

*Supported in part by the National Science Foundation and the Air Force Office of Scientific Research.

†Present address: Union Carbide Corp., Parma Research Laboratories, P. O. Box 6116, Cleveland, Ohio 44101.

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Elastic Properties of Vanadium. II. The Role of Interstitial Hydrogen†

D. I. Bolef, R. E. Smith,* and J. G. Miller

Arthur Holly Compton Laboratory of Physics, Washington University, Saint Louis, Missouri 63130

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A detailed study was made of anomalies in the temperature dependence of the thermal expansion and of the elastic constants of several single crystals of vanadium. The anomalies were characterized by a transition temperature T_C , different for each crystal and lying in the temperature range 160–270 K. A simple thermodynamic theory based on a hydride-precipitation model due to Westlake accounts for the experimental results. The applicability of this model points to the precipitation of interstitial hydrogen as the cause of the observed anomalies.

I. INTRODUCTION

In the preceding paper¹ (referred to as I) we presented the results of a study of the elastic properties of single-crystal vanadium from 4.2 to 300 K. The emphasis in I was on the over-all temperature dependence of the elastic properties of vanadium in this temperature range. Striking anomalies were, however, observed at specific temperatures in both the thermal expansion and in the elastic constants

C_{11} and $C' = \frac{1}{2}(C_{11} - C_{12})$. These occurred, depending upon the particular vanadium specimen, in the temperature range 160–270 K. In this paper we describe these anomalies in greater detail and present a simple thermodynamic theory, based on Westlake's model of interstitial hydrogen precipitation in bcc metals, which is found to be in excellent agreement with the experimental results.

Anomalies in the temperature dependence of many of the physical properties of vanadium have been

reported: lattice parameter,²⁻⁵ electrical resistance,^{2,3,6-9} thermal expansion,^{2,4,10} magnetic susceptibility,^{7,11} and thermoelectric power.¹² One proposed explanation^{3,8} of these phenomena was that of the onset of an antiferromagnetic ordering. Nuclear-magnetic-resonance^{13,14} and neutron-diffraction¹⁵ experiments failed, however, to show any evidence of a magnetic transition. A detailed critique of previous experiments and a proposed explanation for the anomalies have been given by Westlake.¹⁶ As a result of his extensive work on vanadium-hydrogen alloys,¹⁷ Westlake suggested that precipitation of hydrogen impurities in so-called "pure" vanadium could account for the anomalies in the temperature range 180–250 K in which they had been observed. Suggestions that an ordering transition of unspecified gaseous interstitials was responsible for the anomalies had previously been made.^{2,7,12} The hydrogen-precipitation hypothesis is not inconsistent with any of the anomalies which have been verified for vanadium.¹⁶ In particular, the structural change from cubic to tetragonal symmetry indicated by x-ray diffraction experiments⁵ may be a consequence of the onset of hydrogen precipitation.

In Sec. II a thermodynamic theory based on Westlake's model is outlined. Experimental results specifically bearing on the anomalies are presented in Sec. III. In Sec. IV results are compared with the predictions of the theory. A preliminary report of this work has been published.¹⁸

II. THEORY

The hypothesis¹⁷ that hydrogen precipitation is responsible for the observed anomalies in the temperature dependence of many physical properties of pure vanadium suggests that a dilute-solution theory may be applicable.^{19,20} At sufficiently high temperatures one assumes that all of the hydrogen atoms wander randomly through the vanadium lattice. As the temperature is lowered, a point is reached at which the number of hydrogen atoms present in the specimen is equal to the maximum number capable of being dissolved in the "solvent," in this case the vanadium lattice. This represents a saturated solution. As the temperature is lowered further, more hydrogen atoms are present than can be accommodated so that hydrogen atoms are forced out of solution forming a precipitate, presumably vanadium hydride.

We define $N(T)$ as the maximum number of hydrogen atoms (expressed in at. %) which can be dissolved in vanadium at the temperature T ; $N(T)$ is the "limit of solubility." From Westlake's work,¹⁷ $N(T) = \kappa e^{-B/T}$, where $\kappa = 3.4 \times 10^2$ and $B = 1467$ K. If n_0 is the total amount of hydrogen present in the crystal, then for $N(T) > n_0$ all of the hydrogen is in solution, while for $N(T) < n_0$ the fraction $n(T) = n_0$

$-N(T)$ is in the ordered vanadium-hydride phase. We define a transition temperature T_c , at which precipitation of hydrogen begins, by $N(T_c) = n_0$. The amount $n(T)$ of precipitated hydrogen is thus

$$\begin{aligned} n(T) &= n_0 [1 - \exp\{-B(1/T - 1/T_c)\}], & T < T_c \\ n(T) &= 0, & T > T_c. \end{aligned} \quad (1)$$

