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Richard Williams

Citation: Journal of Applied Physics 37, 3411 (1966); doi: 10.1063/1.1708872

View online: http://dx.doi.org/10.1063/1.1708872

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Determination of Deep Centers in Conducting Gallium Arsenide*

RICHARD WILLIAMS

RCA Laboratories, Princeton, New Jersey
(Received 20 April 1966)

A technique has been developed for determining the properties of deep centers in conducting, n-type gallium arsenide. A Schottky barrier is produced at the surface by means of a blocking contact of gold or electrolyte. A reverse bias is applied and the ionization of deep centers in the dark causes the barrier capacitance to change with time. After this, electrons may be injected into the barrier by strongly absorbed light and captured by the deep centers that have previously ionized. Again, the kinetics of the process can be determined from measurements of the barrier capacitance as a function of time. The concentration, energy level, and capture cross section of the dominant center have been determined. It is a donor lying 0.74 eV below the conduction band edge and typically present in concentrations around 10¹⁶/cm³. From capture-cross-section data it appears to be negatively charged when occupied. This property is sufficient to limit minority-carrier lifetimes to very small values.

INTRODUCTION

ONSIDERABLE attention has been devoted to the properties of deep centers in GaAs. Experiments have been done mainly with high resistance or semiinsulating crystals. These have been prepared either accidentally while trying to produce high-purity GaAs or by deliberate incorporation of impurities with compensation. The latter method was used by Haisty, Mehal, and Stratton¹ to study the level associated with oxygen. A summary of earlier work and a critical compilation of the deep centers which have been reported was given by Blanc, Bube, and Weisberg.^{2,3} Many of the deep centers are due to impurities and are probably present in conducting crystals where free carrier concentrations are 10¹⁵/cm³ or greater. In what follows, a method is described for determining deep centers in such crystals and it is shown that their presence can have an important effect on minority carrier lifetime.

METHOD

For simplicity the discussion will be restricted to *n*-type GaAs. The method described, however, is not restricted to *n*-type materials or to GaAs. Consider a crystal of *n*-type GaAs on which there is a transparent blocking contact. Such a contact is produced by an electrolyte solution or by a thin layer of evaporated gold. Under reverse bias of a few volts a Schottky barrier forms. The resulting potential distribution is shown in the energy band diagram of Fig. 1. At the instant the barrier is formed after application of the bias voltage the total charge concentration in the barrier region, which determines the properties of the barrier, is that due to shallow donors which are always ionized. If there are deep donor centers at an energy below that

of the Fermi level in the bulk then these will ionize in the barrier region. The rate of ionization depends on the temperature and their depth in energy. The properties of the Schottky barrier change as these centers ionize and change the total concentration of charge in the barrier. In particular, the small signal ac capacitance increases with time. When all the deep centers are ionized there is no further change with time. The difference between the initial and final values of capacitance, under these conditions, is a measure of the total concentration of deep centers. Whether or not this change takes place slowly enough to permit convenient measurements is determined largely by the temperature and the depth of the center. It turns out that there is often a center present in substantial concentrations which ionizes at room temperature over a period of about 60 sec. Once the centers are ionized it is possible to fill them again by illuminating the surface with strongly absorbed light. This is illustrated in Fig. 1. It is important that the light be absorbed in a layer which is thin compared to the barrier thickness. Penetrating light gives rise to competing processes which empty the centers as fast as the light can fill them. The absorption constant for blue light4 is above 105 cm-1 so that it is absorbed in a layer thin compared to the barrier thickness. Holes produced near the surface are swept out without entering the barrier. Some of the electrons are captured by the empty centers. Centers which capture an electron lose it later by thermal ionization. Thus

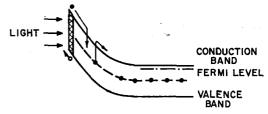


Fig. 1. Energy-band diagram showing potential distribution at a blocking contact under reverse bias. Ionization of deep centers and filling of them by photoinjected electrons are shown.

