

# Elastic Properties of Vanadium. I. Temperature Dependence of the Elastic Constants and the Thermal Expansion\*

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The thermal expansion and adiabatic elastic constants of several single crystals of vanadium were investigated over the temperature range 4.2–300 K. Although certain anomalies in the thermal expansion and in the elastic constants were observed at specific temperatures, in this paper emphasis is placed on the over-all elastic properties of vanadium, and attention is focused on those specimens in which the anomalies were less striking. The anomalies and their origin are the subject of a second paper which follows. The 4.2-K values of the elastic constants of a specimen exhibiting essentially no anomalous behavior were measured to be  $C_{11}=23.70$ ,  $C_{44}=4.708$ ,  $C'=5.793$ ,  $C_{12}=12.20$ , and the bulk modulus  $B=15.98$ , all in units of  $10^{11}$  dyn/cm<sup>2</sup>. Except for  $C_{44}(T)$ , the over-all temperature dependence of the elastic constants agrees with that predicted by current theoretical models.  $C_{44}(T)$ , however, exhibited an upward concavity over much of the temperature range, and was characterized by an athermal value lower than the measured 4.2-K value. Above 150 K the coefficient of thermal expansion was approximately constant for those specimens showing no anomalies, with a value  $\alpha \cong 8.5 \times 10^{-6}/\text{K}$ . Below 150 K,  $\alpha$  decreased monotonically to 0 at  $\sim 10$  K. The value of the Debye temperature extrapolated to 0 K was calculated to be  $\Theta_D$  (elastic) = 403 K.

## I. INTRODUCTION

We report the results of extensive measurements of the temperature dependences of the elastic constants and thermal expansion of several single crystals of vanadium. The emphasis in the present paper (I) is on the over-all temperature dependence of the elastic properties of vanadium in the temperature range 4–300 K. The present results are to be compared with earlier work on the elastic constants of single-crystal vanadium by Alers<sup>1</sup> (4.2–300 K) and by Bolef<sup>2</sup> (300 K); on the thermal expansion of polycrystalline vanadium by Erfling<sup>3</sup> and by White<sup>4</sup>; and on single-crystal vanadium by Smirnov and Finkel'<sup>5,6</sup> and by Suzuki and Miyahara.<sup>7</sup> In the following paper<sup>8</sup> (II) we report results on vanadium single crystals in which striking anomalies in the temperature dependences of the elastic constants and thermal expansion were observed. In that paper we propose a phenomenological theory, based on Westlake's hydrogen-precipitation model,<sup>9,10</sup> to account for the anomalies and to demonstrate that the theory and experiment are in excellent agreement.

That interest exists in the elastic properties of bcc transition metals is evidenced by a number of recent articles which propose theoretical models of cohesive energy and of electronic structure which rely, in part at least, on a knowledge of the elastic constants<sup>11,12</sup> and their temperature dependence.<sup>13</sup> Measurements of thermal expansion contribute to our knowledge of anharmonic properties of crystal lattices; they permit us to calculate, in particular, the Grüneisen constant and the Debye temperature, parameters conventionally used as measures of lat-

tice anharmonicity. The quantities directly measured in the present investigation are (a) the thermal expansivity  $\Delta l/l_0$  and (b) the cubic elastic constants  $C_{11}$ ,  $C_{44}$ , and  $C' = \frac{1}{2}(C_{11} - C_{12})$ . From these one may calculate the derived quantities: thermal-expansion coefficient, bulk modulus, elastic anisotropy, Cauchy ratio, Debye temperature, and Grüneisen constant. The temperature dependence of both the directly measured and the derived elastic quantities are presented in this paper.

## II. EXPERIMENTAL PROCEDURE

The single-crystal specimens V(I), V(II), and V(III A) were cut from a single ingot obtained from the Linde Company. The ingot (1.25 cm diam) was grown by a Verneuil process using an arc as the heat source. Specimen V(II) was obtained by cutting (perpendicular to the [110] axis) approximately  $\frac{1}{3}$  off the length of V(I). V(III A) was in turn obtained by cutting a piece (parallel to the [110] axis) from V(II). Cuts were made with a diamond metallurgical cutoff wheel under water cooling. The crystals were oriented using Laue x-ray back-reflection photographs. In each of these specimens sets of faces were prepared perpendicular to the [100] crystallographic axis and perpendicular to the [110] axis; in V(III A), an additional set of faces perpendicular to the [101] axis was prepared. Specimens V(IV) and V(V) were obtained from Metals Research in the form of cylinders of 0.6 cm diam whose axes were along the  $\langle 110 \rangle$  crystal axes. These specimens, electron-beam grown, were zone refined three times. Sets of faces were prepared perpendicular to the [100] axis for V(IV) and perpendicular to the [110] axis for V(V).

TABLE I. Orientation and lengths of vanadium specimens.  
 $T = 298$  K unless otherwise specified.

