

TABLE I.  $\Delta H_v(298)$  = Heat of vaporization<sup>a</sup> at 298°K [ev].  $E$  = Modulus of elasticity<sup>b</sup> [kg/mm<sup>2</sup>].  $\mu$  = Poisson constant.  $v_s = [E(1-\mu)/\mu(1-2\mu)]^{1/2}$  = bulk sound velocity in 10<sup>5</sup> cm/sec.  $V_0^*$ (Hg) = Threshold energy for sputtering by Hg ions under normal incidence [ev], corrected for neutralization energy and work function.  $M = 2(2em_0V_0^*)^{1/2}m_m/(m_0+m_m)$  = momentum transferred at  $V_0^*$  [ev-sec/cm].

	$\Delta H_v(298)$	$E$	$\mu$	$v_s$	$V_0^*$ (Hg)	$M \times v_s$
Al	3.26	7220	0.34	6.45	120-140	34 - 36.6
Si	3.91	11 500	0.42	11.2	60- 70	43 - 46.4
Ti	4.92	10 500	0.36	6.35	110-130	51.6- 56
V	5.2	15 000	0.35	6.24	120-130	56.2- 58.4
Cr	3.68	19 000	0.31	6.15	60- 80	37.6- 45.6
Fe	4.2	21 550	0.29	6.1	60- 70	41.6- 44.8
Co	4.56	20 380	0.31	5.6	80-100	46 - 51.4
Ni	4.41	19 700	0.32	5.6	70- 90	42.4- 48.4
Cu	3.56	12 500	0.35	4.7	50- 70	32.2- 36
Ge	3.4	8000	0.32	4.6	40- 50	31.2- 34.8
Zr	5.43	6970	0.37	4.33	120-130	60.4- 62.4
Cb	7.6	16 000	0.35	5.5	120-130	77.4- 80
Mo	6.75	33 630	0.31	6.7	80-100	78.4- 87.4
Rh	6.0	38 640	0.26	6.15	70- 80	70.8- 75.6
Pd	4.05	12 360	0.39	4.5	50- 80	44.6- 56.4
Ag	3.04	8160	0.37	3.68	40- 50	32.8- 36.6
Sb	2.74	5600	0.33	4.3	30- 40	36 - 41.2
Hf	7.4	8500	0.37	3.34	150-180	76.8- 83.6
Ta	8.7	18 820	0.35	4.25	120-140	89 - 96.6
W	8.75	41 520	0.30	5.36	80-100	92.8-104
Re	8.21	53 000	0.26	5.65	70- 80	91.4- 98
Pt	5.86	17 320	0.39	3.98	70- 90	66 - 75.2
Au	3.94	7900	0.42	3.22	40- 50	40.8- 45.6
Pb	2.02	1600	0.44	2.17	20- 40	20 - 28.2
Th	6.5	7970	0.26	2.89	120-140	68.6- 74
U	5.43	13 380	0.30	3.08	70- 80	56 - 60
B	3.91	—	—	(13.1-14.7)	200-250	(42.8)
C	7.45	—	—	(14.7-16)	500-600?	(82)?

<sup>a</sup>L. Brewer in *Chemistry and Metallurgy of Miscellaneous Materials, Thermodynamics* (McGraw-Hill Book Company, Inc., New York, 1950), National Nuclear Energy Series, Plutonium Project Record, Vol. 19B, Div. IV, p. 13.

<sup>b</sup>W. Köster in "General Metallurgy," *FIAT Review of German Science, 1939-46* (1950), Vol. 31.

perpendicular impacts. The study of deposits, sputtered under these conditions, shows that a well-defined minimum ion energy ( $V_0^*$ ) is characteristic for every gas-metal combination.

