Low-Temperature Thermal Expansion of V_3Si

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Measurements are described of the thermal expansion α of two samples of V_3Si. One shows a large anomaly in α resulting from the structural transformation, which starts above 30°K and continues below the superconducting transition temperature T_c. The other sample shows only about 1% structural transformation, and the associated anisotropy in the discontinuity of α at T_c shows that quadratic terms in the strain dependence of T_c are unusually large.

The superconductor V_3Si has a high transition temperature,[1] $T_c \sim 17$°K, and exhibits a progressive transformation from cubic to tetragonal structure over a range of temperature somewhat above T_c.[2] The sound velocity shows no discontinuity at T_c but its temperature derivative shows a discontinuity about four orders of magnitude larger than the typical value for most superconductors. Testardi *et al.*[3] claim that this indicates a small linear strain dependence, $\Gamma_i = \partial T_c/\partial \epsilon_i$, of T_c, with an unusually large quadratic strain dependence, $\Delta_{ij} = \partial^2 T_c/\partial\epsilon_i \partial\epsilon_j$. The pressure dependence of T_c appears to be inconsistent with this result.[4] We find that the anisotropy of the thermal-expansion anomaly at T_c in a sample of V_3Si which is almost nontransforming appears to support Testardi's claim.

We have measured the linear thermal expansion of two samples of V_3Si from 1.5 to 30°K. The thermal expansion along a cube axis of one sample, V_3Si A, is anomalously large and positive, consistent with this axis being the a axis in the tetragonal phase. Our measurements are performed with a capacitance dilatometer, which gives much greater sensitivity than the x-ray method. With the greater sensitivity we find that the structural transformation begins at a higher temperature than previously thought and continues below T_c. The anomaly in the thermal expansion at T_c in V_3Si A is somewhat obscured by the structural transformation, and the data for V_3Si B are more informative about the strain dependence of T_c. This sample was measured along a cube axis and also along a perpendicular $\langle 011\rangle$ axis, and the thermal expansion above T_c (which is much smaller than in V_3Si A) has an anisotropy consistent with the transformation of only about 1% of the sample, with the c axis along the cube axis. When the anisotropic change in the thermal-expansion coefficient at T_c is analyzed accordingly, the resultant values of Γ_1 and $\Delta_{11}-\Delta_{12}$ are in reasonably good agreement with those of Testardi *et al.*[3]

Since the behavior of V_3Si is sensitive to strain, precautions were taken in mounting the samples in the capacitance dilatometer to minimize strain due to differential thermal contraction on cooling. A 1.5-mm hole was spark drilled down the axis of V_3Si A (diameter ~ length ~ 10 mm), so that it could be held against the copper base plate of the dilatometer under the light pressure of a spring washer. Rubber cement was used to fasten V_3Si B (dimensions ~ $9\times 6\times 6$ mm^3) to the base plate since it was mounted with each of two perpendicular axes in turn along the measuring direction. The small amount of transformation in this sample ensures at least that the strain does not change significantly in the region of measurement, though there may be a constant radial strain transverse to the measuring direction due to differential thermal contraction at higher temperatures.

The change in the thermal expansion at T_c is obtained from the free-energy difference, which for a second-order transition with a parabolic relation between critical field $H_c(T)$ and temperature T may be written, for T below T_c,

$$F^N - F^S = \frac{H_c^2(T,\epsilon)}{8\pi} = \frac{A^2}{8\pi}[T_c(\epsilon)-T]^2. \tag{1}$$

The coefficient A^2 is determined from the specific-heat discontinuity at T_c,

$$C_V^N - C_V^S = -T\left[\frac{d^2}{dT^2}(F^N-F^S)\right]_{T_c} = \frac{-A^2 T_c}{4\pi}. \tag{2}$$

From Eq. (1) we obtain[5]

$$\overleftrightarrow{c}\cdot\left(\frac{d\overleftrightarrow{\epsilon}^N}{dT} - \frac{d\overleftrightarrow{\epsilon}^S}{dT}\right)_{T_c} = \frac{+A^2}{4\pi}\frac{dT_c(\epsilon)}{d\overleftrightarrow{\epsilon}}, \tag{3}$$

where $\overleftrightarrow{c}$ is the elastic modulus tensor at T_c. Fol-

Table I. Uniaxial strain for V_3Si samples between 1.5 and 30°K.