Vanadium specimen	Direction of propagation	Length (cm)
(I)	[110]	1.2887
	[100]	1.1252
(II)	[110]	0.4176
	[100]	1.1657
(III A)	[110]	0.3625
	[100]	0.4996
(IV)	[100]	0.3668
(V)	[110]	1.2416 (293 K)
(Alers)	[110]	1.4765

Preliminary grinding and polishing was done using AO 302 aluminum oxide on a cast-iron lap, followed by AO 303  $\frac{1}{2}$  aluminum oxide on a lead lap. Final polishing was done using Linde A sapphire powder on lead laps or on onionskin paper. Pure odorless kerosene was used as the lubricant. The finished faces were flat and parallel to within  $6 \times 10^{-5}$  cm. Before polishing the surfaces were etched for ten minutes in a solution of 1 HCl : 1 HNO<sub>3</sub> : 1 H<sub>2</sub>O to a depth of  $6 \times 10^{-3}$  cm. Etching revealed the existence of a grain boundary around the periphery of specimens V(I) and V(II), of approximately 1-mm width. These portions of the crystals were avoided in the elastic-constant measurements.

Orientations and lengths of the finished specimens utilized in both Papers I and II are given in Table I. [A description of V(Alers) is given in Ref. 1.] Lengths were measured with gauge blocks and a high-magnification dial gauge to a precision of  $\pm 5 \times 10^{-5}$  cm. The theoretical density of 6.092 g/cm<sup>3</sup> at 298 K was obtained from the known atomic weight and from unit-cell dimensions as determined by x-ray diffraction. The temperature dependence of the density was obtained from the measured thermal expansivity. With the exception of V(I) [110], the exposed faces were measured (by x-ray diffraction) to be perpendicular within 1° to the crystal axis listed in column 1 of Table I. For V(I) [110], the face perpendicular was measured to be off axis by  $2.5^\circ \pm 1^\circ$ . Chemical analyses of the vanadium crystals are given in Table II. Analyses of portions of the Linde ingot were made at various stages in its history; the analyses were made on small pieces which had been contiguous with the larger pieces used in the experiment.

The careful work of Westlake<sup>9,10</sup> has emphasized the unreliability of quoted hydrogen-impurity concentrations in vanadium unless the physical measurements are preceded immediately by vacuum annealing and charging to the desired concentration. This was not done in the present experiment. Our

experience demonstrates, furthermore, the correctness of Westlake's warning that "the hydrogen content is easily altered during sample preparation."<sup>9</sup> The analyses for metal impurities were done by emission spectroscopy; for gases by vacuum-fusion techniques. The analyses listed in Table II for V(IV) and V(V) are those supplied by Metals Research; that for V(Alers) by Alers.<sup>1</sup>

The thermal-expansion dilatometer used in the present work was of conventional design.<sup>14,15</sup> The specimen was mounted in a fused quartz tube with a fused quartz rod resting on it. On top of the rod is the core of a linear variable differential transformer (LVDT). When an audio voltage is impressed on the primary of the LVDT, the voltage across the secondary is a linear function of the position of the LVDT core. The change in length  $\Delta l$  of the specimen was measured relative to  $l_0$ , the specimen length at 273 K. Although in any given run relative changes in  $\Delta l/l_0$  of  $5 \times 10^{-6}$  could be measured, inaccuracies in the calibration procedure limited reproducibility from run to run to 2 or 3%.

The continuous-wave (cw) ultrasonic techniques used to measure acoustic velocities have been described previously.<sup>16,17</sup> A stable oscillator supplies rf power to a piezoelectric quartz transducer on one face of the crystal specimen. A receiver is connected to a transducer on the opposite face. The frequency spectrum of power reaching the receiver consists of a series of Lorentzian lines peaking sharply at frequencies  $\omega_n$  at which the conditions for standing-wave resonance are obeyed. The acoustic velocity  $v_s$  is given by

$$v_s = \frac{\omega_n l_s}{n\pi} \left[ 1 - \frac{2\rho_T l_T}{\rho_s l_s} \left( \frac{\omega_T - \omega_n}{\omega_n} \right) \right], \quad (1a)$$

where

$$n = \frac{\omega_n}{\Delta\omega} \left( 1 - 2 \frac{\rho_T l_T}{\rho_s l_s} \right). \quad (1b)$$

Here  $n$  is the integral number of half-wavelengths in the specimen of length  $l_s$  and density  $\rho_s$ ;  $\omega_T$ ,  $\rho_T$ , and

TABLE II. Chemical and vacuum-fusion analyses of crystal specimens (ppm by weight).

Specimens	H <sub>2</sub> <sup>a</sup>	N <sub>2</sub>	O <sub>2</sub>	Si	C	Metal impurities
(I)	120	33	860	100	...	Al(400), Fe(250), total all others < 100 ppm
(II)	...	...	...	100	...	[similar to V(I)]
(III A)	350	670	870	100	...	[similar to V(I)]
(IV)	3	450	36	200	80	Mo, Nb, W, Ti < 100 ppm; all others < 10 ppm
(V)	40 <sup>b</sup>	500 <sup>b</sup>	1000 <sup>b</sup>	200	.80	total < 100 ppm
(Alers)	60	80	80	<10	100	total < 100 ppm

<sup>a</sup>See Westlake's warning in Sec. II.

<sup>b</sup>Analysis of starting material from supplier (Metals Research).