$V_0^*$ (Hg), (normal incidence of Hg ions) was measured for 26 metals (Table I). These threshold energies cannot be brought

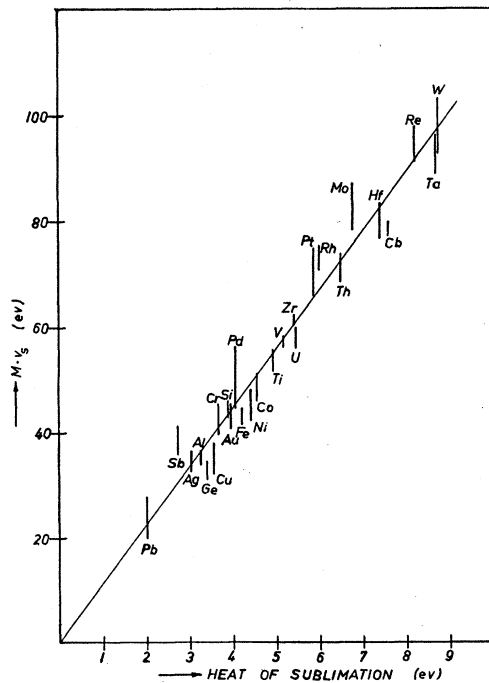


FIG. 1. Product of transferred momentum and bulk sound velocity versus heat of sublimation.

into agreement with existing threshold theories.<sup>2,4</sup> It turns out, however, that they follow (so far without exception) a simple law: The product of the momentum transferred at  $V_0^*$  from the ion to the metal atom (central collision between free elastic spheres), with the bulk sound velocity of the metal, is proportional (factor  $\approx 11.2$ ) to the heat of sublimation (Fig. 1); hence, threshold energies can be calculated from

$$V_0^* = \left( \frac{1.68 \times 10^6 (m_0 + m_m) \phi}{m_0^2 v_s m_m} \right)^2,$$

where  $V_0^*$  is in ev;  $m_0$  = atomic weight of ion;  $m_m$  = atomic weight of metal;  $v_s$  = bulk sound velocity of metal in cm/sec; and  $\phi$  = heat of sublimation of metal in kcal/mol. Part of  $V_0^*$  is supplied by the neutralization energy  $V_i$  and part is used for overcoming the work function  $W$  of the material; hence,  $V_0^* = V_0 + V_i - W$ , where  $V_0$  is identical with the measured voltage difference between sputtering electrode and plasma. A correction of  $v_s$  for temperature (200-300°C) is small enough in most cases to stay within the experimental error and is omitted.

This law is in good agreement with other experimental results, such as those for Pt in Xe,<sup>5</sup> and those from recent work of Bradley<sup>6</sup> concerning alkali metals in inert gases. Hence, there is reason to believe that this law is of a general nature and is applicable to all gas-metal combinations, as long as "physical" and not "chemical" sputtering (e.g., C in H<sub>2</sub>) takes place.

The bulk sound velocity of boron, not listed in the literature, would hereby be determined to be  $14 \times 10^5$  cm/sec (between Si and diamond). Measurements with C (graphite) seem to indicate that it is the maximal sound velocity which determines the threshold energy. Unfortunately, sufficient data concerning  $v_s$  max from measurements in metal single crystals are not available in the literature for the introduction of this additional correction.

The significance of the sound velocity here, although not yet fully understood, is obviously to introduce the elastic constants of the material, which determine what part of the transferred energy with the momentum directed to the inside of the material arrives at the surface with a momentum reversed in direction. This part has to be at least equal to the binding energy of a surface atom before sputtering ensues.

A more detailed paper will be submitted later.

<sup>1</sup>G. Wehner, *J. Appl. Phys.* (to be published).

<sup>2</sup>K. H. Kingdon and I. Langmuir, *Phys. Rev.* **22**, 148 (1923).

<sup>3</sup>Research Staff of General Electric Company, Ltd., London, *Phil. Mag.* **45**, 98 (1923).

<sup>4</sup>E. S. Lamar and K. T. Compton, *Science* **80**, 541 (1934).

<sup>5</sup>G. Wehner and G. Medicus, *J. Appl. Phys.* (to be published).

<sup>6</sup>R. C. Bradley, paper presented at 1953 Conference on Gaseous Electronics, Washington, D. C. (unpublished).