In the discussion that follows we use the notation

$$W(T, T_c) \equiv [1 - \exp\{-B(1/T - 1/T_c)\}].$$

Since the solution is extremely dilute, one may expand the Helmholtz thermodynamic free energy of the system in terms of $n(T)$, $F(T) = F_0(T) + F_1(T)n(T)$, where F_0 is the Helmholtz free energy of the vanadium specimen in the absence of any precipitated vanadium hydride. The Gibbs potential $G(T)$ may be similarly expanded. The physical quantities of interest are derivatives of G or F with respect to variables such as pressure, strain, etc. In the region $T > T_c$ the measured elastic properties (see I) depend approximately linearly on T . We assume that in the absence of the hydride-precipitation phenomenon the elastic properties continue to depend linearly on T for $T < T_c$ down to temperatures of the order of 100 K. The behavior of the several specimens studies in I, which exhibit different transition temperatures, supports this assumption. We treat F_1 as independent of T over the limited temperature range of interest.

An experimental quantity $X(T)$ is given by

$$X(T) = X_0(T) + \alpha n_0 W(T, T_c), \quad (2)$$

where $X_0(T)$ and α are appropriate derivatives of $F_0(T)$ and F_1 , respectively. An example is

$$C_{11}(T) = C_{11}^0(T) + \gamma_{11} n_0 W(T, T_c),$$

where $C_{11}^0(T) = \partial^2 F_0(T) / \partial e_1^2$, $\gamma_{11} = \partial^2 F_1 / \partial e_1^2$, and e_1 is the appropriate strain. If we assume B to be

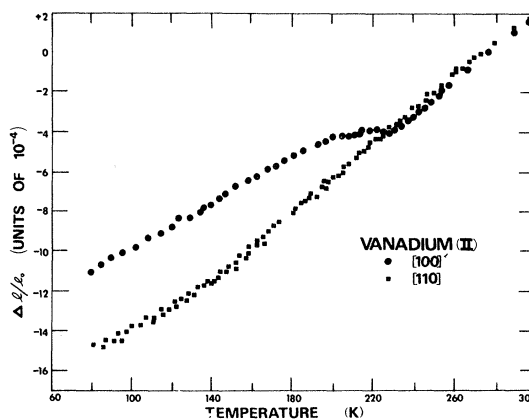


FIG. 1. Thermal expansivity $\Delta l/l_0$ for V(II) along [100] and [110] crystal axes.

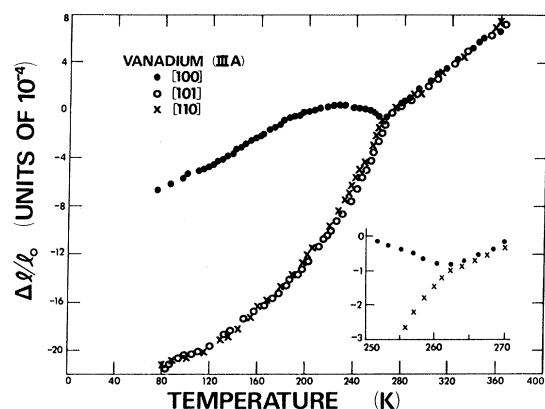


FIG. 2. Thermal expansivity $\Delta l/l_0$ for V(III A) along [100], [101], and [110] crystal axes. Insert shows details of curves near the critical temperature T_c .

known (Westlake's value of $B = 1467$ K), the function $W(T, T_c)$ is completely specified by T_c . The quantity xn_0 is determined by matching theory to experimental results at some temperature $T < T_c$. The quantity x which is obtained from F_1 is a material property of the vanadium-hydride precipitate and should be the same for all vanadium specimens. If one evaluates xn_{01} for a specimen with transition

temperature T_{c1} using the experimental data for $X_1(T)$, then for any other specimen with transition temperature T_{c2} the quantity xn_{02} is predicted to be

$$xn_{02} = xn_{01} \exp[-B(1/T_{c2} - 1/T_{c1})]. \quad (3)$$

Thus Eqs. (1)–(3) and a fit to the data for one specimen are sufficient to predict the behavior for all vanadium specimens over the entire temperature range; there are no adjustable parameters.

III. EXPERIMENTAL RESULTS

The experimental procedures for preparation and analysis of specimens, and for the measurements of thermal expansion and elastic constants have been described in I.

