of points indicate two regions in the sample, and a martensitic transformation is seen in one of them at $T_m \approx 21$ K. The uncertainty in measurement is less than the size of the points except below T_M . All points are not shown at low temperatures.

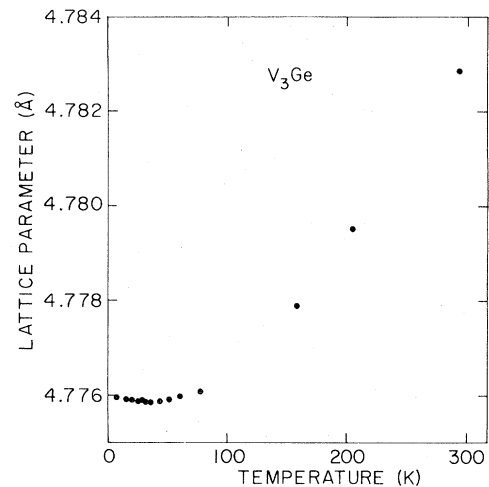


FIG. 2. Lattice parameter of V_3Ge as a function of temperature. The uncertainty in measurement is less than the size of the points. All points are not shown at low temperatures.

though not as pronounced.

We believe that the V_3Si sample contains two kinds of regions of different Si concentration, one of which is T- V_3Si and the other is NT- V_3Si . Using the relation between the room-temperature LP and the Si concentration established by Bruning,¹⁷ we infer that the region with larger LP has 24.7 ± 0.05 at. % Si, while the region with lower LP has 25.4 ± 0.05 at. % Si.¹⁸ Comparing this with Chiang's correlation,¹⁹ the region with larger LP should be NT- V_3Si in agreement with our observation. The martensitic transition of T- V_3Si is arrested at the temperature corresponding to the lower T_c observed by Dyan and co-workers. Thus the region with larger LP has a larger T_c , and this is in agreement

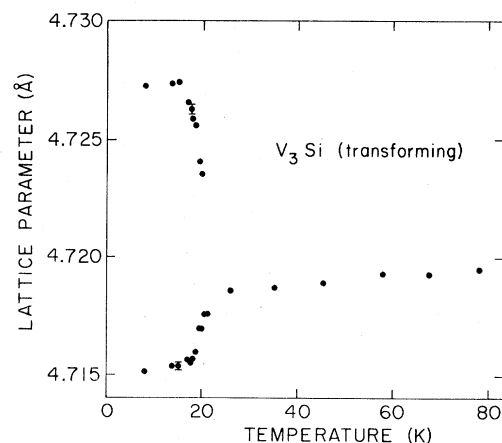


FIG. 3. The martensitic transformation is seen in the region having a lower room temperature LP.

with Bruning. It appears consistent to infer, therefore, that the double superconducting transition seen by Dayan and co-workers was actually the observation of the two distinct T_c 's of the T- V_3Si and NT- V_3Si regions in their sample.

In Fig. 4 we compare the measured value of $(c/a - 1)$ in T- V_3Si with the theory of Bilbro and McMillan.²⁰ There is reasonable agreement, though the accuracy of our measurements is not good enough to comment on the predicted decrease of $(c/a - 1)$ below T_c . The calculation of Bilbro and McMillan is for $T_c = 17$ K, and so quantitative comparison with our measurement would not be justified. We do not see any change in the unit cell volume at T_m . The volume change seen by Chandrasekhar and co-workers²¹ is 10 ppm, which is less than the error in our measurement.

We note that we do not see any diffraction spots corresponding to tetragonal domains at temperatures above T_m . This contradicts the proposal of Abou-Ghantous and co-workers²² that tetragonal domains form in all samples and as the temperature is lowered a connectivity between these domains is established at T_m . Their explanation of the observations of Dayan and co-workers is, consequently, also not valid.

