

Elastic Moduli of Vanadium

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Using the technique of zone melting by electron bombardment, $\frac{3}{8}$ -in. diameter single crystals of vanadium were grown in a high vacuum. Two crystals were prepared from seeds such that their lengths were parallel to the [100] and the [110] crystal directions. With these orientations, the elastic moduli C_{11} , C_{44} , and $\frac{1}{2}(C_{11}-C_{12})$ were measured directly from 4.2°K to 300°K using the ultrasonic pulse-echo technique. The results are, in units of 10^{11} dyne cm^{-2} ,

| Temp. | C_{11} | C_{44} | $\frac{1}{2}(C_{11}-C_{12})$ |
|-------|----------|----------|------------------------------|
| 300°K | 22.795 | 4.255 | 5.460 |
| 4.2°K | 23.240 | 4.595 | 5.652 |

The moduli at 4.2°K were used to calculate a Debye θ_0 of 399.3°K which disagrees with the θ_0 of 338°K obtained from calorimetry. The room temperature moduli agree very well with all other determinations. The moduli were used to calculate a phonon frequency distribution which is compared with the distribution measured by slow neutron scattering.

INTRODUCTION

THE Born-von Kármán theory¹ of crystal lattices predicts the phonon frequency distribution function of a solid if the interatomic force constants are assumed. Since the force constants also determine the elastic constants, it is possible in principle, to use measured elastic constants to define the force constants and thence to determine a frequency distribution. A comparison between the measured and calculated distributions then serves to assess the validity of the force constant model chosen. Until recently, it has been impossible to obtain a measured frequency distribution and it was necessary to carry the theory a step further and calculate the specific heat before a comparison could be made. Recent studies of inelastic neutron scattering show that if the scattering cross section is incoherent, the energy spectrum of scattered neutrons is easily converted to the lattice vibration frequency distribution. Because of the special properties of vanadium, the neutron scattering from this metal is almost completely incoherent and its phonon frequency distribution function has now been measured by several workers.^{2,3} It is therefore important to know the elastic constants of pure vanadium as accurately as possible.

The bulk modulus,⁴ Young's modulus^{5,6} and the rigidity modulus⁵ of polycrystalline vanadium have been measured but these do not uniquely define the single crystal constants C_{11} , C_{12} , and C_{44} which are needed by

the theory.⁷ An attempt to get the single crystal constants from thermal diffuse x-ray scattering has been made by Sandor and Wooster⁸ but the results give only the two ratios C_{12}/C_{11} and C_{44}/C_{11} . Accurate values of all three constants can be obtained by ultrasonic techniques if large single crystals are used. However, such specimens are very difficult to fabricate because of vanadium's high melting point (1900°C) and its extreme reactivity with oxygen and nitrogen. Recently the use of vacuum arc melting techniques and of floating zone purification techniques have yielded sufficiently large vanadium single crystals. The elastic constants reported here were determined on crystals grown by the floating zone method while room temperature measurements made simultaneously with the present work in another laboratory¹⁰ used crystals prepared by the arc method.

SPECIMEN PREPARATION

As pointed out above, the major problem of determining the three elastic moduli of vanadium is in the preparation of sufficiently large single crystals. A further complication is imposed if it is important to control the crystallographic orientation of the specimen. Both of these problems were overcome with the aid of D. K. Donald of the Electrical Department of the Ford Motor Scientific Laboratory who designed and built a floating zone purification apparatus.¹¹ In this equipment a polycrystalline rod about $\frac{3}{8}$ in. in diameter is supported vertically inside a bell jar which is evacuated to 10^{-6} mm of Hg. Around the rod, a movable filament electron source with focusing electrodes directs a beam of high-

¹ M. Born and T. von Kármán, *Physik. Z.* **13**, 297 (1912).

² A. T. Stewart and B. N. Brockhouse, *Revs. Modern Phys.* **30**, 250 (1958).

³ C. M. Eisenhour, I. Pelah, D. J. Hughes, and H. Palevsky, *Phys. Rev.* **109**, 1046 (1958).