A. Thermal Expansion

The thermal expansivity $\Delta l/l_0$ as a function of temperature for the crystals V(II) and V(III A) is shown in Figs. 1 and 2. The length at $T = 273.2$ K is denoted by l_0 . The curve for $\Delta l/l_0$ in the [100] direction of V(II) (Fig. 1) shows a marked break at 233 K; no noticeable break is observed for $\Delta l/l_0$ in the [110] direction. For V(III A) (Fig. 2) anomalies occur for the [100], [110], and [101] directions at approximately 260 K. A detailed inspection of the original data indicates that the break for the [100]

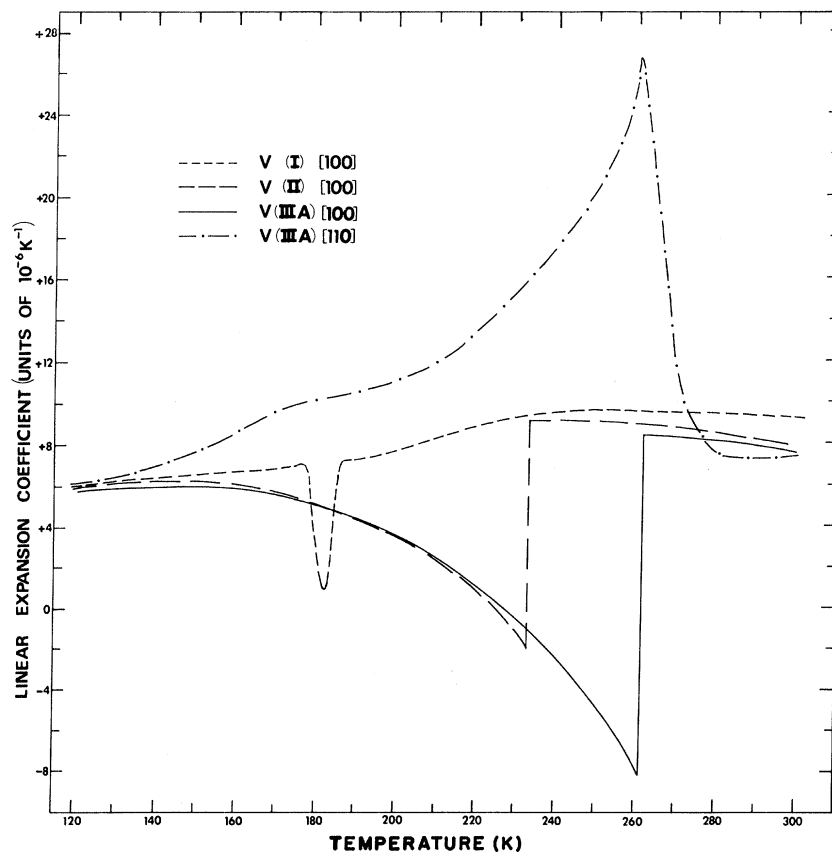


FIG. 3. Thermal-expansion coefficient for V(I), V(II), and V(III A), calculated from the slopes of the smoothed curves of $\Delta l/l_0$.

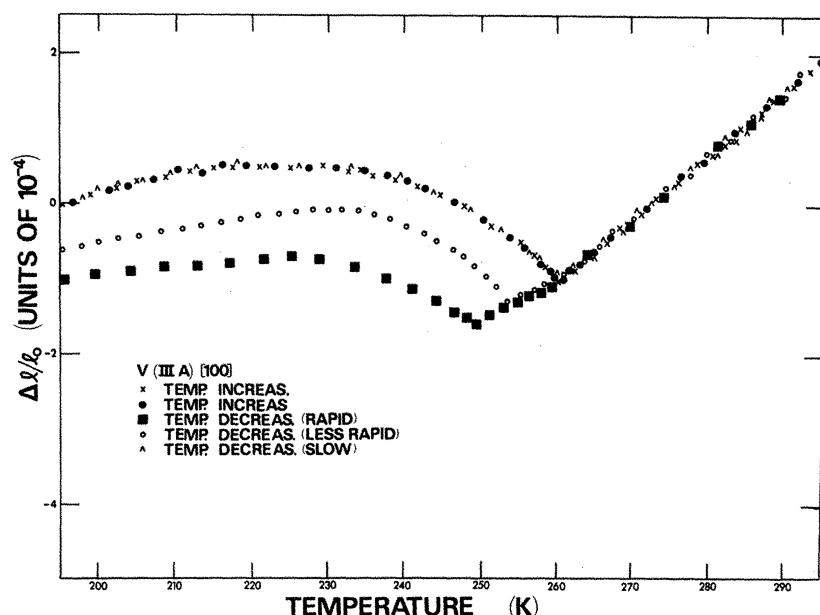


FIG. 4. Thermal expansivity for V(III A) [100] taken with temperature increasing and temperature decreasing. Rates of cooling are indicated.