* The research reported in this paper was sponsored by the

U. S. Army Research and Development Laboratory, Fort Belvoir, Va., and RCA Laboratories.

1 R. W. Haisty, E. W. Mehal, and R. Stratton, J. Phys. Chem. Solids 23, 829 (1962).

² J. Blanc, R. H. Bube, and L. R. Weisberg, J. Phys. Chem. Solids 25, 225, (1964).

³ J. Blanc, Ř. H. Bube, and H. E. MacDonald, J. Appl. Phys. 32, 1666 (1961).

⁴ M. D. Sturge, Phys. Rev. 127, 768 (1962).

there is a steady state population of deep centers in which a certain fraction is filled and the rest are empty. The fraction filled depends on the light intensity, the thermal ionization rate, and the capture cross section for electrons. Analysis of the kinetics of this process gives an equation relating various properties of the center to experimentally determined changes of capacitance.

In the crystals examined, the results could be fit by a model with a single deep level. The kinetics are analyzed for the ionization and capture of electrons by such a center. For the case of electron capture a useful simplification can be made by using a ballistic model. The average field in the barrier is between 10⁴ and 10⁵ V/cm. Since the electron mobility in GaAs is several thousand cm²/V·sec, the drift velocity in the barrier is nearly equal to the thermal velocity of the electron. It is a good approximation to consider the electrons moving in straight lines in the direction of the field. A similar ballistic model has been used to describe trapping in silicon dioxide.5

We consider first the thermal ionization of filled centers in the barrier after the bias voltage is applied. The barrier thickness is y and the total concentration of centers, filled plus empty, is N_{tot} . All are filled with electrons at t=0, the instant the voltage is applied. The concentration of filled centers remaining at time t is N(t). We set dN(t)/dt proportional to the rate constant k.

$$ydN(t)/dt = -ykN(t). (1)$$

The solution is:

$$N(t) = N_{\text{tot}} e^{-kt}.$$
 (2)

It is not valid in general to neglect retrapping but for the specimens used it is a good approximation. It is shown later that electrons are swept out of the barrier after their thermal release without being retrapped.

The filling of traps by light involves a balance between capture of carriers injected by the light and thermal release from centers which have already captured an electron. The capture rate is given by the product of the number of electrons/cm²·sec passing through the barrier j/e, the capture cross section S_e , and the concentration of empty centers present at any time. The thermal release rate is given by the right side of Eq. (1). The total capture rate is the sum of the two processes:

$$ydN(t)/dt = y(jS_e/e)[N_{tot}-N(t)]-ykN(t)$$
 (3)

$$N(t) = N_{\infty}(1 - e^{-\infty t}).$$
 (4)

We define $N_{\infty} = N_{\text{tot}}/(1+ke/jS_e)$ and $\alpha = k+jS_e/e$.

These equations are used in the following way. The small-signal ac capacitance is measured using a 100 kc/sec measuring frequency. After application of a dc bias the initial capacitance value at t=0 rises over a

period of 60 sec or so to a higher value. Capacitance is measured at various times. From the Schottky barrier equation, which is given below, one obtains N(t) as a function of time. This gives N_{tot} and k from Eq. (2). When the final steady value of capacitance is reached in the dark the specimen is illuminated with strongly absorbed light. The capacitance now drifts to smaller values, indicating that electrons are being trapped in the barrier. Values of capacitance measured at various times may be fitted to Eq. (4) to give N_{∞} and α . j/e, which is simply the photocurrent per unit area, is directly measured. This is sufficient to determine S_e . From k and S_e the energy depth E is obtained, thus giving all the properties essential to describe the center.