$l_T$  are, respectively, the unloaded resonant frequency, the density, and length of the transducer;  $\Delta\omega$  is the frequency separation between adjacent mechanical resonances. This cw technique is capable of measuring  $\nu_s$  to better than 0.2%; changes in  $\nu_s$  can be measured to a few parts in  $10^6$ .<sup>18,19</sup>

Measurements were made at 10 MHz using quartz transducers. Bonds of Nonaq vacuum grease and silicone grease were found to be suitable over the temperature range investigated. The compressional constant  $C_{11}$  and shear constant  $C_{44}$  were obtained from the measured velocities of longitudinal and transverse acoustic waves propagated along the [100] crystalline axis. The shear constants  $C_{44}$  and  $C' = \frac{1}{2}(C_{11} - C_{12})$  and the compressional constant  $C_L = \frac{1}{2}(C_{11} + C_{12} + 2C_{44})$  were obtained from the velocities of transverse and longitudinal acoustic waves propagated along the [110] axis.

Over the period (approximately 5–10 min) during which a measurement of acoustic velocity or thermal expansion was made, a temperature controller held the temperature constant to within 0.2 K or better. Temperature was measured to within  $\pm 0.1$  K with gold-cobalt-copper or copper-constantan thermocouples.

### III. EXPERIMENTAL RESULTS

#### A. Thermal Expansion

The thermal expansivity  $\Delta l/l_0$  as a function of temperature for V(I) is shown in Fig. 1. The length at  $T = 273.2$  K is denoted by  $l_0$ . The curve for the [100] direction shows a slight "break" at  $\sim 182$  K (see insert); that for the [110] direction is smooth throughout the entire temperature range. For comparison, the data of Erfling<sup>3</sup> on polycrystalline vanadium is also plotted in Fig. 1. In Table III the

values of  $\Delta l/l_0$  at  $10^\circ$  intervals are compared (over the overlapping temperature ranges) with those of Refs. 3, 5, and 7.

In Fig. 2 are shown the curves for the thermal-expansion coefficient  $\alpha = (1/l)(dl/dT)$  for V(I) [100] obtained by graphically computing the slopes of the corresponding thermal-expansivity curves of Fig. 1. In the insert of Fig. 2 is shown an expanded portion of the [100] curve of  $\alpha(T)$  in the temperature range of the anomaly. The very sharply defined anomaly in  $\alpha[100]$  does not show up on the relatively coarse scale of the full plot. For comparison, the data of Erfling<sup>3</sup> are also plotted in Fig. 2. White's very precise data,<sup>4</sup> not shown here, were primarily taken at temperatures below 30 K. In Table IV are given the values of  $\alpha(T)$  at intervals of 10 K. The results of Erfling, Smirnov, and Finkel', and White are also given.

#### B. Elastic Constants

The measured values of the adiabatic elastic constants of V(I) and V(II) over the temperature range 4.2–300 K are shown in Figs. 3–6. A cw reflection (single-transducer) technique was used to obtain this data. Data points were taken at intervals of 1 or 2 K. An indication of the scatter of the data is given by the inserts in each figure, which repeat, on an expanded scale, the elastic-constant data for 4.2–30 K. The anomalies [at  $\sim 182$  K for V(I),  $\sim 235$  K for V(II)] are marked for the cases of  $C_{11}$  (Fig. 3) and  $C'$  (Fig. 4). Within the resolution of the present experiment,  $C_{44}$  (Fig. 5) and  $C_L$  (Fig. 6) do not exhibit anomalies in any of the vanadium specimens investigated. The differences in the absolute values of the elastic constants in the linear region among different specimens fall within the limits of the quoted absolute error of  $\pm 0.2\%$  for

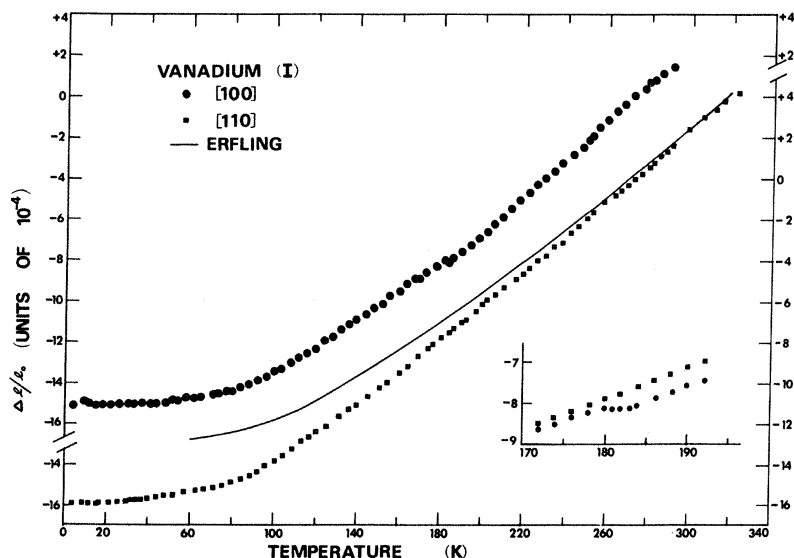


FIG. 1. Thermal expansivity  $\Delta l/l_0$  for V(I) along [100] and [110] crystal axes. For comparison, the data of Erfling for polycrystalline vanadium are shown. An expanded portion of the [100] expansivity curve, in the vicinity of the anomaly, is shown in the insert.