direction occurs at 262 K and is extremely sharp, while that for the [110] and [101] directions, occurring in the same temperature range, is more diffuse. This difference is shown more clearly by the expanded curves for $\Delta l/l_0$ given in the insert of Fig. 2. The thermal-expansivity curve for V(I) was given in I; an anomaly occurs at 182 K. Thermal-expansivity measurements on V(IV) indicated a slight anomaly in the [100] direction at $T_c = 160$ K.

The thermal-expansion coefficient $\alpha = (1/l_0)dl/dT$ for V(I) [100], V(II) [100], V(IIA) [100], and V(III A) [110] is plotted as a function of temperature in Fig. 3. The values of $\alpha(T)$ were obtained graphically from the slope of the corresponding smoothed curves of the thermal expansivity. The sudden and oppositely directed changes in the thermal expansion for the [100] and [110] crystal axes of V(III A) are clearly shown in this figure, as are the critical temperatures for the three crystal specimens.

In Fig. 4 are shown on an expanded scale some data corresponding to the thermal-expansivity curves for V(III A) [100] in the vicinity of T_c . Of the five runs shown, three were taken with temperature decreasing, two with temperature increasing. In the latter cases the temperature T_c at which the break occurred was independent of the rate of heating, which varied from 1 K/min to 1 K/10 min. In the former cases a marked "supercooling" of the anomaly was observed when the rate of temperature decrease was fast (of the order of 1 K/min). For very slow rate of decrease (of the order of 1 K/10 min), the curves for temperature decreasing were found to agree with those for temperature increasing. Similar "supercooling" behavior was exhibited for thermal expansivity of V(III A) along

the [110] crystal axis.

B. Elastic Constants

Expanded curves of the acoustic velocities corresponding to C_{11} , C_{44} , and C' in the temperature range of the anomalies in V(I) and V(II) are shown in Figs. 5-7, respectively. The ordinates are given

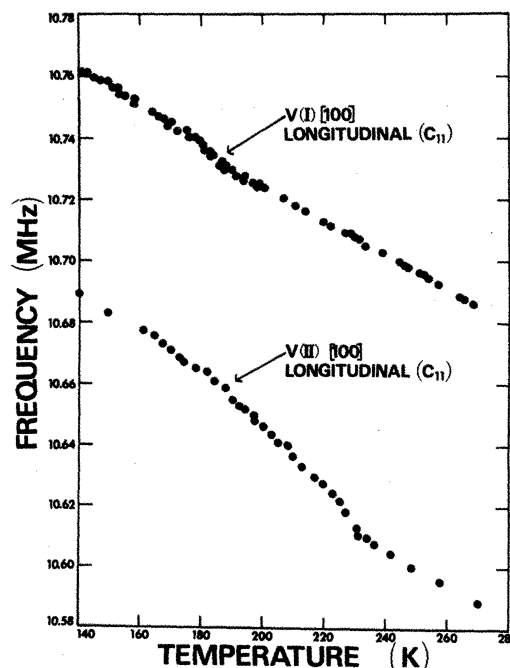


FIG. 5. Mechanical resonance frequencies (corresponding to C_{11}) for V(I) and V(II) in the temperature range about T_c .

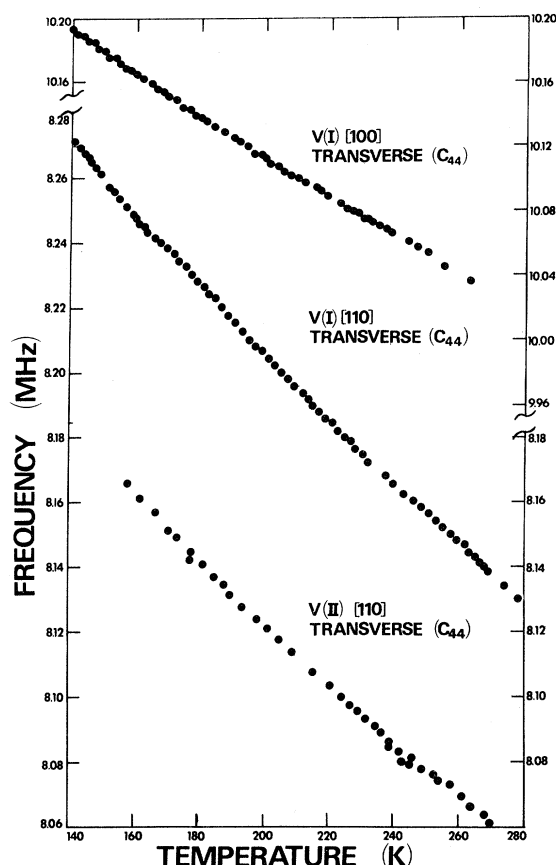


FIG. 6. Mechanical resonance frequencies (corresponding to C_{44}) for V(I) and V(II) in the temperature range about T_c .