Sample	Measuring direction	ϵ(30°K) (10^{-6})	Identification of direction	$(\alpha_N-\alpha_S)_T$ (10^{-6} °K^{-1})$_c$
V_3Si *A*	⟨100⟩	890	*a* axis	57
V_3Si *B*	⟨100⟩	−4(−10)[a]	*c* axis	−1.63
	⟨011⟩	20	*a* plane	−0.14

[a]The value $\epsilon(30°K) \simeq -10\times10^{-6}$ is obtained by making a plausible extrapolation of the ⟨100⟩ curve in Fig. 2 from above T_c to zero temperature. In the case of the ⟨011⟩ curve, the corresponding correction for the strain resulting from superconductivity to obtain the strain ϵ(30°K) associated with the structural transformation is negligibly small.

lowing Testardi *et al.*,[3] we write,

$$T_c(\epsilon)=T_c(0)+\vec{\Gamma}\cdot\vec{\epsilon}+\tfrac{1}{2}\vec{\epsilon}\cdot\overleftrightarrow{\Delta}\cdot\vec{\epsilon}, \tag{4}$$

so that for a nontransforming cubic crystal the change in the isotropic linear-thermal-expansion coefficient α at T_c is

$$(\alpha_N-\alpha_S)_{T_c}{}^0=\frac{A^2}{4\pi}\left(\frac{\Gamma_1}{c_{11}+2c_{12}}\right). \tag{5}$$

For a crystal which has undergone a cubic to tetragonal transformation at $T>T_c$, the strain at T_c relative to the cubic state is $\epsilon=(\frac{2}{3}\delta,-\frac{1}{3}\delta,-\frac{1}{3}\delta)$, where $\delta=c/a-1$. In this case the change in the thermal-expansion coefficient at T_c has the same tetragonal symmetry as the transformed crystal; Eqs. (3) and (4) give[5]

$$(\alpha_N-\alpha_S)_{T_c}=(\tfrac{2}{3}\Delta\alpha,-\tfrac{1}{3}\Delta\alpha,-\tfrac{1}{3}\Delta\alpha),$$

$$\Delta\alpha=\tfrac{2}{3}\delta\frac{A^2}{4\pi}\left(\frac{2}{c_{11}-c_{12}}\right)(\Delta_{11}-\Delta_{12}). \tag{6}$$

Since V_3Si *B* is almost nontransforming, we can roughly estimate the isotropic strain ϵ^0(30°K) by averaging the data in Table I, as explained below. With the resultant very small correction, $\epsilon^0(30°K)\simeq 10\times10^{-6}$, we find for V_3Si *A* a uniaxial strain, $\epsilon(30°K)=880\times10^{-6}$, which is to be compared with the value of 830×10^{-6} for the strain