The lattice parameters of NT- V_3Si and V_3Ge below 80 K are shown in Figs. 5 and 6, together with quadratic least-squares fit to the data. It is evident that the thermal expansivity α becomes negative in both cases. Using these fits, and from similar fits to the remaining data, we have obtained the values of α shown in Figs. 7 and 8. Results of some other measurements reported in literature are also

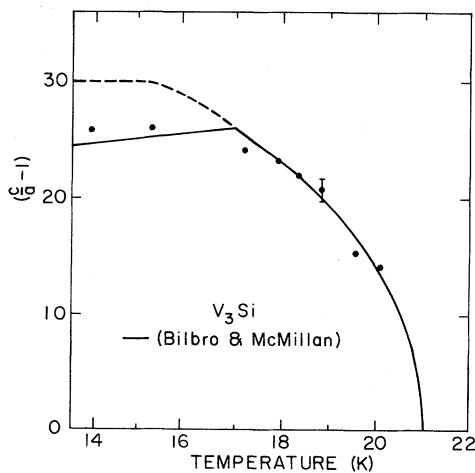


FIG. 4. Tetragonality we observed in T- V_3Si is compared with the calculated values of Bilbro and McMillan (Ref. 20), in their units. See text for details.

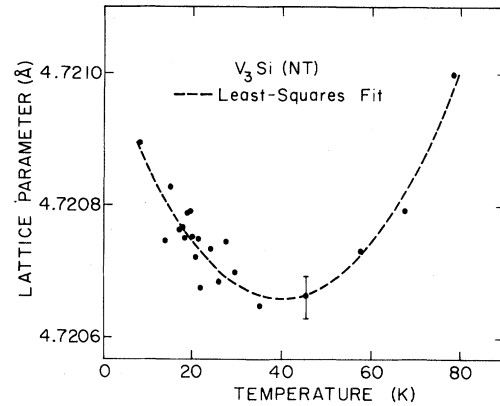


FIG. 5. Low-temperature LP's for NT- V_3Si , together with a quadratic least-squares fit, are shown. The error indicated is for the relative measurement of LP.

shown. Testardi¹⁴ has obtained a logarithmic fit to his thermal expansion data, and the fit is shown in the figures. His data on V_3Si are limited to above 80 K. Forsterling and Hegenbarth²³ made x-ray measurements on V_3Si and obtained α . Their measurements do not extend below 28 K, and the disagreement of their Debye-Waller factors with other measurements on T- V_3Si raises the possibility that their sample was NT- V_3Si . Also their room temperature LP and reported Si concentration are not consistent with the correlation established by Bruning.¹⁷ Smith and co-workers²⁴ used a capacitance dilatometer to measure α for various bulk V_3Si samples with different "nominal concentrations" of Si, and obtained a range of values for the low temperature α . Their room-temperature LP values are not accurate enough to estimate the Si concentrations, and it is not clear which of their samples were T- V_3Si and which NT- V_3Si . Smith and Finlayson²⁵ have report-

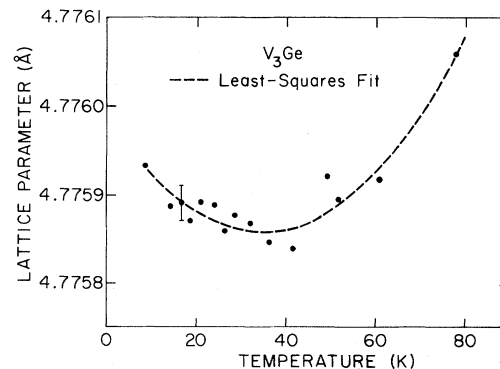


FIG. 6. Low-temperature LP's for V_3Ge are shown, together with a quadratic least-squares fit. The error indicated is for the relative measurement of LP.

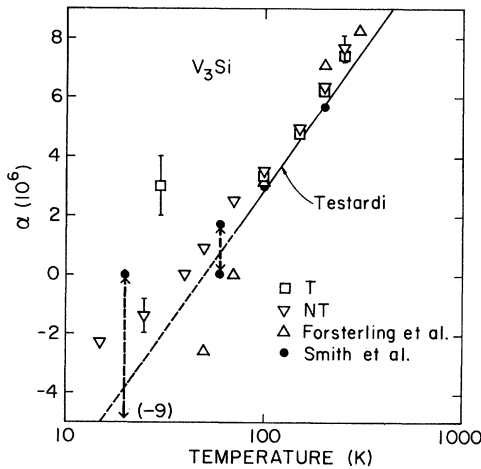


FIG. 7. Our measured values of thermal expansivity for T-V₃Si and NT-V₃Si are shown, and the error is indicated. Previous data of Testardi (Ref. 14), Försterling *et al.* (Ref. 23), and Smith *et al.* (Ref. 24) are also shown. At low temperatures Smith *et al.* obtained a range of values with different samples. The broken line indicates Testardi's extrapolation of the fit to his data.

ed a negative α for V₃Ge, and their results are shown in Fig. 8. Our measurements are on well-characterized samples, and we had the opportunity to simultaneously measure α for T- and NT-V₃Si.