For a Schottky barrier, the relation between capacitance per unit area C, dielectric constant K, total charge concentration N, and the dc applied voltage V, is given⁶ by the equation

$$N = (8\pi/Ke)C^{2}(V + V_{d}). \tag{5}$$

Here V_d is the diffusion voltage. For the specimens used V_d is about 1.4 V which is the bandgap in GaAs. Under these conditions the one-carrier model used for Eq. (5) is no longer valid since thermally generated minority carriers near the surface make a substantial contribution to the charge in the barrier. This affects the capacitance and makes it impossible to get accurate barrier heights from capacitance data. The largest effects are under forward bias when minority carriers are injected into the barrier region. Under reverse bias the minority carriers are confined to a thin layer near the surface and Eq. (5) should be a reasonable approximation. However, the value of V_d must be estimated by an independent method not involving Eq. (5).

The measured capacitance includes a large contribution, due to the charge of ionized donors, which does not change with time, either in the dark or under illumination. It is the changing component of the capacitance which gives the concentrations described by Eqs. (1)-(4). In analyzing results the total value of N was computed from Eq. (5) for each capacitance value and the background concentration of ionized donors was subtracted.

EXPERIMENTAL DETAILS

Experiments were done on wafers from three different GaAs crystals. The crystals were obtained from the RCA Semiconductor division and had been grown by the horizontal Bridgman method. They were Sn-doped. The ingots from which the wafers came were n-type with free carrier concentrations between 1015 and 10¹⁶/cm³ and the electron mobilities were 4000 to 5100 cm²/Vsec. To obtain reproducible results and good Schottky barriers it was necessary to etch the wafers

⁵ R. Williams, Phys. Rev. 140, A569, (1965).

⁶ H. K. Henisch, Rectifying Semiconductor Contacts (Oxford University Press, New York, 1957), p. 214.

7 R. F. Schwarz and J. F. Walsh, Proc. IRE 41, 1715 (1953).

after cutting to remove at least 100μ of the workdamaged surface. Wafers were etched in boiling Clorox (sodium hypochlorite) solution followed by a light etch in aqua regia. Ohmic indium contacts were applied at 350°C in a hydrogen atmosphere to an area which had been sandblasted. For the electrolyte contacts the crystal was mounted as shown in Fig. 2 on the bottom of a plastic box. There was a hole in the box permitting an electrolyte solution to come in contact with the crystal. The electrolyte was 0.5 molar H₂SO₄ in deionized water. The crystal was sealed to the box with paraffin wax. The other electrode in the solution was a platinum sheet of about 1-cm² geometric area which had been sandblasted to increase the surface area. Under illumination light passed through the solution and was absorbed at the GaAs surface in contact with the electrolyte. On two specimens the blocking contacts were thin layers of evaporated gold of such thickness that they transmitted 10% of incident blue light. A tungsten lamp source was used with a Corning 5-58 filter which passes only light of wavelengths shorter than 4700 Å. For such wavelengths the absorption

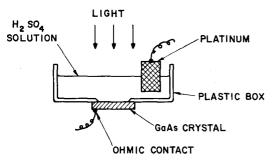


Fig. 2. Method of mounting crystal to provide an electrolyte contact which can be illuminated.

constant⁴ is greater than 10^5 cm⁻¹. The barrier thickness in the experiments was about $0.5 \,\mu$. Thus the condition of the model, that the light be absorbed in a layer thin compared to the barrier thickness is met to a fair degree but not to a high degree of approximation. Capacitance measurements were made with a Boonton 74D bridge. The measuring signal had a frequency of $100 \, \text{kc/sec}$ and an amplitude of about $10 \, \text{mV}$.

RESULTS

Figure 3 shows the capacitance as a function of voltage for one of the specimens under various conditions. The data are plotted in the way which is usual for data of this kind, i.e., $1/C^2$ vs V. The upper line shows the capacitance in the dark at the instant the dc bias voltage is applied. These data were taken by switching the bias voltage on and off repeatedly and adjusting the bridge settings until the detector indicated balance when the bias was switched on. In practice this gives the capacitance roughly 0.1 sec after the bias is switched on.