en in terms of the experimentally measured quantity, the mechanical resonance frequency $\omega_n/2\pi$, which is directly proportional to the acoustic velocity [see I, Eq. (1)]. The transition temperatures, evidenced by sudden changes in slopes, are 182 K and 233 K for V(I) and V(II), respectively. The upward concavity (discussed in I) of the curves (Fig. 6) corresponding to C_{44} is characterized by changing slope without, however, the sharp "break" evident in Figs. 5 and 7. In the case of the curves for the remaining directly measured elastic quantity C_L (not shown) there is no noticeable change in slope in the temperature range 100–300 K for V(I), but slight "breaks," at the transition temperatures noted above, for V(II) and V(III A).

The specimens V(IV), V(V), and V(Alers) all exhibited relatively small anomalies in C' at approximately 180 K. These three specimens were all similar in that they were grown by electron-beam bombardment, had approximately the same initial hydrogen-impurity content (~ 0.2 at. %), had no more than two cuts made on them, and were cylindrical in shape. (There is some indication that the act of

cutting can introduce additional hydrogen into the crystal.) The curves for C' , C_{44} , and C_L for V (Alers) are reproduced in Fig. 8 from data supplied by Alers.²¹ The over-all behavior of V(Alers) is similar to that of the specimens investigated in the present work.

In Fig. 9 we show data corresponding to anomalies at $T_c = 267$ K for C_{11} and C' in V(III A) which, of all of the specimens, exhibited the most marked anomalies. Data taken with temperature increasing and temperature decreasing illustrate a "supercooling" phenomenon analogous to that for the thermal expansion shown in Fig. 5. As in the case of the thermal expansion, it was found that the faster the rate of cooling, the lower the temperature T_c at which the anomaly occurred. Changing the rate of heating, however, produced no change in T_c , and T_c (heating) always corresponded to T_c obtained with the slowest cooling rate. T_c (elastic constant) for V(III A) occurred at 267 K; this disagrees with the

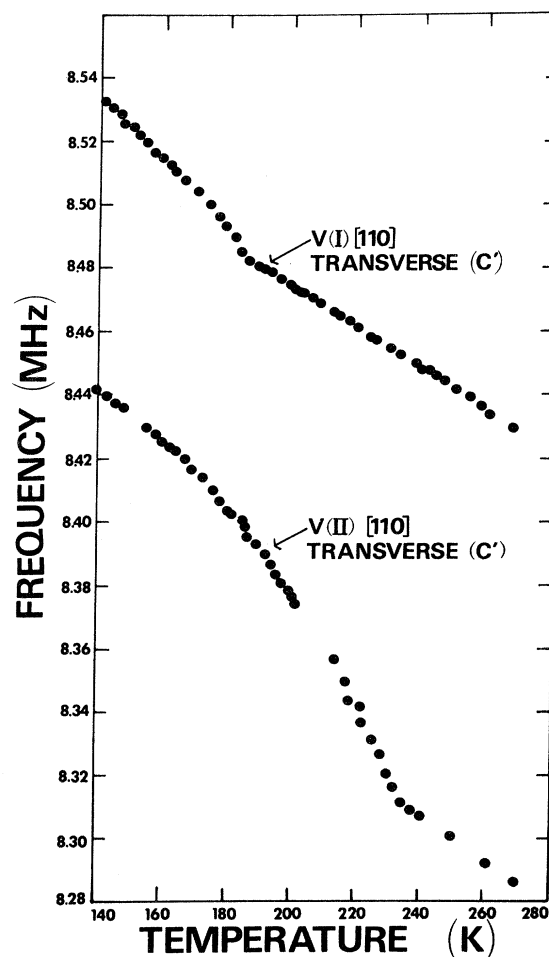


FIG. 7. Mechanical resonance frequencies [corresponding to $C' \equiv \frac{1}{2}(C_{11} - C_{12})$] for V(I) and V(II) in temperature range about T_c .