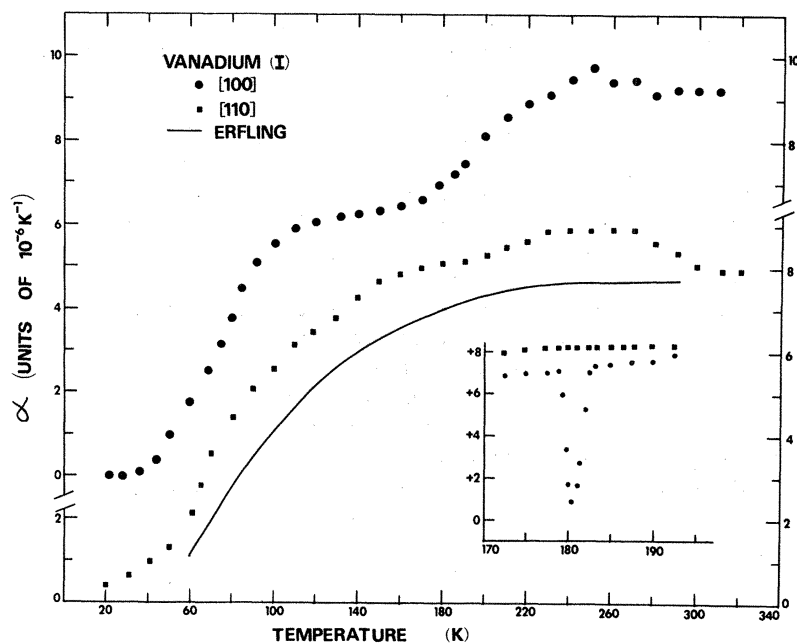


FIG. 2. Thermal expansion coefficients  $\alpha$  for V(I) [100] and V(I) [110]. For comparison, the data of Erfling for polycrystalline vanadium are shown. An expanded portion of the [100] curve, in the vicinity of the anomaly, is shown in the insert.

$C_{44}$  and  $C_{11}$ . The discrepancy in the values for  $C'$  ( $\sim 1\%$ ) may be attributed in part to the misorientation of the acoustic-propagation axis from the [110] crystal axis (see Table I). Consistency checks were made by comparing the measured values of  $C_L$  with those calculated using the other elastic constants, e.g.,  $C_L = C_{11} - C' + C_{44}$ . Agreement for V(I) over the entire temperature range was within 0.1%.

The curves of Figs. 3-6 represent the elastic constants directly measured by the present investigators. From these data we have calculated the following derived elastic quantities: the elastic constant  $C_{12} = C_{11} - 2C'$ , shown in Fig. 7; the bulk modulus  $B \equiv \frac{1}{3}(C_{11} + 2C_{12}) = C_{11} - \frac{4}{3}C'$ ; the anisotropy

ratio (for cubic crystals)  $A = C_{44}/C'$ ; and the Cauchy ratio  $C_{44}/C_{12} = C_{44}/(C_{11} - 2C')$ . A summary of the directly measured and derived elastic properties of V(I) from  $T = 4.2$  to  $T = 300$  K is given in Table V. Included in the table are the "athermal" values of the elastic constants, obtained by extrapolation of the linear high-temperature curve to absolute zero. The "athermal" values of the elastic constants are those which may be related to theories of the interatomic forces in the harmonic approximation.<sup>20</sup> In Table VI, finally, we present the temperature coefficients of the elastic constants  $T_c = (1/C)(dC/dT)$  in units of  $10^{-4} \text{ K}^{-1}$ , where we follow the convention of Hearmon in his comprehensive compilation of elastic constants.<sup>21</sup>

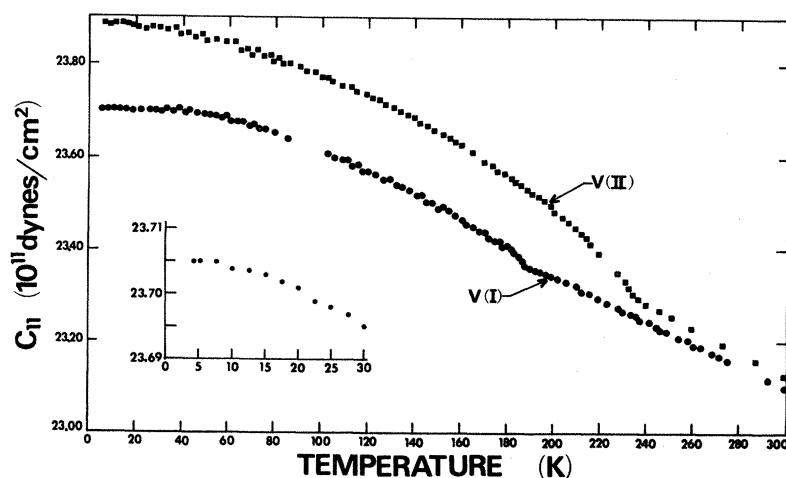


FIG. 3. Compressional elastic constant  $C_{11} = \rho v_l^2$  [100] for V(I) and V(II). Insert is for V(I) between 4.2 and 30 K.

TABLE III. Thermal expansivity  $\Delta l/l_0$  for vanadium (units of  $10^{-4}$ ).