We find that α for T-V₃Si and NT-V₃Si are, within experimental error, equal at high temperature (≥ 70 K) and that these values, as well as those for V₃Ge, are in reasonable agreement with existing data. At lower temperature (but above T_m) α for T-V₃Si remains positive, while α for NT-V₃Si is

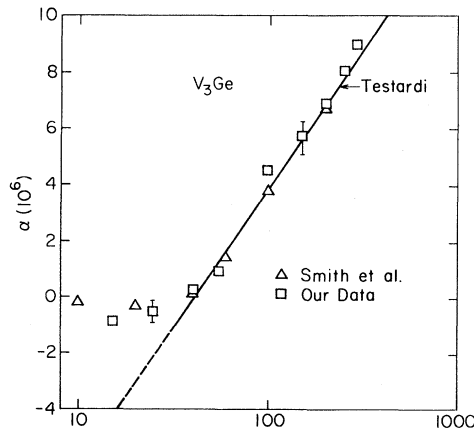


FIG. 8. Our measured values of thermal expansivity for V₃Ge are shown, and the error is indicated. Previous data of Testardi (Ref. 14) and Smith *et al.* (Ref. 25) are also shown. The broken line indicates Testardi's extrapolation of the fit to his data.

negative below about 40 K. Also α for V₃Ge is negative below about 35 K.

III. DISCUSSION

The negative α that we have observed could be caused by a negative electronic contribution and/or by a negative contribution from lattice modes. The former would give a negative electronic Grüneisen parameter γ_e , while the latter would make the lattice Grüneisen parameter γ_L negative. Let us first consider γ_L which is given by the weighted average

$$\gamma_L = \frac{\sum_i C_i \gamma_i}{\sum_i C_i}, \quad (1)$$

where C_i are the thermal occupancies of the various lattice modes and

$$\gamma_i = - \frac{\partial \ln \omega_i}{\partial \ln V}$$

are the individual mode γ 's. Carcia and Barsch¹⁰ used the measured values of $\partial C_s / \partial P$ and an anisotropic Debye model to obtain γ_i 's for the longitudinal and transverse acoustic models in NT- and T-V₃Si. With the dominant contribution to γ_L being the acoustic mode γ_i 's at low temperature, they had predicted a negative α for NT-V₃Si and a positive α for T-V₃Si, which is in agreement with our observations. The experimentally observed^{10,11} temperature dependence of $(\partial C_s / \partial P)$ can be explained by the model of Ting.²⁶ He gets quantitative agreement with the data for T-V₃Si with E_F located *above* a peak in the electronic density of states, which is in accordance with the model of Bhatt and McMillan. For NT-V₃Si he needs to place E_F *below* a peak in the density of states.

The electronic contribution becomes important at low temperature, and we now consider the conditions under which γ_e would be negative. γ_e is given by

$$\gamma_e = 1 + \left[\frac{\partial \ln N(E_F)}{\partial \ln V} \right]_T, \quad (2)$$

where $N(E_F)$ is the density of states at the Fermi level. Thus if E_F lies above a peak in the density of states γ_e would be positive as

$$\left[\frac{\partial \ln N(E_F)}{\partial \ln V} \right]_T$$

would be positive while if it lies below a sharp peak it could be negative. (The application of pressure raises E_F .²⁶) Thus both the phonon and the electronic contributions to α would be negative if E_F

lies below a sharp peak in the density of states, and the difference in the position of E_F can qualitatively explain the observed differences between T-V₃Si and NT-V₃Si. Because of the similar behavior of V₃Ge and NT-V₃Si, we tentatively place E_F below a sharp peak in the density of states for V₃Ge.