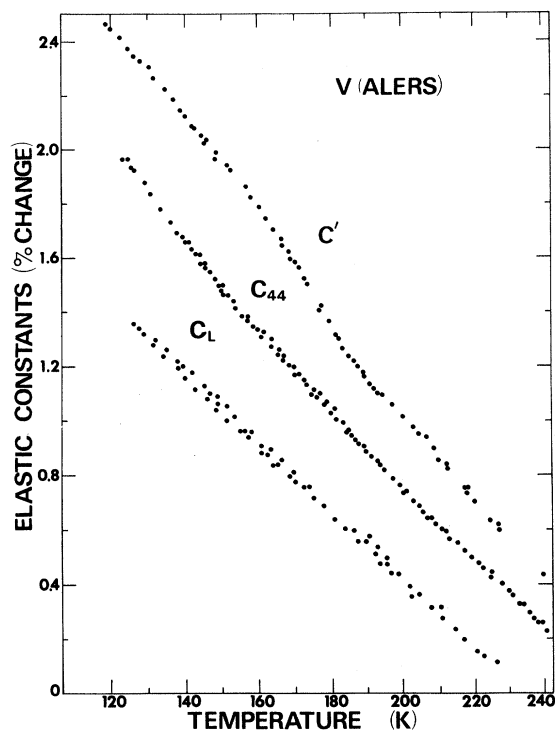


FIG. 8. The elastic constants C' , C_{44} , and C_L for V(Alers) in the region of T_c . Data provided by Alers.

value of T_c (thermal expansion) ≈ 262 K. This discrepancy is not understood. A possible explanation based on the pressure dependence of T_c has been proposed.²⁰

IV. DISCUSSION OF RESULTS

Comparison between the theory of Sec. II and the experimental data for thermal expansivity $\Delta l/l_0$ and for the elastic constants C_{11} and C' is shown in Figs. 10–12. In each case Eq. (2) was matched to the experimental curve at one temperature below T_c for one crystal; then the entire temperature dependence for both crystals was determined using Eqs. (2) and (3). The assumed forms of the temperature dependence were

$$\frac{\Delta l}{l_0} = \left(\frac{\Delta l}{l_0} \right)_0 + \beta n_0 W(T, T_c), \quad \beta \equiv \frac{\partial G_1}{\partial P} \quad (4)$$

$$C_{11} = C_{11}^0 + \gamma_{11} n_0 W(T, T_c), \quad \gamma_{11} \equiv \frac{\partial^2 F_1}{\partial e_1^2} \quad (5)$$

$$C' = C'_0 + \gamma' n_0 W(T, T_c), \quad \gamma' = \frac{1}{2} \left(\frac{\partial^2 F_1}{\partial e_1^2} - \frac{\partial^2 F_1}{\partial e_1 \partial e_2} \right) \quad (6)$$

where the e_i 's are the strains and P is the pressure. For $\Delta l/l_0$ the data were matched at 253 K for the [100] expansivity in V(IIIA) (Fig. 10), yielding $\beta(n_0)_{\text{IIIA}} = 6.90 \times 10^{-4}$ for $T_c(\text{IIIA}) = 261$ K. For C_{11} and C' the data were matched at 180 K for V(II), yielding $\gamma_{11}(n_0)_{\text{II}} = 0.142 \times 10^4$ dyn/cm² and $\gamma'(n_0)_{\text{II}}$

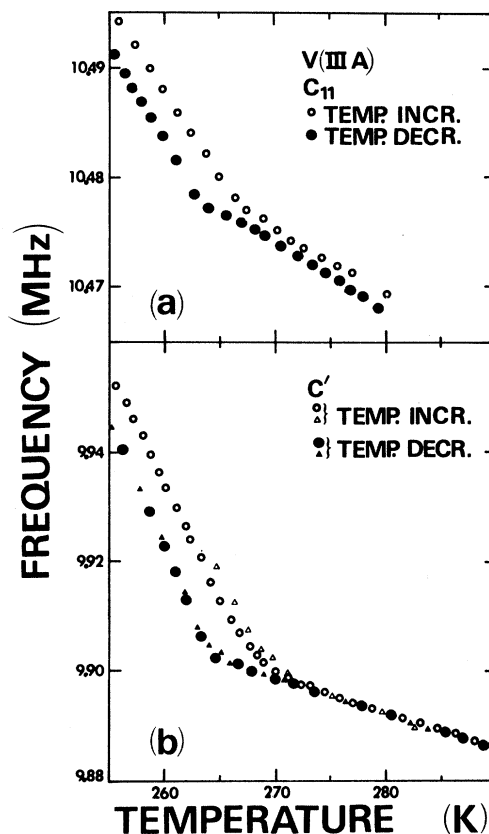


FIG. 9. Mechanical resonance frequencies for V(IIIA) in the temperature range about T_c for temperature increasing and temperature decreasing; corresponding to (a) C_{11} , and (b) $C' \equiv \frac{1}{2}(C_{11} - C_{12})$.