T(K)	V(I)		Ref. 5 [100]	Ref. 7 [100]	Ref. 3
	[100]	[110]			
4.2-20	-15.05	-15.91			
30	-15.05	-15.82			
40	-15.05	-15.69			
50	-15.00	-15.53			
60	-14.85	-15.32			-12.8
70	-14.70	-15.01			-12.6
80	-14.4	-14.80			-12.3
90	-13.8	-14.31			-12.0
100	-13.3	-13.60			-11.7
110	-12.8	-13.03			-11.3
120	-12.3	-12.40	-10.53		-10.8
130	-11.6	-11.72			-10.3
140	-10.9	-11.00	-10.13		-9.7
150	-10.2	-10.35			-9.1
160	-9.6	-9.50	-8.65		-8.4
170	-9.0	-8.62			-7.7
180	-8.4	-7.80	-7.10	-8.6	-7.0
190	-7.7	-7.00		-7.9	-6.3
200	-6.9	-6.12	-5.54	-7.2	-5.6
210	-6.0	-5.30		-6.4	-4.8
220	-5.1	-4.56	-4.62	-5.6	-4.1
230	-4.2	-3.78		-4.6	-3.3
240	-3.3	-2.85	-3.04	-3.3	-2.6
250	-2.3	-1.93		-2.3	-1.8
260	-1.4	-1.01	-1.32	-1.3	-1.0
270	-0.4	-0.25		-0.3	-0.2
280	+0.7	+0.51	+0.53	+0.5	+0.5
290	+1.4	+1.51		+1.05	+1.3
300	+2.70	+2.70	+2.38	+2.4	+2.0

## IV. DISCUSSION

The over-all behavior of the thermal expansivity (Fig. 1) and thermal-expansion coefficient (Fig. 2) is consistent with the results of previous investigators. Even in V(I), however, which of all the vanadium specimens on which results are reported in both Papers I and II showed the most "normal" behavior, anomalies in the thermal expansion were evident; in the expansivity, a change in slope in the temperature range 180-185 K; in the thermal-expansion coefficient (see insert, Fig. 2) a marked dip centered at 182 K; and in both, a departure from the isotropy in thermal expansion which ordinarily characterizes a crystal with cubic symmetry. The anomaly in V(I) (at  $\sim 182$  K) was most marked for expansion along the cube axis. Only a slight concavity in the  $\alpha(T)$  curve for the [110] axis (Fig. 2) appeared to reflect the anomalous behavior, whereas for the [100] axis a broad concavity in  $\alpha(T)$ , as well as the sharp dip at 182 K, was evident. The forms of  $(\Delta l/l_0)(T)$  and  $\alpha(T)$  curves for V(I) are compared in Figs. 1 and 2 with the results of Erling for a polycrystalline specimen of vanadium in which no anomaly was reported. Considering vari-

ations from specimen to specimen, and the relative crudeness of the present thermal-expansion measurements (absolute accuracy  $\pm 2\%$ ), the agreement between the present results and those of previous investigators<sup>3-7</sup> is good.

The variation of the measured elastic constants (Figs. 3-6) as a function of temperature is well described at high temperatures (above 200 K and neglecting anomalies) by a straight line of negative slope. This linear behavior is consistent with that predicted by current theories of vibrational modes of crystal lattices.<sup>20</sup> At temperatures below  $\sim 200$  K, the elastic constants  $C_{11}$ ,  $C'$ , and  $C_L$  are characterized by a decreasing (negative) slope, with a slope of essentially zero below 10 K. The temperature coefficients of these three elastic constants differ in magnitude, with  $T_{C'} > T_{C_L} > T_{C_{11}}$  (see Table VI), but not in form. This behavior, predicted theoretically,<sup>20</sup> is characterized also by the fact that the athermal values (value at 0 K from extrapolation of the high-temperature linear portion of the curve) are larger than the measured values at  $\sim 4.2$  K. The shear constant  $C_{44}$  exhibits a temperature behavior markedly different from those of the three other directly measured elastic quantities (see Fig. 4). Over most of the temperature range ( $80 \text{ K} < T < 300 \text{ K}$ ) the  $C_{44}(T)$  curve shows a marked upward concavity; its temperature coefficient is considerably larger than that of the other elastic constants, and its athermal value is considerably less than the measured 4.2-K value. Such an anomalous athermal value of  $C_{44}$  and upward concavity of the  $C_{44}(T)$  have been noted previously for a quite different (but also cubic) crystal (RbMnF<sub>3</sub>).<sup>22</sup>

An apparent disagreement of about 2% exists between the 4.2-K values of the elastic constants of the present work and those of Alers (see Table V). Approximately half of this discrepancy arises, however, because of a difference of about 1% between the value of density used here and that used by Alers. It seems reasonable to tentatively attribute the remaining differences to effects related to the presence of interstitial hydrogen and of dislocations, the densities of which differ markedly from specimen to specimen.<sup>23,24</sup> The specimen designated V(I) of Ref. 2 is identical to V(I) of the present paper. (Slight changes in lengths resulted from minor repolishing of the prepared faces.) In agreement with our quoted accuracy of better than 0.2%, the present values of the elastic constants at 300 K differ by no more than 0.15% from those of Ref. 2 when proper account is taken of the values of density employed.