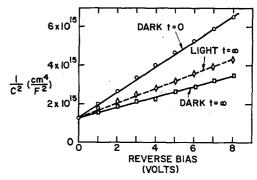


Fig. 3. Plot of $1/C^2$ vs reverse bias. C is the capacitance per unit area of contact measured under various conditions.

The capacitance in the dark then increased until it reached the final values indicated by the lowest line of Fig. 3. This required about 60 sec. Any charge appearing in the barrier in less than a tenth of a second may be calculated from the initial capacitance. From the difference between initial and final values the total concentration of deep centers is obtained. The middle curve in Fig. 3 shows the capacitance at its final steady state value under illumination with strongly absorbed light. By varying the light intensity any value of capacitance may be obtained between the two extreme values found in the dark.

The proportionality between $1/C^2$ and V stated in Eq. (5) is seen in the data of Fig. 3. The lines, however, cannot be extrapolated to determine V_d . A different value of V_d would be given by each line and none is a reasonable value. This is apparently due to the contribution of minority carriers to the space charge in the barrier region as mentioned above. Equation (5) is clearly only an approximation under these conditions but it should be better the higher the reverse bias.

The magnitude of V_d may be estimated from the opencircuit photovoltaic voltage. Figure 4 shows the opencircuit photovoltage as a function of light intensity using an unfiltered tungsten lamp as light source. This was measured in a special way because there is an electrochemical reaction which gives a small current in the dark and if the input resistance of the electrometer used for the voltage measurement is too high this gives a measured potential in the dark. If the electrometer

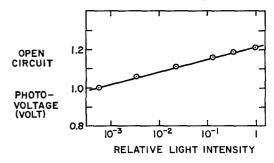


Fig. 4. Open-circuit photovoltaic emf as a function of light intensity.

input resistance is $10^9 \Omega$ or lower the electrochemical reaction does not give significant open-circuit voltage in the dark. The photovoltage is still independent of the electrometer input resistance so it is a true open-circuit photovoltage which is measured. At the highest intensity the photovoltage is 1.0 V and the slope of voltage vs light intensity is 77 mV per decade of light intensity. A similar photovoltage has been reported by Pleskov⁸ for an electrolyte electrode. Lower values have been reported by the author⁹ and by Haisty¹⁰ for various electrolytes. Differences are due to differences in electrolyte, surface preparation, and semiconductor doping.

If the photovoltage is due to band bending in the GaAs rather than to electrochemical effects then it may be used to estimate V_d . Two pieces of evidence suggest that this is the case. First the slope of voltage vs light intensity is close to the theoretical value given by the simple diode theory.11 The theoretical slope is 59 mV per decade of light intensity. Secondly, measurements of current as a function of voltage were made on the same specimen in the dark under forward bias. Here the current is controlled by the electrochemical reaction of hydrogen evolution. The slope of current vs voltage, which may be compared to that of voltage vs light intensity given above, is 176 mV per decade. This is comparable to Tafel slopes¹² which have been reported for cases where the current-voltage relation is determined by electrochemistry. Since the photovoltage data are quite different we interpret them as an effect of band bending in the semiconductor.

Since a photovoltage as large as 1.0 V was measured, the diffusion voltage V_d must be larger than this. The photovoltage is a forward bias applied to the semiconductor. A steady state is reached when the flow of carriers to the surface due to this forward bias is equal to the flow away from the surface of those carriers produced by the light. For the specimen in Fig. 4 the short-circuit current at the highest light intensity was 5.0×10^{-3} A/cm². The flow of electrons to the surface must be equal to this and this implies that, at the highest light intensity, there is still a band bending of 0.5 eV. The total bending at equilibrium is therefore 1.5 eV. The value of V_d should not be greater than the energy of the band gap, 1.4 eV. This indicates some uncertainty in estimating V_d by this method. We shall take the value to be 1.4 eV in the subsequent calculations which are not highly sensitive to the exact value of V_d . For the specimens with the gold electrodes the barrier is lower and the minority carriers are present in relatively low concentrations. A barrier height of 1.0 eV was indicated by both capacitance and photovoltage