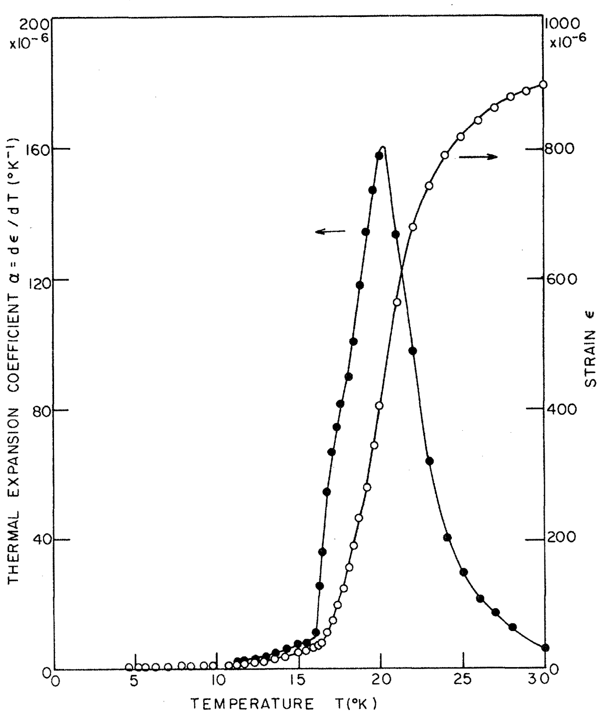

FIG. 1. Thermal expansion and expansion coefficient of V_3Si *A* along the ⟨100⟩ axis.

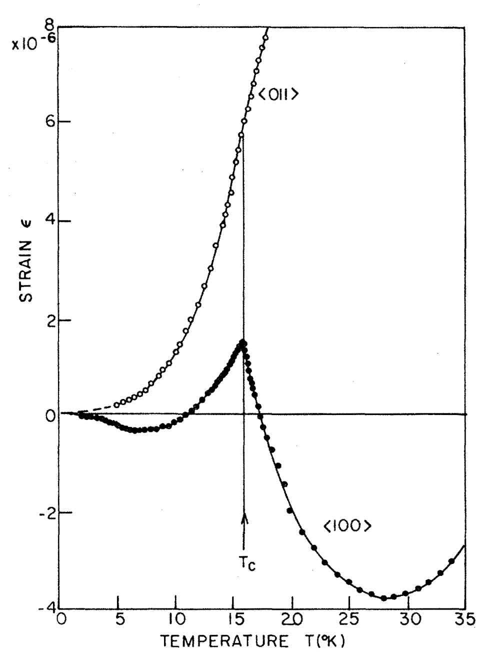

FIG. 2. Thermal expansion of V_3Si *B* along two crystal axes.

along the a axis of a completely transforming crystal obtained by x-ray measurements.[2] We conclude that V_3Si A transforms completely with the a axis in the tetragonal phase along the measuring direction. We find that the thermal-expansion coefficient is still anomalously large at 30°K ($\alpha \simeq 6\times 10^{-6}\,°K^{-1}$), so that the transformation must begin somewhat above this temperature. As shown in Fig. 1, α shows a discontinuity[6] at T_c in the sense that it rises rapidly from $10\times 10^{-6}\,°K^{-1}$ at 16°K to $67\times 10^{-6}\,°K^{-1}$ at 17°K, and then increases more slowly at higher temperatures. The maximum value of α is $\sim 160\times 10^{-6}\,°K^{-1}$ at ~20°K. It is interesting to note that the thermal expansion of V_3Si A shows anomalous temperature dependence even below T_c and is considerably larger than that of V_3Si B at all temperatures, which indicates that the structural transformation continues into the superconducting state.

Both the uniaxial strain $\epsilon(30°K)$ and the discontinuity in the thermal-expansion coefficient $(\alpha_N - \alpha_S)$ are anisotropic in V_3Si B (Fig. 2 and Table I). If we suppose that fractions f_1, f_2, and f_3 transform with the tetragonal c axis along $\langle 100\rangle$, $\langle 010\rangle$, and $\langle 001\rangle$, respectively, and use the value, $\epsilon(30°K) = 880\times 10^{-6}$, along the a axis of the completely transforming sample, we obtain two equations (in units of 10^{-6}),

$$\begin{aligned}
\epsilon^{100}(30°K) &= -10 = \epsilon^0(30°K) - 1760 f_1 + 880(f_2+f_3),\\
\epsilon^{110}(30°K) &= +20 = \epsilon^0(30°K) + 880 f_1 - 800[\tfrac{1}{2}(f_2+f_3)],
\end{aligned}\tag{7}$$