⁴ P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, London, 1952).

⁵ C. E. Lacy and C. J. Beck, *Trans. Am. Soc. Metals* **48**, 579 (1956).

⁶ W. Rostoker, A. S. Yamamoto, and R. E. Riley, *Trans. Am. Soc. Metals* **48**, 560 (1956).

⁷ D. N. Singh and W. A. Bowers, *Phys. Rev.* **116**, 279 (1959).

⁸ E. Sandor and W. A. Wooster, *Acta Cryst.* **12**, 332 (1959).

⁹ W. Rostoker, *The Metallurgy of Vanadium* (John Wiley & Sons, New York, 1958).

¹⁰ D. I. Bolef and M. Menes, *Bull. Am. Phys. Soc.* **5**, 40 (1960). The author is indebted to D. I. Bolef for communicating their results to him prior to publication.

¹¹ D. K. Donald (to be published).

energy electrons at the bar. In this way a narrow zone may be melted and moved along the length of the bar. For preparing the vanadium single crystals, a section of the $\frac{3}{8}$ -in. bar was machined down to $\frac{1}{8}$ -in. diameter. The passage of the molten zone through this neck formed a small diameter single crystal which then served as a seed for the section of larger diameter. By mounting the seed in a jig and using x-rays to orient it, the crystallographic orientation of the crystal grown from it could be controlled.

The vanadium metal used for the present measurements was purchased in the form of a $\frac{3}{4}$ -in diameter rod from Electro Metallurgical Company¹² and had an initial purity greater than 99.5%. During the single crystal growth ten or fifteen molten zones were passed through the sample to increase its purity. After growth analysis showed 0.008% N₂ and O₂, 0.006% H₂, and less than 0.01% C and metallic impurities. Measurements of the ratio of the room temperature resistivity to the low-temperature residual resistivity¹¹ were only 12 to 15 which is not very large compared to other pure metals but is much higher than is usually observed for vanadium. Two $\frac{3}{8}$ -in. diameter \times 1-in long crystals were prepared. One had its length 7° away from a [100] direction and the other was within 3° of the [110] direction. It was possible to cut two parallel faces on each crystal whose normals were at a slight angle to the specimen length but which were within $\frac{1}{2}$ ° of the principal crystal axes [100] or [110]. In this way, a quartz transducer attached to one surface could generate sound waves which would propagate along the [100]

TABLE I. The adiabatic elastic constants of vanadium at various temperatures. 10^{11} dyne cm^{-2}

| $T^\circ\text{K}$ | C_{11} | C_{44} | $\frac{1}{2}(C_{11}-C_{12})$ | C_{12} | $\frac{1}{3}(C_{11}+2C_{12})$ |
|-------------------|----------|----------|------------------------------|----------|-------------------------------|
| 300 | 22.795 | 4.255 | 5.460 | 11.870 | 15.508 |
| 275 | 22.831 | 4.275 | 5.473 | 11.884 | 15.531 |
| 250 | 22.869 | 4.300 | 5.486 | 11.898 | 15.554 |
| 225 | 22.905 | 4.323 | 5.500 | 11.910 | 15.575 |
| 200 | 22.951 | 4.353 | 5.520 | 11.910 | 15.588 |
| 175 | 23.995 | 4.385 | 5.542 | 11.916 | 15.609 |
| 150 | 23.042 | 4.418 | 5.566 | 11.908 | 15.617 |
| 125 | 23.085 | 4.447 | 5.588 | 11.914 | 15.638 |
| 100 | 23.132 | 4.483 | 5.612 | 11.906 | 15.646 |
| 75 | 23.177 | 4.523 | 5.630 | 11.920 | 15.672 |
| 50 | 23.216 | 4.560 | 5.645 | 11.930 | 15.692 |
| 25 | 23.239 | 4.587 | 5.650 | 11.940 | 15.705 |
| 0 | 23.240 | 4.595 | 5.652 | 11.936 | 15.702 |

or [110] direction and be reflected back without interference from the sides of the specimen. The details of the cutting process has been described elsewhere.¹³ The final length of the [100] specimen was 1.3352 cm and of the [110] specimen, 1.4765 cm.