The over-all behavior of the  $C_{12}(T)$  and  $B(T)$  curves (see Table V) is similar to that for the three regularly behaved constants  $C_{11}(T)$ ,  $C'(T)$ , and  $C_L(T)$  which were measured directly. The temperature dependences of  $C_{12}$  and  $B$  are, however,

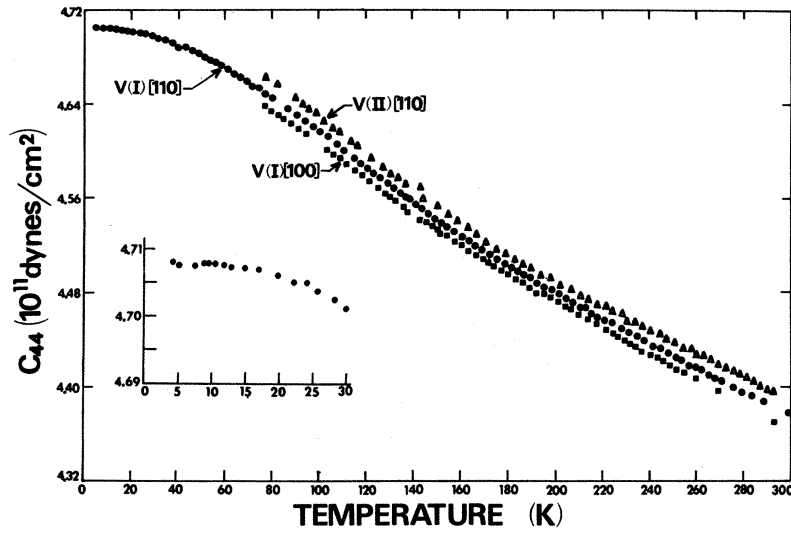


FIG. 4. Shear elastic constant  $C_{44} = \rho v_{t_1}^2$  for V(I) and V(II). Insert is for V(I) [110] between 4.2 and 30 K.

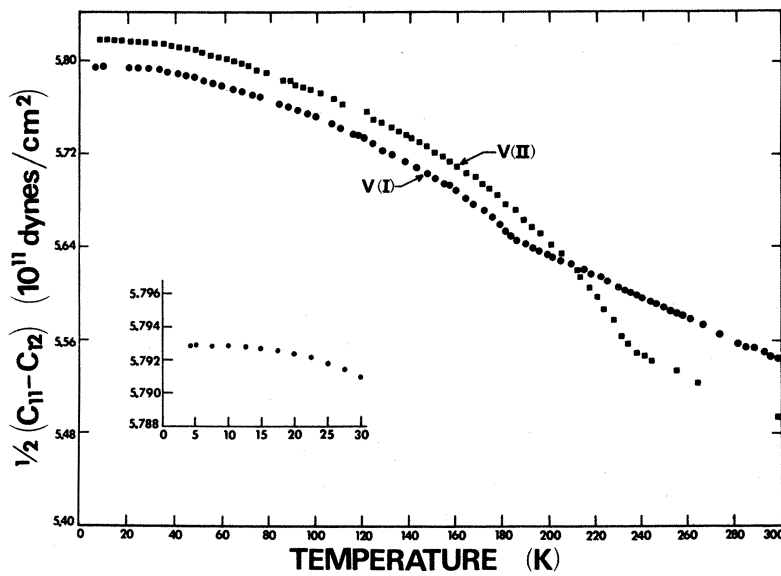


FIG. 5 Shear elastic constant  $C' \equiv \frac{1}{2}(C_{11} - C_{12}) = \rho v_{t_2}^2$  for V(I) and V(II). Insert is for V(I) between 4.2 and 30 K.

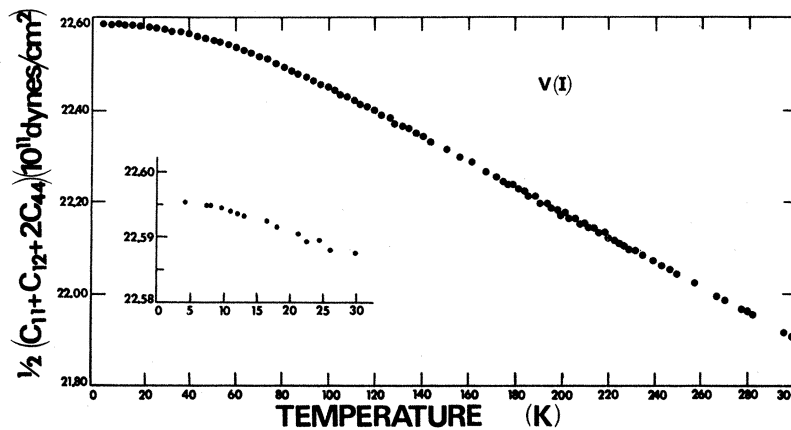


FIG. 6. Compressional elastic constant  $C_L \equiv \frac{1}{2}(C_{11} + C_{12} + 2C_{44}) = \rho v_l^2$  [110] for V(I).  $C_L$  for V(II) did not differ in any respect from that shown here. Insert is for V(I) between 4.2 and 30 K.

TABLE IV. Thermal-expansion coefficient  $\alpha$  for vanadium (units of  $10^{-3} \text{K}^{-1}$ ). First two columns calculated from smoothed curves of  $\Delta l/l_0$  (Fig. 1).