$= 0.0924 \times 10^{11}$ dyn/cm² for $T_c(\text{II}) = 233$ K. The derivative with respect to temperature of a quantity x shows a discontinuity at T_c of magnitude $x n_0 B / T_c^2$. Although difficulty in obtaining an accurate value for the temperature derivative from the experimental data precluded a quantitative comparison be-

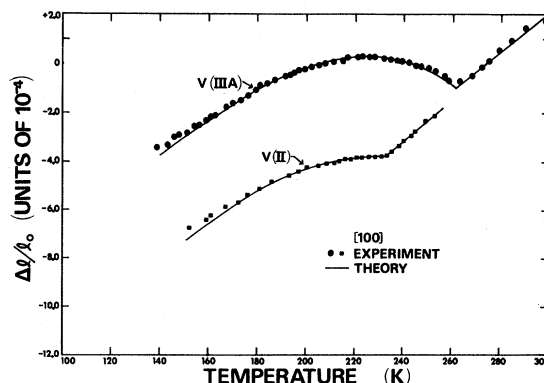


FIG. 10. Matching of theory (solid lines) to experimental points for $\Delta l/l_0$ [100] in V(II) and V(IIIA). $\beta(n_0)_{\text{IIIA}} = 6.90 \times 10^{-4}$; $T_c(\text{IIIA}) = 261$ K.

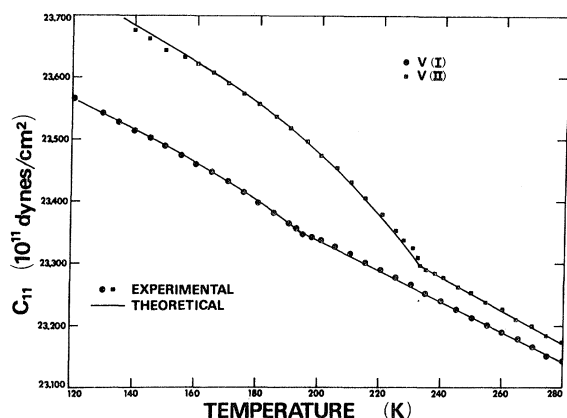


FIG. 11. Matching of theory (solid lines) to experimental points to C_{11} in V(I) and V(II). $\gamma'(n_0)_{II} = 0.142$; $T_c(II) = 233$ K.

tween theory and experiment, this behavior is clearly illustrated in Fig. 3 for the thermal-expansion coefficient $\alpha \equiv (1/l_0) dl/dT$.

The theoretical curves of Figs. 10–12 were calculated using Westlake's value 1467 K of B , which is known¹⁷ to apply to hydrogen in vanadium. If the experimental data of the present work is used to evaluate B , a value of $1370 \text{ K} \pm 10\%$ is obtained, in agreement, to within our experimental error, with the Westlake value. Since B depends critically on the size, mass, and, perhaps, bonding character of the interstitial atomic species involved, the close agreement with Westlake's results may be taken to exclude the possibility that other interstitial gas atoms, such as carbon, nitrogen, or oxygen, contribute significantly to the observed temperature anomalies in the elastic properties of the vanadium specimens we have studied.

Although the theory in Sec. II is macroscopic in character, some qualitative statements concerning the microscopic nature of the transition at $T = T_c$ are in order. The data indicate that the transition can be supercooled but not superheated (see Figs. 4 and 9). This may be understood by noting that upon heating hydrogen atoms may "boil" off from the vanadium-hydride precipitate, the process being limited only by the relatively fast diffusion rate for hydrogen in vanadium. Upon cooling, however, hydrogen atoms must satisfy energetics requirements and locate in specific positions in the lattice in order to form the vanadium-hydride precipitate. The relatively slow rate for this rather selective process may account for the supercooling. The formation of vanadium-hydride "clusters" may also play a role in the supercooling phenomena.²⁰

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*Present address: Union Carbide Corp., Parma

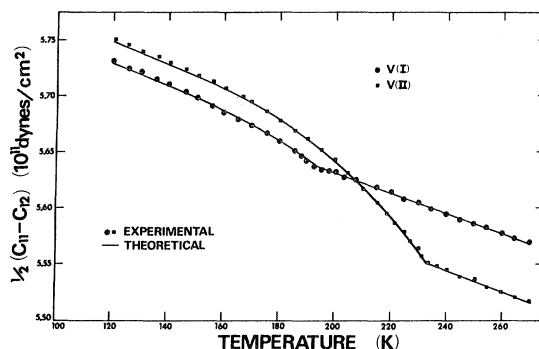


FIG. 12. Matching of theory (solid lines) to experimental points for C' in V(I) and V(II). $\gamma'(n_0)_{II} = 0.0924$; $T_c(II) = 233$ K.