## Infrared Absorption of NiO

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THE Verneuil method<sup>1</sup> (or flame-fusion method) of growing crystals is well known and has been utilized for some time in producing crystals of sapphire, rutile, etc. Recently this method has been used at this laboratory to produce single crystals of NiO. These crystals are dark green to black in color and are easily cleaved. Their crystal structure is face-centered cubic with a lattice spacing of 4.17Å which agrees with previously published data.<sup>2</sup> The melting point, as determined during the actual growth, is slightly above 1900°C.

The over-all resistivity at room temperature of these crystals, as measured by a megohm bridge, is  $7.0 \times 10^6$  ohm cm, this value being somewhat less than the  $10^8$  ohm cm usually reported in the literature for NiO in the polycrystalline form.<sup>3</sup>

A  $1 \times 5 \times 10$  mm plate was cleaved from the NiO single-crystal boule; infrared transmission in the wavelength range of  $1\mu$  to  $15\mu$  was observed with this specimen using a Perkin Elmer Model-112

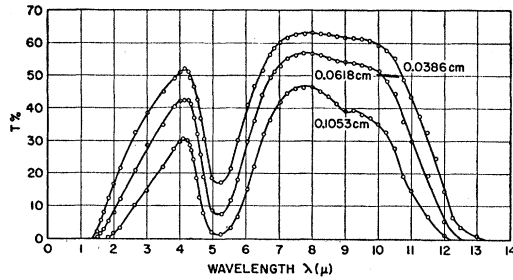


Fig. 1. Transmission spectrum of NiO from  $1\mu$  to  $14\mu$  for sample thickness 0.1053 cm, 0.0618 cm, and 0.0386 cm.

double-pass spectrophotometer. Since this finding pointed towards some interesting information concerning the semiconducting properties of NiO, a more careful study was begun. Because refractive index information is necessary to convert transmission to absorption coefficient, and few refractive index data are available,<sup>4</sup> the following technique was adopted to obtain both refractive index and absorption coefficient data from the transmission spectrum.

The transmission  $T$  of a plane parallel plate of thickness  $x$  can be expressed by the equation<sup>5</sup>

$$T = \frac{(1-R)^2 e^{-\alpha x}}{1 - R^2 e^{-2\alpha x}}, \quad (1)$$

where  $\alpha$  is the absorption coefficient and  $R$  is the reflection coefficient defined as  $R = [(n-1)/(n+1)]^2$ , with  $n$  as the refractive

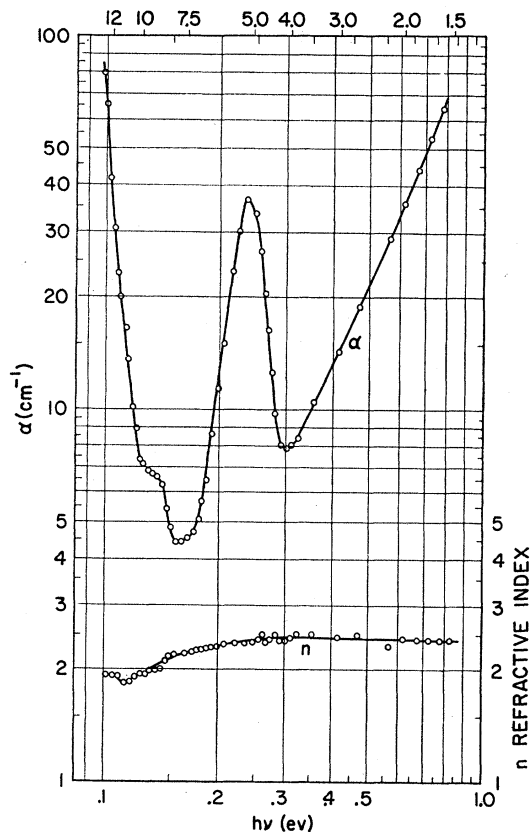


Fig. 2. Absorption coefficient  $\alpha$  ( $\text{cm}^{-1}$ ) and refractive index  $n$  of NiO versus photon energy in eV.

index. The  $n$  and  $\alpha$  values could be derived from an algebraic simultaneous solution of the equations for two different thicknesses; however, in this case, a graphical solution was used which combined the data on specimens of three different thicknesses. The graphical solution was obtained by plotting from Eq. (1),  $T$  versus  $\alpha x$  with  $n(R)$  as a parameter. Trial values of  $n$  then permitted the determination of  $\alpha$  for known  $x$  and  $n$ ;  $\alpha$  and  $n$  values which were independent of thickness  $x$  were thereby chosen.