The elastic constants were measured using the ultrasonic pulse echo technique as described previously.¹⁴ Because of the small diameter of the single crystals, a few modifications had to be made. One half-inch diameter, 10 megacycle transducers were used but only a section $\frac{1}{4}$ in. in diameter was covered with the electrode. They were driven at 30 megacycles per second to minimize beam spreading effects and interference from the side walls. The pulsed oscillator and receiver were purchased from the Arenberg Ultrasonic Laboratory.¹⁵ The method of obtaining measurements as a function of temperature has been described elsewhere.^{13,16} In the present case Nonaq stopcock grease was used as a binder between the transducer and specimen.

RESULTS

The [110] oriented crystal was used to determine the two shear wave velocities from which the elastic moduli $\frac{1}{2}(C_{11}-C_{12})$ and C_{44} are obtained directly. Using longitudinal and shear waves in the [100] crystal, the moduli C_{11} and C_{44} were measured directly. For these results, the room temperature density was taken as 6.022 g/cm³ as calculated from the x-ray lattice parameter.¹⁷ At lower temperatures the density and sample length must be corrected for thermal expansion. Since no such measurements are available, a simple dilatometer was constructed using fused silica rods and a precision dial indicator to measure the specimen length change between room temperature and 77°K. Based on these results, a correction amounting to at most 0.16%

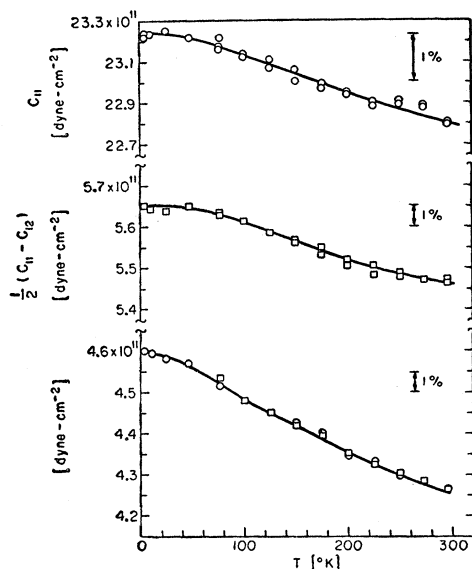


FIG. 1. Temperature variation of the elastic moduli of vanadium. The open circle points were obtained on a [100] oriented crystal. The square data points were obtained on a [110] crystal.

¹² Fine Metals and Chemicals Department, P. O. Box 268, Niagara Falls, New York.

¹³ J. R. Neighbours and G. A. Alers, Phys. Rev. **111**, 707 (1958).

¹⁴ G. A. Alers and J. R. Neighbours, J. Phys. Chem. Solids **7**, 58 (1958).

¹⁵ 94 Green Street, Jamaica Plain 30, Massachusetts.

¹⁶ D. L. Waldorf, J. Phys. Chem. Solids (to be published).

¹⁷ C. S. Barrett, *Structure of Metals* (McGraw-Hill Book Company, Inc., New York, 1952).

TABLE II. Comparison of the present results with those of Bolef and Menes (reference 10) and of Bridgman (reference 4).

| | C_{11} | $\frac{1}{2}(C_{11}-C_{12})$ | C_{44} | $\frac{1}{3}(C_{11}+2C_{12})$ |
|--------------|----------|------------------------------|----------|-------------------------------|
| Present | 22.80 | 5.46 | 4.26 | 15.51 |
| Bolef, Menes | 22.82 | 5.48 | 4.32 | 15.51 |
| Bridgman | ... | ... | ... | 15.8 |

was applied to the moduli measurements. Figure 1 shows the results. The circle points were obtained from the [100] crystal while the square data points come from the [110] crystal. Excellent internal consistency between the two crystals is shown by the agreement obtained on the C_{44} modulus. Table I gives the values for the measured moduli as well as the other elastic parameters which can be calculated from them as a function of temperature. The tabulated values were read from smooth curves drawn through the data points. The absolute accuracy of the moduli C_{11} , C_{44} , and $\frac{1}{2}(C_{11}-C_{12})$ is $\pm \frac{1}{2}\%$.