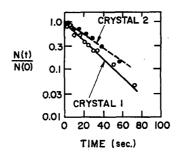


Fig. 5. Kinetics of the emptying of filled centers in the dark. N(0) is the number filled at t=0. N(t)is the number of filled centers remaining at time t as determined by capacitance measurements.

measurements. From Fig. 3 the initial charge concentration in the barrier may now be computed from Eq. (5). For an applied voltage of 4 V the concentration of shallow donors plus any centers which ionize in less than 0.1 sec is 1.9×10¹⁶/cm³. A Hall measurement on the same specimen gives a bulk free-carrier density of 0.73×10¹⁶/cm³. It is not certain whether this discrepancy is due to centers which lie below the Fermi level in the bulk but ionize too quickly to be measured by this method or whether it is simply experimental error.

Ionization of deep centers in the dark is shown in Fig. 5. Here and in subsequent figures the concentration of filled centers is plotted directly. Time is measured from the instant the dc bias is switched on. The concentration of occupied centers decreases exponentially with time, indicating a single discrete level. This gives N_{tot} and k for the center.

The effect of illumination on the occupancy of the centers is shown in Fig. 6. The solid lines are plots of Eq. (4) for the values of α and N_{∞} which give the best fit to the experimental points. With the measured values of j/e these data suffice to give all the properties of the center. In Table I these properties are collected. On one specimen the parameters were determined in two different ways. The second way, only partly independent of that already described, is to vary j/e by varying the light intensity. The final steady state concentration of filled centers obtained in this way is plotted in Fig. 7 as a function of i/e. The solid line is the function $N_{\text{tot}}/(1+ke/jS_e)$ used in Eq. (4). N_{tot} and k

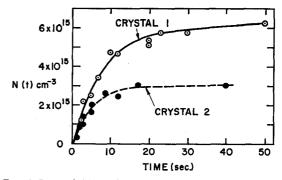


Fig. 6. Rate of filling of empty centers by strongly absorbed light of such intensity that $j/e=1.4\times10^{18}/\mathrm{cm^2\cdot sec}$. The lines are plots of Eq. (4), choosing N_∞ and α to give the best fit to the experimental points.

⁸ Yu. V. Pleskov, Dokl. Akad. Nauk SSSR 143, 1399 (1962).

⁹ R. Williams, J. Chem. Phys. 32, 1505 (1960).

¹⁰ R. W. Haisty, J. Electrochem. Soc. 108, 790 (1961).

¹¹ See Ref. 6, Ch. VII.

¹² E. C. Potter, *Electrochemistry* (Cleaver-Hume Press, London, 1956), p. 135.

	Crystal No. 1 electrolyte electrode	Crystal No. 1 electrolyte electrode ^b	Crystal No. 1 gold electrode	Crystal No. 2 electrolyte electrode	Crystal No. 3 gold electrode
k(sec-1)	0.046	0.046	0.071	0.033	0.045
$j/e(e/cm^2 \cdot sec)$	1.4×10^{13}	varied	4.1×10^{13}	3.4×10^{13}	1.4×10^{13}
$\alpha (\text{sec}^{-1})$	0.102		0.124	0.196	0.177
N_{∞} (cm ⁻³)	6.2×10^{15}		4.0×10^{15}	3.0×10^{15}	3.6×10^{15}
$N_{\rm tot}({\rm cm}^{-3})$	1.0×10^{16}	0.95×10^{16}	1.0×10^{16}	0.9×10^{16}	4.9×10^{15}
$S_{\epsilon}(\text{cm}^2)$	4.0×10^{-15}	4.0×10^{-15}	1.3×10^{-15}	4.8×10^{-15}	9.3×10^{-15}
E(eV)	0.73	0.73	0.74	0.74	0.75

Table I. Experimentally determined properties of deep centers.

are taken from previous data and used to obtain an independent value of S_e .