which give $f_1 - \frac{1}{2}(f_2+f_3) = 1.14\,\%$ and an isotropic strain $\epsilon^0(30°K) = 10\times 10^{-6}$. The equations for the discontinuities of the thermal-expansion coefficient at T_c follow from Eqs. (5) and (6) and have a form similar to Eqs. (7), if we assume that the structural transformation and superconducting transition of the fractions with different c axes determine the anisotropy of $\epsilon(30°K)$ and $(\alpha_N - \alpha_S)_{T_c}$ in a similar way:

$$\begin{aligned}
(\alpha_N-\alpha_S)_{T_c}^{100} &= \frac{A^2}{4\pi}\left\{\frac{\Gamma_1}{c_{11}+2c_{12}} + \frac{4\delta}{9}\left(\frac{2}{c_{11}-c_{12}}\right)(\Delta_{11}-\Delta_{12})[f_1-\tfrac{1}{2}(f_2+f_3)]\right\},\\
(\alpha_N-\alpha_S)_{T_c}^{100} &= \frac{A^2}{4\pi}\left\{\frac{\Gamma_1}{c_{11}+2c_{12}} - \frac{2\delta}{9}\left(\frac{2}{c_{11}-c_{12}}\right)(\Delta_{11}-\Delta_{12})[f_1-\tfrac{1}{2}(f_2+f_3)]\right\}.
\end{aligned}\tag{8}$$

We substitute in Eq. (8) from Table I with the values[5] $A^2/4\pi = 3.82\times 10^4$ erg/cm^3 °K^2, $c_{11}+2c_{12} = 5.14\times 10^{12}$ erg/cm^3, $\frac{1}{2}(c_{11}-c_{12}) = 0.08\times 10^{12}$ erg/cm^3, and $\frac{1}{3}\delta = 880\times 10^{-6}$, and obtain $\Gamma_1 = -80°K$ and $(\Delta_{11}-\Delta_{12}) = -16\times 10^4\,°K$. If V_3Si A is assumed to transform completely with the a axis along the measuring direction, and the discontinuity in the thermal expansion at T_c estimated from Fig. 1 is $57\times 10^{-6}\,°K^{-1}$, the resultant value of $(\Delta_{11}-\Delta_{12})$ from Eq. (6) is $-20\times 10^4\,°K$. These values agree reasonably well with those estimated by Testardi *et al.*,[3] $|\Gamma_1| < 50°K$ and $(\Delta_{11}-\Delta_{12}) = -19\times 10^4\,°K$, in view of the fact that this upper limit for Γ_1 was estimated from a null measurement of the discontinuity of the velocity of sound at T_c in a transforming sample.[5]

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[5]L. R. Testardi, Phys. Rev. B 3, 95 (1971). The apparent reversal in sign between Eqs. (1) and (3) results from the fact that the latter equation describes the free energy only for T below T_c. In Eq. (3) we neglect the term $\vec{\epsilon}\cdot d\vec{c}/dT$, which Testardi shows to be negligible compared with the term $(A^2/4\pi)dT_c/d\vec{\epsilon}$ even in a transforming crystal for which $\epsilon \neq 0$ at T_c.

[6]The transition temperature, $T_c \gtrsim 16°K$, observed in both V_3Si A and V_3Si B is somewhat lower than that reported in the literature. L. R. Testardi, J. E. Kunzler, H. J. Levinstein, J. P. Maita, and J. H. Wernick [Phys. Rev. B 3, 107 (1971)] find that nontransforming samples of V_3Si have $T_c \sim 17.1°K$ while transforming samples have $T_c \sim 16.8°K$.

The difference of 0.3°K may be too small to measure in the present experiment since the thermal expansion of the transforming sample V_3Si A (Fig. 1) is qualitatively different from that of the nontransforming sample V_3Si B (Fig. 2) possibly because of an inhomogeneous strain in the former, so that T_c is characterized differently in the two samples. However, the low value of T_c we observe for both samples can only be attributed to error in our thermometer. We used a germanium resistance thermometer calibrated by Cryocal, Riviera Beach, Fla., and were unable to check the calibration later since the thermometer was damaged.