DISCUSSION

The 4.2°K values of the elastic moduli were used to calculate a Debye θ_0 using a computer as described previously.¹⁸ The results were θ_0 (elastic) = 399.3°K. Low-temperature specific heat measurements on vanadium¹⁹, give a value for θ_0 (calorimetric) of $338 \pm 5^\circ\text{K}$ which is in definite disagreement. This difference in θ values is surprising since it has been shown¹⁸ that the θ_0 (elastic) and θ_0 (calorimetric) are in excellent agreement for all other cubic metals examined. It is not likely that the difference arises from a gross error in the elastic constants since other measurements are in very good agreement with those presented here. Table II shows a comparison between the various available measurements. It is not likely that the low-temperature specific heat data are at fault because the measurements are quite accurate and were taken at temperatures below $\theta/50$ where Debye theory is usually satisfactory. Furthermore, great care was exercised in suppressing the effects of superconductivity.

It is of interest to compare these two θ values with the phonon frequency distribution as determined from the most recent neutron scattering experiments.³ At low frequencies the measured distribution should be parabolic and have a shape described by the Debye theory. Figure 2 shows the two Debye distributions for $\theta = 338^\circ\text{K}$ (calorimetric) and $\theta = 388^\circ\text{K}$ (elastic) superimposed on the measured distribution. It might be concluded that $\theta = 388^\circ\text{K}$ gives a slightly better fit. This θ value was calculated from the room temperature elastic constants since this is the temperature at which the neutron scat-

tering experiments were performed. Strictly speaking the θ obtained from low-temperature calorimetry (338°K) should be adjusted downward before comparing it with the phonon distribution at room temperature. However, such an adjustment would only serve to make the Debye distribution based on the calorimetric θ deviate more from the neutron data. In view of the slightly better agreement between the measured phonon frequency distribution and the θ determined from the elastic constants, it might be concluded that the low-temperature specific heat includes a contribution which varies as T^3 in addition to the lattice T^3 term. It would be worthwhile to extend specific heat data to temperatures greater than $\theta/50$ and to examine the deviations from the T^3 law.

The main purpose for measuring the elastic constants was to use the values to define a set of force constants from which the frequency distribution might be calculated. One force constant model discussed in the literature which can be used easily to construct a distribution is that given by Montroll and Peaslee.²⁰ This is a two force constant model in which central forces are assumed to connect an atom with its nearest and next nearest neighbors. The force constants are related to the elastic constants by²¹

$$\alpha_1 = 3aC_{44}/2 \text{ (nearest neighbors)}$$

$$\alpha_2 = a(C_{11}-C_{12})/2 \text{ (next nearest neighbors),}$$

where a is the lattice parameter. The solid line curve shown in Fig. 2 is the frequency distribution predicted by Montroll and Peaslee's two central force constant model. It is obvious that such a model represents too extreme an oversimplification and only describes the general features of the observed distribution. The same

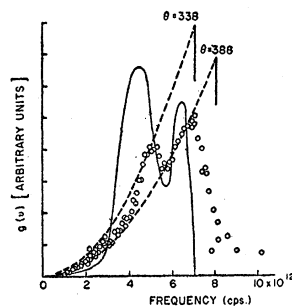


FIG. 2. Phonon frequency distribution function of vanadium. The data points are the neutron scattering results of Eisenhaur *et al.*, (reference 3). The two dashed curves are distribution functions predicted by Debye theory using θ values determined from the elastic constants (388°K) and from calorimetry (338°K). The light line distribution is predicted from a two central force constant model (reference 20).

¹⁸ G. A. Alers and J. R. Neighbours, *Revs. Modern Phys.* **31**, 675 (1959).

¹⁹ W. S. Corak, B. B. Goodman, C. B. Satterthwaite, and A. Wexler, *Phys. Rev.* **102**, 656 (1956).