T(K)	V(I)		Reference 5 [100]	Reference 4 [100]	Reference 3
	[100]	[110]			
20	0	40		13	
30	10	65		35	
40	30	96			
50	100	130			
60	170	210			110
70	250	350			190
80	370	440			270
90	515	500			345
100	550	550			400
110	590	620			460
120	605	640			515
130	615	680			550
140	620	730	645		590
150	630	770			630
160	640	780	785		660
170	655	795			700
180	680	800	800		710
190	700	815			720
200	820	825			725
210	855	835			750
220	885	845			750
230	890	855			760
240	950	885	830		760
250	970	885	865		765
260	935	885	895		770
270	940	885			775
280	900	855	910		785
290	920	830			800
300	920	810	925	775	

small (see Table VI). The behavior of both  $A(T)$  and  $C_{44}(T)/C_{12}(T)$  is markedly affected by the contribution of  $C_{44}(T)$ , resulting in (i) a characteristic upward concavity and (ii) an athermal value less than that measured at 4.2 K.

The Debye temperature  $\Theta_D$  (elastic) as a function of temperature was calculated using the relation

$$\Theta_D(\text{elastic}) = \frac{h}{k} \left( \frac{3N}{4\rho V} \right)^{1/3} \left( \frac{C_{11}}{\rho} \right) g,$$

where  $h$  is Planck's constant,  $k$  the Boltzmann constant,  $N/V$  is the number density of atoms, and  $g$  is a function of  $C'/C_{11}$  and  $C_{44}/C_{11}$  which is obtained conveniently from graphs due to Marcus and reproduced in a review article by Alers.<sup>25</sup> The results are given in Table V. The 403-K value for  $\Theta_D$  (elastic) extrapolated to 0 K obtained from the present data is to be compared with the corresponding value 399.3 K of Alers. The calorimetric values of  $\Theta_D$  have been measured by Corak *et al.*<sup>26</sup> to be  $\Theta_D$  (calorimetric) = 338 K extrapolated to 0 K and by Clusius *et al.*<sup>27</sup> to be  $\Theta_D$  (calorimetric) = 425 K at 20 K. Detailed discussions of Debye temperatures, the relationship of values obtained by different techniques, and their temperature dependences have been given by Alers<sup>25</sup> and by Herbstein.<sup>28</sup>

A detailed discussion of the anomalies in the elastic properties of vanadium is given in Paper II.<sup>8</sup> Here we simply note that the anomalies—sharp “breaks” in elastic constants as functions of temperature—occur for  $C_{11}$  and  $C'$ , but not for  $C_{44}$  and  $C_L$ . Regarding anomalies in the “derived” elastic properties of V(I): The scatter in the data for  $C_{12}(T)$  makes one hesitate to claim an anomaly at 185 K; there is a small, but nonetheless distinct, anomaly in  $B(T)$ ; an “inverted” anomaly, as expected, appears in the curve of  $A(T)$ ; and, as expected, no observable anomaly is present in the Cauchy ratio  $C_{44}/C_{12}$ .

The thermal expansion and the temperature dependence of the elastic constants are due to anharmonicity in the potential energy of a crystal.<sup>20</sup> A parameter conventionally used to characterize the degree of lattice anharmonicity in the quasiharmonic approximation is the Grüneisen constant  $\gamma = 3\alpha B/\rho C_v$ , where  $C_v$  is the specific heat at constant volume. From the measured values of  $\alpha(T)$ ,  $B(T)$ , and the specific heat,<sup>29</sup> we obtain  $\gamma_{300 \text{ K}} \approx 1.35$ ,  $\gamma_{200 \text{ K}} \approx 1.4$ , and  $\gamma_{100 \text{ K}} \approx 1.50$ . These values are higher than those given by Corruccini and Gniewick (cited by Collins and White<sup>30</sup>) but closer to those for other bcc transition metals quoted by Collins and White.<sup>30</sup>

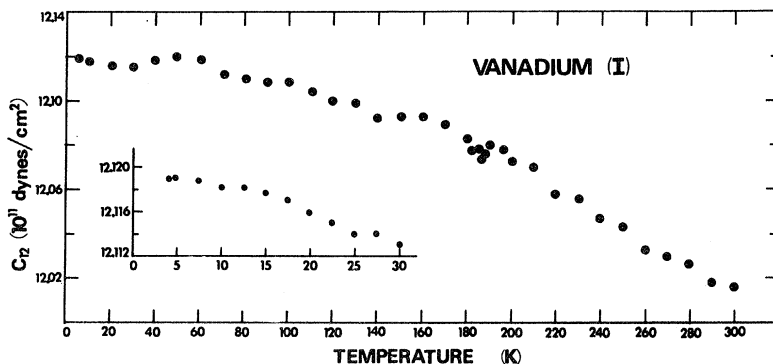


FIG. 7. Derived elastic constant  $C_{12}$  for V(I) calculated from the data of Figs. 3 and 5 using  $C_{12} = C_{11} - 2C'$ . Insert shows details between 4.2 and 30 K.

TABLE V. Elastic properties of V(l).