The  $1 \times 5 \times 10$  mm cleaved plate was ground and polished optically flat and parallel and the transmission spectrum obtained. This same plate was then ground and repolished for two thinner specimens. The transmission spectra (Fig. 1) for the three thicknesses (0.1053 cm; 0.0618 cm; 0.0386 cm) are replotted as absorption coefficient versus photon energy in Fig. 2, utilizing the graphical solution outlined above. Refractive index data obtained from the solution are also included and agree fairly well with those published.<sup>4</sup>

The branch of the curve for energy values greater than 0.3 eV may be the tail of the fundamental absorption which is to be expected at about 2 eV according to the electrical measurements of Wright and Andrews<sup>6</sup> on polycrystalline NiO. These authors present data indicating the existence of impurity optical activation energies between 0.3 and 0.6 eV. The 0.24-eV absorption peak may be an impurity ionization energy corresponding at least in order of magnitude to that expected above. There is also a satellite absorption peak at 0.13 eV. The increasing absorption coefficient below this peak is probably a lattice vibration absorption. The validity of this conclusion is enhanced by the suddenly decreasing refractive index at these low frequencies, a circumstance which probably would not result from impurity absorption.

We would like to thank Dr. G. G. Palmer, who supplied us with the NiO crystals, and Dr. F. G. Keihn, who made the x-ray determinations on them for us.

<sup>1</sup> A. Verneuil, Compt. rend. 135, 791 (1902); Ann. chim. et phys. 3, 20 (1904).

<sup>2</sup> H. P. Rooksby, Nature 152, 304 (1943).

<sup>3</sup> E. J. W. Verwey, in *Semiconducting Materials* (Butterworths Scientific Publications Ltd., London, 1951), p. 155.

<sup>4</sup> C. J. Ksanda, Am. J. Sci. 22, 131 (1931); A. Kundt, Sitzber. deut. Akad. Wiss. Berlin, 255-272 (1888).

<sup>5</sup> R. B. Barnes and M. Czerny, Phys. Rev. 38, 338 (1931).

<sup>6</sup> R. W. Wright and J. P. Andrews, Proc. Phys. Soc. (London) 62, 446 (1949).

## Bulk Photoconductivity in Lead Sulfide\*

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EXTENSIVE investigations have been carried out upon photoconducting evaporated and chemical layers of PbS (for a review see Smith<sup>1</sup>). Sosnowski *et al.*<sup>2</sup> and Gibson<sup>3</sup> have presented models of photoconductivity in evaporated layers based on the modulation of intercrystalline potential barriers. Experimental evidence of bulk photoconductivity in PbS crystals, however, has not been published to our knowledge. We have studied this property in three cleaved synthetic PbS crystals at liquid nitrogen temperature.

The dark conductivities at room temperature for samples  $S_{11}$ ,  $S_{12}$ ,  $S_{13}$  were 34, 21, and 23  $\text{ohm}^{-1} \text{cm}^{-1}$ , respectively. All electrode and probe contacts to the crystals were made by electroplating them with rhodium and then soldering the lead wires to the rhodium. All samples showed slight internal rectification.

The potential difference developed between a probe fixed at the right electrode and a probe moved along the crystal  $S_{12}$  at room temperature is shown in Fig. 1(a). Two different traversing paths are represented. Potential barriers are present within the crystal at A, B, C, and D.

At 77°K the frequency response to chopped radiation from a tungsten source was taken over the range of 20 to 9000 cps to