²⁰ E. W. Montroll and D. C. Peaslee, *J. Chem. Phys.* **12**, 98 (1944).

²¹ J. de Launay, *Solid-State Physics* (Academic Press, Inc., New York, 1956), Vol. 2, Chap. 4, p. 273.

force constant model has also been studied by Clark²² who has arrived at the same conclusion as is reached here. A more general force constant model has been applied to vanadium by Singh and Bowers,⁷ but the elastic constants they used deviate considerably from the measured values.

²² C. B. Clark, *Bull. Am. Phys. Soc.* **5**, 41 (1960).

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Photoconductivity in Gallium Sulfo-Selenide Solid Solutions

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The photoconductivity characteristics of solid solutions of GaSe and GaS have been investigated for proportions of GaS between 10% and 50%. The difference between the room temperature band gaps of GaSe and GaSe(50)·GaS(50) is 73% of the total difference between the band gaps of GaSe (2.03 eV) and GaS (2.58 eV). The optical quenching energy and the thermal quenching energy of sensitizing centers are independent of the solid solution composition, thus giving additional evidence that these centers are associated with the crystal cation and that the photoconductivity observed is associated with holes.

INTRODUCTION

PHOTOCONDUCTIVITY in GaSe crystals has been described in a previous publication.¹ The major results of that investigation may be briefly summarized:

- (1) GaSe has a layer-type crystal structure as indicated by easy cleavage perpendicular to the *c* axis.
- (2) The photoconductivity characteristics of GaSe were not dependent on whether the applied field was parallel or perpendicular to the *c* axis.
- (3) GaSe crystals were high conductivity *p* type as prepared from the melt, but low conductivity crystals with high photosensitivity could be prepared by compensating with chlorine or tin impurity.
- (4) Rectification tests at room temperature indicated photoconductivity by holes. Crystals were of too high a resistivity to permit Hall effect measurements to date.
- (5) Both optical quenching and thermal quenching of photoconductivity were observed. The energy for optical quenching, about 1.0 eV, however, was twice the energy for thermal quenching, about 0.5 eV.
- (6) Analysis of the thermal quenching data indicated a capture cross-section ratio for the sensitizing centers of 3×10^6 .

GaS has the same crystal structure as GaSe² and a complete range of solid solutions should be possible. Evidence has been obtained from analysis of the properties of Group II-Group VI compounds indicating that the ionization energy of donor imperfections is associated primarily with the cation of the compound, and

that the ionization energy of acceptor imperfections is associated primarily with the anion of the compound.³ It is reasonable that a similar correlation should exist in the properties of Group III-Group VI compounds. It would be expected therefore, to find a variation in the ionization energy of the sensitizing centers with composition in GaSe·GaS solid solutions if the sensitizing centers were associated with acceptor-type imperfections (as is found in the CdSe·CdS system), but not if the sensitizing centers were associated with donor-type imperfections. Normally one would expect sensitizing centers to be associated with acceptor-type imperfections (negatively charged) if the photocurrent were carried primarily by electrons (as in CdS and CdSe), and with donor-type imperfections (positively charged) if the photocurrent were carried primarily by holes. If the photocurrent in GaSe is carried by holes, therefore, as indicated by the previous investigation, it would be expected that the ionization energy of sensitizing centers would be relatively independent of composition in GaSe·GaS solid solutions. It is the purpose of this paper to present the results which confirm this expectation.

EXPERIMENTAL

Crystals of GaSe·GaS solid solutions were grown in essentially the same manner as described previously for the growth of GaSe crystals.¹ Reaction between the elements was followed by gradient freeze crystallization. Since the melting points of GaSe (960°C) and GaS (about 1020°C) are not appreciably different, all solid solutions had melting points within a small temperature

¹ R. H. Bube and E. L. Lind, *Phys. Rev.* **115**, 1159 (1959).

² H. Hahn and G. Frank, *Z. anorg. u. allgem. Chem.* **278**, 340 (1955).

³ R. H. Bube and E. L. Lind, *Phys. Rev.* **110**, 1040 (1958).