Measurements on one specimen, first with 4 V applied and then with 6 V applied, gave substantially identical values for the quantities in Table I. The dark current through the barrier varied from 1.0×10⁻⁶ A/cm² at 4 V to 4.0×10^{-6} at 6 V. This indicates that hole trapping is not a significant process in determining the kinetics here and is taken up in the Discussion.

The data obtained with the gold electrodes were very similar to those obtained with the electrolyte contact to wafers from the same crystal. Somewhat different values of S_e were obtained with the gold electrodes, probably indicative of the scatter of results inherent in this method.

DISCUSSION

From the good fit of Eqs. (2) and (4) to the experimental points we infer that the important effects are due to a discrete center at a single energy level. The capture cross section for electrons is about 5×10⁻¹⁵ cm². This indicates capture by a neutral center rather than a charged center. From the total concentration, the thickness of the barrier and Se we estimate that no more than one out of every 500 electrons passing through the barrier is captured. For this reason the neglect of retrapping in the kinetic analysis is justified. Note that if the center is neutral for the capture of an electron then it is negative when occupied. Such a center presents a Coulomb-attractive capture cross section for holes, S_h . The order of magnitude¹³ for S_h should be 10^{-12} cm². A hole passing through the barrier would have an almost unit probability of being captured. For this reason the dark current would give a serious departure from the model analyzed if it were due mainly to transport of holes through the barrier. As indicated above large changes in the dark current due to changes in applied voltage do not change the kinetics seen experimentally. For this reason it is believed that the dark current must be due to some process which does not lead to the transport of holes through the barrier. Examples of such processes are tunneling of electrons

from the cathode, surface generation of hole-electron pairs, and surface leakage.

The energy depth E of the center may be obtained¹⁴ from the equation relating k to the effective density of states in the conduction band N_c and the electron thermal velocity v:

$$k = N_c v S_e e^- E/kT. (6)$$

 N_c may be obtained from the equation¹⁴:

$$N_c = 2(2\pi m_e * kT)^{\frac{3}{2}}/h^3. \tag{7}$$

The value reported¹⁵ for m_e^*/m_e is 0.071. From this we obtain for the room-temperature effective density of states in the conduction band, $N_c = 6.0 \times 10^{17} / \text{cm}^3$. With the measured values of k and Eq. (6) we obtain for E an average value of 0.74 eV. This is the energy of the center below the bottom edge of the conduction band at room temperature.

This energy corresponds to a center^{1,2,16,17} which has been reported by several authors. They have measured the depth, concentration and other properties but not the capture cross section. The center appears to be

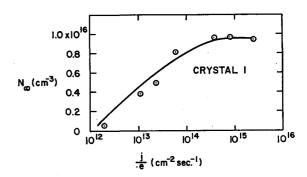


Fig. 7. N_{∞} for various values of j/e obtained by varying the light intensity. The line is a plot of $N_{\text{tot}}/(1+ke/jS_e)$.

Quantities determined by measuring capacitance as a function of time under constant illumination.
b Quantities determined by measuring final steady state capacitance at various light intensities.

¹³ A. Rose, Concepts in Photoconductivity (Interscience Publishers, New York, 1963), pp. 121-126.

¹⁴ R. H. Bube, *Photoconductivity of solids*, (John Wiley & Sons, Inc., New York, 1960), pp. 51, 48.

¹⁵ O. Madelung, *Physics of III-V Compounds* (John Wiley & Sons, Inc., New York, 1964), p. 353.

¹⁶ N. M. Voronkova, D. N. Nasledov, and S. V. Slobodchikov, Phys. July 5, 2250 (1963) [Exp. High Translet Sourist Physics 1964].

Fiz. Tverd. Tela 5, 3259 (1963) [English Transl.: Soviet Phys.-Solid State 5, 2383 (1964)].