Chu and Diatschenko¹² argue that Ting's model rules out the possibility of the T-V₃Si to NT-V₃Si transformation they observe at about 19 kbar. As application of pressure raises E_F , and as Ting has $E_F(\text{T-V}_3\text{Si}) > E_F(\text{NT-V}_3\text{Si})$, they argue within a rigid-band model that the permitted transformation is NT-V₃Si to T-V₃Si. We shall argue below how the data of Ref. 12 could be explained.

Following Bhatt and McMillan, we assume the peak in the density of states to be at $E_{\vec{q}}$, where a Peierls-type distortion of wave vector \vec{q} causes the martensitic transition. (The exact location of \vec{q} does not affect the discussion that follows). The energy gained by the distortion then decreases as E_F moves away from $E_{\vec{q}}$ in either direction. The martensitic transition temperature is given by

$$T_m = T_m^{\text{max}} - B(E_F - E_{\vec{q}})^2. \quad (3)$$

The sample is T-V₃Si if the energy gain is large enough to have $T_m > T_c$, and is NT-V₃Si if $T_m < T_c$. If $E_F > E_{\vec{q}}$, then $\partial T_m / \partial P < 0$, and the T-V₃Si sample of Chu and Diatschenko becomes nontransforming as E_F rises away from $E_{\vec{q}}$ under pressure. This NT-V₃Si has $E_F < E_{\vec{q}}$ and should have a positive α and a positive $\partial T_c / \partial P$, thus distinguishing it from our zero pressure NT-V₃Si.

The zero pressure NT-V₃Si sample has $E_F < E_{\vec{q}}$, but the energy gained by a Peierls-type distortion is small and we have $T_m < T_c$. Under application of pressure E_F rises toward $E_{\vec{q}}$, the energy gained by the distortion increases and at high enough pressure we have $T_m > T_c$ and NT-V₃Si becomes T-V₃Si. This T-V₃Si, however, has $E_F < E_{\vec{q}}$ and, following Bhatt and McMillan, the tetragonal phase to which it transforms will have $c/a < 1$. Under such pressures it will also have $\partial T_c / \partial P < 0$ and $\partial T_m / \partial P > 0$. Chu and Diatschenko see a transition in their NT-V₃Si sample at about 29 kbar when T_c drops sharply. We believe this to be the NT-V₃Si to T-V₃Si transition we have just discussed, and this could be verified by an x-ray study above 29 kbar. Fasol and co-workers²⁷ have also seen a transition in NT-V₃Si at about 32 kbar. Following the same arguments as

above, and because of the similarities in NT-V₃Si and V₃Ge that we have mentioned, we speculate that V₃Ge would show a martensitic transformation, with $c/a < 1$, under high pressure. We have assumed that the T-V₃Si samples studied here $E_F > E_{\vec{q}}$. We see from Eq. (3), however, that T_m depends only on $|E_F - E_{\vec{q}}|$, while in the model of Bhatt and McMillan the sign of $(c/a - 1)$ depends on the sign of $E_F - E_{\vec{q}}$. If the position of E_F can vary continuously in the neighborhood of $E_{\vec{q}}$ in different V₃Si samples (the position of E_F could be correlated to the Si concentration), then it raises the possibility of having a V₃Si sample with $E_F < E_{\vec{q}}$ and $T_m > T_c$. Such a sample would have $c/a < 1$. It is not clear whether the c/a ratio of enough transforming V₃Si samples have been measured to make a definite statement on this possibility.

The remaining question is why $(\partial T_c / \partial P)$ for NT-V₃Si and T-V₃Si (at pressures when it remains in the cubic phase) samples¹² are so nearly equal when the pressure dependence of the soft-mode frequency and of $N(E_F)$ favor a large value for NT-V₃Si. Cowan and Carbotte²⁸ have argued for Nb₃Sn that the phonon softening does not affect T_c strongly, and the electron-optical phonon coupling is a more important factor. Recent Raman scattering data indicate²⁹ that the electron-optical phonon coupling constant strongly determines T_c for V₃Si. It is possible that the pressure dependence of this coupling constant is the same for both T- and NT-V₃Si when they are in the cubic phase, and this could account for their nearly equal $\partial T_c / \partial P$.

There have been some measurements on V₃Si samples which do not show the martensitic transformation, which we have not discussed. In these measurements the transformation is inhibited either because of strain induced by a copper coating,³⁰ or because the sample is not annealed.³¹ Our discussion on NT-V₃Si does not include such samples.

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