$T$ (K)	$\rho$ (g/cm <sup>3</sup> )	$C_{11}$ (10 <sup>11</sup> dyn/cm <sup>2</sup> )	$C_{44}$ (10 <sup>11</sup> dyn/cm <sup>2</sup> )	$\frac{1}{2}(C_{11}-C_{12})$ (10 <sup>11</sup> dyn/cm <sup>2</sup> )	Bulk modulus (10 <sup>11</sup> dyn/cm <sup>2</sup> )	$C_{12}$ (10 <sup>11</sup> dyn/cm <sup>2</sup> )	Anisotropy	$\frac{C_{44}}{C_{12}}$	$\Theta_D$ (eI) (K)
Athermal	6.135	23.820	4.680	5.808	16.07	12.204	0.806	0.383	
4.2(Alers)	6.032	23.240	4.595	5.652	15.702	11.936	0.812	0.384	399.3
4.2	6.119	23.705	4.7080	5.7929	15.981	12.119	0.813	0.388	403.8
10	6.119	23.704	4.7077	5.7928	15.980	12.118	0.813	0.388	403.8
20	6.119	23.701	4.7060	5.7924	15.979	12.116	0.812	0.388	403.8
30	6.119	23.695	4.7014	5.7910	15.974	12.113	0.812	0.388	403.7
40	6.119	23.696	4.6940	5.7878	15.979	12.120	0.811	0.387	403.6
50	6.119	23.687	4.6866	5.7836	15.975	12.120	0.810	0.387	403.5
60	6.119	23.675	4.6730	5.7773	15.973	12.120	0.809	0.386	403.2
70	6.118	23.654	4.6594	5.7714	15.960	12.111	0.807	0.385	403.0
80	6.118	23.643	4.6453	5.7662	15.955	12.110	0.806	0.384	402.7
90	6.117	23.624	4.6314	5.7577	15.947	12.109	0.804	0.382	402.3
100	6.117	23.609	4.6145	5.7502	15.943	12.109	0.802	0.381	401.9
110	6.116	23.586	4.6020	5.7407	15.932	12.105	0.802	0.380	401.5
120	6.116	23.566	4.5869	5.7331	15.922	12.100	0.800	0.379	401.2
130	6.114	23.544	4.5731	5.7226	15.914	12.099	0.799	0.378	400.6
140	6.113	23.514	4.5553	5.7019	15.900	12.092	0.798	0.376	399.9
150	6.112	23.490	4.5389	5.6984	15.893	12.093	0.797	0.375	399.3
160	6.111	23.436	4.5268	5.6851	15.883	12.093	0.796	0.374	398.6
170	6.110	23.436	4.5158	5.6730	15.872	12.090	0.796	0.374	398.3
180	6.108	23.401	4.5040	5.6589	15.856	12.083	0.796	0.373	397.6
190	6.107	23.631	4.4910	5.6405	15.840	12.080	0.796	0.372	396.9
200	6.106	23.338	4.4800	5.6329	15.828	12.072	0.795	0.371	396.4
210	6.105	23.317	4.4693	5.6234	15.820	12.070	0.795	0.370	395.7
220	6.103	23.287	4.4567	5.6146	15.801	12.058	0.794	0.370	395.0
230	6.102	23.266	4.4457	5.6051	15.793	12.056	0.793	0.369	394.7
240	6.100	23.237	4.4354	5.5948	15.777	12.047	0.793	0.368	394.3
250	6.099	23.215	4.4264	5.5858	15.767	12.043	0.792	0.368	394.0
260	6.097	23.186	4.4164	5.5769	15.750	12.032	0.792	0.367	393.7
270	6.096	23.165	4.4033	5.5675	15.741	12.030	0.791	0.366	393.3
280	6.095	23.145	4.3947	5.5585	15.733	12.028	0.791	0.365	392.9
290	6.093	23.116	4.3841	5.5497	15.716	12.017	0.790	0.365	392.6
300	6.092	23.098	4.3768	5.5403	15.712	12.017	0.790	0.364	392.1

## V. SUMMARY

In this paper we emphasized the over-all temperature-dependent behavior of the thermal expansion and elastic constants of vanadium, despite the intrusion of certain anomalies. In Paper II we report

TABLE VI. Temperature coefficients of elastic constants  $(1/C) dC/dT$  computed from smoothed curves of Figs. 3-7. All values are negative. Units of  $10^{-4} K^{-1}$ .

$T(K)$	$T_{C_{11}}$	$T_{C_{44}}$	$T_{C'}$	$T_{C_L}$	$T_{C_{12}}$	$T_B$
25	0.21	0.98	0.24	0.15	0.02	0.16
50	0.37	2.14	0.90	0.64	0.07	0.30
75	0.60	2.90	1.50	0.96	0.09	0.41
100	0.87	3.10	1.50	1.23	0.13	0.61
150	•••	2.90	•••	1.25	0.33	0.77
200	1.02	2.46	1.60	1.25	0.45	0.76
250	1.03	2.50	1.60	1.25	0.46	0.83
300	1.03	2.52	1.63	1.26	0.46	0.76

in detail on the structure and nature of these anomalies, and propose a simple thermodynamic theory Brandt, R. B. Ferguson, and R. W. Guernsey aided in experimental aspects. We are indebted to J. Paterson, J. Senko, and W. Harris for impurity analysis of the vanadium specimens. I. Wu aided in data analysis.

to explain them. Quantitative agreement between our results for those specimens exhibiting little or no anomalous behavior and the results of previous investigators has convinced us that it is physically meaningful to characterize the elastic properties of vanadium by the data presented in this paper.

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

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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 paper<sup>1</sup> (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