Eight-Vertex Model in Lattice Statistics

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The solution of the zero-field "eight-vertex" model is presented. This model includes the square lattice Ising, dimer, ice, F, and KDP models as special cases. It is found that in general the free energy has a branch-point singularity at a phase transition, with a continuously variable exponent.

It has been pointed out[1] that many of the previously solved two-dimensional lattice models, notably the Ising and "ice"-type models, can be regarded as special cases of a more general model. Adopting the arrow terminology used by Lieb,[3] we can formulate this model as follows: Place arrows on the bonds of a square, N-by-N lattice and allow only those configurations with an even number of arrows pointing into each vertex. Then there are eight possible different configurations of arrows at each vertex (hence our name for the model), as shown in Fig. 1. Next we assign energies $\epsilon_1, \cdots, \epsilon_8$ to these vertex configurations and the problem is to evaluate the partition function

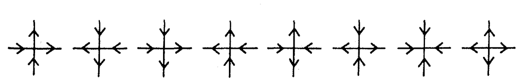
$$Z = \sum \exp(-\beta \sum_{j=1}^{8} N_j \epsilon_j), \tag{1}$$

where the summation is over all allowed configurations of arrows on the lattice, and N_j is the number of vertices of type j.

Let $\omega_j = \exp(-\beta\epsilon_j)$, and suppose the model to be unchanged by reversal of all arrows (in ferroelectric terminology this implies that there are no electric fields). Then we can write

$$\omega_1 = \omega_2 = a, \quad \omega_3 = \omega_4 = b,$$
$$\omega_5 = \omega_6 = c, \quad \omega_7 = \omega_8 = d. \tag{2}$$

We have succeeded in solving this model for arbitrary values of a, b, c, and d, and outline here the main results. The details of the derivation will be published elsewhere.[3]



1 2 3 4 5 6 7 8

FIG. 1. The eight arrow configurations allowed at a vertex.

The method of attack on the problem was guided by some recent results[4] for an inhomogeneous system satisfying the "ice condition" ($d = 0$), in which we observed that the Bethe *Ansatz* approach worked provided that the transfer matrices of any two rows commuted. This led to an algebraic identity which later reflection has shown to be the diagonal representation of an identity between the transfer matrices and another matrix function Q.

Applying these ideas to the $d \neq 0$ situation, suppose that a, b, c, and d can vary from row to row. We find that the transfer matrices for any two rows commute provided that

$$a:b:c:d = \mathrm{sn}(\eta - v) : \mathrm{sn}(\eta + v) : \mathrm{sn}(2\eta) : -k\,\mathrm{sn}(2\eta)\,\mathrm{sn}(\eta - v)\,\mathrm{sn}(\eta + v), \tag{3}$$

where $\mathrm{sn}(u)$ is the usual elliptic function[5] of modulus k; k and η are fixed, but v can vary from row to row. Thus we can write the transfer matrix of a typical row as $T(v)$, where v is a variable parameter.

We now look for a matrix identity of the type mentioned above and find that there exists a matrix function $Q(v)$ (in general nonsingular) such that[6]

$$\zeta(v)T(v)Q(v) = \varphi(v - \eta)Q(v + 2\eta) + \varphi(v + \eta)Q(v - 2\eta), \tag{4}$$

where

$$\zeta(v) = [c^{-1}H(2\eta)\Theta(v - \eta)\Theta(v + \eta)]^N, \tag{5}$$

$$\varphi(v) = [\Theta(0)H(v)\Theta(v)]^N, \tag{6}$$

$H(u)$ and $\Theta(u)$ being the elliptic theta functions[5] of modulus k. Both $T(v)$ and $Q(v)$ are 2^N-by-2^N matrices, and $Q(v)$ commutes with any matrix $T(u)$ or $Q(u)$. Thus there exists a representation