¹⁷ W. J. Turner, G. D. Pettit, and N. G. Ainslee, J. Appl. Phys. 34, 3274 (1963).

associated in some way with oxygen impurities. Previous measurements were with high-resistance crystals and it is of interest to find what appears to be the same center in conducting crystals.

The conclusion that the center is negatively charged when filled is of considerable significance in connection with minority-carrier lifetimes. In the bulk, in a conducting crystal, all the centers are filled with electrons since the Fermi level is well above the energy of the center. For a concentration of 1016 centers/cm3 with $S_h = 10^{-12}$ cm² and a hole thermal velocity of 4×10^7 cm/sec the hole lifetime before capture would be 2.5×10^{-12} sec. Thus, this center which appears to be common in GaAs can easily be sufficient in itself to limit minority-carrier lifetimes to very small values.

ACKNOWLEDGMENTS

The author is indebted to J. Blanc, L. Weisberg, and A. Goodman for valuable discussions of this problem, to J. Tietjen for performing the Hall measurement, and to A. Willis for assistance with the experiments.

JOURNAL OF APPLIED PHYSICS

VOLUME 37, NUMBER 9

AUGUST 1966

Comparison of Measured and Predicted Bulk Moduli of Tantalum and Tungsten at High Temperatures

NAOHIRO SOGA*

Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey (Received 17 February 1966; in final form 21 March 1966)

The elastic constants of tantalum have been determined from room temperature to 500°C by means of a dynamic resonance method to obtain the adiabatic bulk modulus at elevated temperature. The adiabatic bulk modulus (B_s) of tantalum is found to be 1897 kbar at room temperature and it decreases almost linearly with a slope (dB_s/dT) of -0.11 kbar/°C as temperature rises. The calculation of the Grüneisen constant γ and a parameter δ , defined as $-(dB_s/dT)/\alpha B_s$, from the present data shows that both parameters are almost independent of the temperature (1.57 for γ and 3.1 for δ). The constancy of γ and δ at high temperatures has also been tested for tungsten by using the recent data of Lowrie and Gonas [J. Appl. Phys. 36, 2189 (1965)]. The results indicate that both γ and δ are virtually constant at high temperature. The applicability of the following equation to estimate the bulk-modulus-temperature relationship for the refractory metals Ta and W has also been tested:

$$B_s^T = B_s^{25} - (\delta \gamma / V) (H^T - H^{25}),$$

where H is the enthalpy and the superscripts indicate values at 25° and T° C.

I. INTRODUCTION

IT has been shown^{1,2} that the Grüneisen constant γ and a parameter δ , defined as $-(dB_s/dT)/\alpha B_s$, where B_s is the adiabatic bulk modulus and α is the volume expansion of a solid, become virtually constant with temperature at high temperatures for magnesium oxide and aluminum oxide. This paper describes investigations of the temperature dependence of γ and δ for the refractory metals tantalum and tungsten.

Both the Grüneisen constant γ and a parameter δ can be defined in terms of the adiabatic bulk modulus (B_s)

$$\gamma = V\alpha B_s/C_p,\tag{1}$$

$$\delta = -\left(1/\alpha B_s\right) (dB_s/dT),\tag{2}$$

where α is the volume expansion and C_p is the specific

heat at constant pressure. Therefore, the adiabatic bulk modulus of a solid at elevated temperature must be known in order to test the constancy of these parameters at high temperatures. For tungsten, the adiabatic bulk modulus at high temperatures has recently been reported by Lowrie and Gonas.3 The single-crystal elastic constants measured by Bolef and DeKlerk4 may also be used to obtain the adiabatic bulk modulus. No data, however, seem to have been published on the elastic constants of tantalum at elevated temperature, although the values at room temperature and at low temperatures are available.^{5,6} Thus, it was decided to measure the elastic constants of tantalum at elevated temperature so that the constancy of the Grüneisen constant and the parameter δ could be tested.

^{*} Work done while on leave from Lamont Geological Observa-

tory of Columbia University, Palisades, New York.

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