The elastic constant C_{44} fails to exhibit the anomalous sharp change in slope characteristic of C_{11} and C' . The microscopic distortion involved in a C_{44} shear strain is such that the average nearest-neighbor bond length in vanadium is unchanged. If the primary effect of the hydrogen-precipitation process were to change the bond length, then one might speculate that the effect on C_{44} would be small. Regarding the absence of a marked anomaly in C_L , cubic symmetry requires that $C_L = C_{44} - C' + C_{11}$. Since C_{44} exhibits no anomaly, and C' and C_{11} exhibit similar anomalies, one expects a diminution, at least, in the anomaly in C_L compared to those in C' and C_{11} . This indeed is the case for all three vanadium specimens (I, II, and IIA) which have been studied in detail. The very slight departure from cubic symmetry below T_c (as evident from the present thermal-expansion results and from the x-ray diffraction work^{4,5}) should have little effect on this fortuitous diminution of the anomaly in C_L .

The thermal-expansion results of the present work indicate a structural change at the transition temperature, in agreement with the results of x-ray diffraction studies.⁵ The present work lends strong support to the hypothesis of Westlake that ordering of interstitial hydrogen is responsible for the anomalies in the elastic constants, thermal expansion, and many of the other physical properties of "pure" vanadium.

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Research Laboratories, P. O. Box 6116, Cleveland, Ohio 44101.

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PHYSICAL REVIEW B

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Lattice Vibrations of Thallium at 77 and 296 K*

T. G. Worlton†

*Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544
and Idaho Nuclear Corporation, Idaho Falls, Idaho 83401
and*

R. E. Schmunk

*Idaho Nuclear Corporation, Idaho Falls, Idaho 83401
(Received 5 October 1970)*

Lattice vibration frequencies of Tl at 77 and 296 K have been measured along the lines Δ and Σ by neutron inelastic scattering. Modified axially symmetric force-constant models were fitted to the neutron data and were used to calculate phonon-dispersion curves along other symmetry directions in the crystal. Frequency distributions calculated from the 77-K models are compared with the results of superconducting tunneling experiments of Clark and Dynes.

I. INTRODUCTION

Phonon-dispersion curves of a large number of hcp metals have been measured by neutron inelastic scattering, including Mg,^{1,2} Be,^{3,4} Zn,⁵ Ho,⁶ Y,⁷ Zr,⁸ Sc,⁹ and Tb.¹⁰ Many hcp metals undergo a transition to a bcc structure at high temperature.¹¹ Transition temperatures of hcp metals which undergo this transition and have been studied by neutron inelastic scattering are 1523 K for Be, 1715 K for Ho, 1760 K for Y, 1135 K for Zr, 1583 K for Tb, and 1608 K for Sc.¹¹ None of the neutron inelastic scattering studies report results above room temperature, so the hcp-bcc transition could be expected to have little effect on phonon modes studied previously.

The present paper reports a study of the lattice vibration frequencies of thallium along the directions $[0001]$ and $[01\bar{1}0]$ at 77 and 296 K. Since Tl under-

goes the hcp-to-bcc transition at 507 K, a relatively low temperature, it was expected that considerable softening of modes which take part in the transition might be observed at room temperature.

Considerable study has been given to the mechanism for the bcc \rightleftharpoons hcp phase transformation. Habit-plane studies in Ti and Zr indicate that the transformation involves $\{112\}\langle 111\rangle$ shears in the bcc phase. Burgers¹² concluded that the $\{0001\}$ planes of the hcp phase of Zr become $\{110\}$ planes of the bcc phase. He showed that this could be accomplished by a primary shear along $\{10.0\}$ planes of the hcp phase in a $\langle 11.0\rangle$ direction. The reverse shear system in the bcc phase is $\{112\}\langle 111\rangle$ with small dilatation strains needed to complete the transformation in either direction. Fisher and Renkin¹¹ have pointed out that the $\{10.0\}\langle 11.0\rangle$ shear in the hcp phase corresponds to the C_{66} elastic shear modulus which displays a strong temperature