

related to a change in the thermal activation energy of the semiconductor due to the applied pressure.

If the activation energy calculated for the various pressures is plotted against the dilatation,  $\Delta V/V$ , a straight line is obtained, provided the value of activation energy of 0.38 ev found from Hall effect measurements by Johnson<sup>3</sup> is used for the value at zero pressure.

From the graph it is found that

$$\Delta E/(\Delta V/V) = 0.041 \text{ ev per one percent dilatation.}$$

Photo-conductive films of tellurium have been prepared by the author, and from measurements of the spectral distribution of sensitivity, a value of the optical activation energy can be obtained. It was found that for different layers the sensitivity fell to half-value at wave-lengths in the range  $3.2\mu$  to  $3.5\mu$ , corresponding to an optical activation energy of 0.35 to 0.38 ev. There is thus good agreement between the optical and thermal activation energies.

It has also been observed that the "threshold" wave-length of sensitivity is temperature dependent, moving to longer wave-lengths on cooling, and the extent of the shift has now been measured. Unfortunately the sensitivity of tellurium cells falls rapidly with increasing temperature, and in general spectral sensitivity measurements cannot be carried out much above 150°K. However, fairly good results were obtained on two cells from 77°K to 161°K and 77°K to 195°K respectively. The observed shifts of  $0.16\mu$  and  $0.20\mu$ , give an energy change:—

$$\Delta E/\Delta T = 2.1 \times 10^{-4} \text{ and } 1.9 \times 10^{-4} \text{ ev/}^\circ\text{C.}$$

As a result of the restricted temperature range, the accuracy is not high, but a mean value of  $\Delta E/\Delta T = 2 \times 10^{-4} \text{ ev/}^\circ\text{C}$  may be taken. Since the thermal expansion coefficient,  $\Delta V/V \cdot \Delta T = 51 \times 10^{-6}/^\circ\text{C}$ , we obtain from the optical measurements,  $\Delta E(\Delta V/V) = 0.04 \text{ ev per one percent dilatation.}$

This figure is almost identical with that calculated from the pressure measurements. Such close agreement is fortuitous, but we may conclude that within the accuracy of the measurements the values of the energy change with dilatation are the same in the two cases. The energy gap is thus determined primarily by the volume, the forbidden zone decreasing in width as the atoms move closer together. Bardeen has suggested that the opposite effect occurs in germanium.

An interesting conclusion to be drawn from the above results is that a film of tellurium operated at 20,000 kg/cm<sup>2</sup> and suitable low temperature, should be photo-conductive at wave-lengths  $\sim 12\mu$ .

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<sup>1</sup> P. W. Bridgman, Proc. Am. Acad. **72**, 159 (1938).

<sup>2</sup> J. Bardeen, Phys. Rev. **75**, 1777 (1949).

<sup>3</sup> V. A. Johnson, Phys. Rev. **74**, 1255 (1948).

## Boride Cathodes

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THE thermionic emission properties of the borides of the alkaline-earth and rare-earth metals and thorium have been investigated. These compounds all have the same formula MB<sub>6</sub> and the same crystal structure consisting of a three-dimensional boron framework in whose interlattice spaces the metal atoms are embedded. The valence electrons of the metal atoms are not accepted by the B<sub>6</sub> complex, thus giving rise to the presence of free electrons which impart a metallic character to these compounds.

This is evident from their high electrical conductivity. Lanthanum boride, for example, has a specific resistance of 27  $\mu\text{ohm-cm}$

at room temperature and a positive resistance-temperature coefficient of 0.071  $\mu\text{ohm}/^\circ\text{C}$ . Hall effect measurements on sintered lanthanum boride show approximately one free electron per lanthanum atom. The strong binding forces between the boron atoms lead to a series of compounds which are very refractory, with melting points above 2100°C. The hexaborides are also very stable chemically; moisture, oxygen and even hydrochloric acid do not react with them.

When this structure is heated to a sufficiently high temperature, the metal atoms at the surface evaporate away. They are, however, immediately replaced by diffusion of metal atoms from the underlying cells. The boron framework does not evaporate but remains intact. This process gives a mechanism for constantly maintaining an active cathode surface. This feature, together with the high electrical conductivity and high thermal and chemical stability, gives ideal properties for a cathode material.

Thermionic emission measurements show the rare-earth metal borides to be superior to the others. The emission constants obtained from Richardson plots for the hexaborides are shown in Table I. Lanthanum boride gave the highest emission and was

TABLE I. Hexaboride electron emission constants determined for Dushman's equation.

| Boride           | A                                             | $\phi$     |
|------------------|-----------------------------------------------|------------|
| CaB <sub>6</sub> | 2.6 amp./cm <sup>2</sup> /deg. K <sup>2</sup> | 2.86 volts |
| SrB <sub>6</sub> | 0.14                                          | 2.67       |
| BaB <sub>6</sub> | 16                                            | 3.45       |
| LaB <sub>6</sub> | 29                                            | 2.66       |
| CeB <sub>6</sub> | 3.6                                           | 2.59       |
| ThB <sub>6</sub> | 0.53                                          | 2.92       |

found to have a relatively low evaporation rate corresponding to a latent heat of evaporation of 169 kcal./mole.

Boride cathodes require no special activation. When they are heated for a few minutes at 1400°C to 1600°C for outgassing, they are found to be completely active. When lanthanum boride is bombarded with mercury ions which exceed energies of approximately 20 ev lanthanum atoms are readily sputtered off the surface making the cathode inactive. However, at 1400°C, the lanthanum atoms diffuse rapidly to the surface, making the cathode active again.

The pulsed emission is the same as the d.c. emission for the boride cathodes.

If these cathode materials are operated in contact with the refractory metals, the boron atoms diffuse into their metal lattices forming interstitial boron alloys with them. When this occurs, the boron framework which holds the alkaline-earth or rare-earth metal atoms collapses, permitting them to evaporate. The hexaborides may be operated in contact with tantalum carbide or carbon.

## On the Spins of Li<sup>6</sup> and B<sup>10</sup>

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IT was pointed out by Feenberg<sup>1</sup> that according to the  $p^n$  shell model, the spins of Li<sup>6</sup> and B<sup>10</sup> are one in  $LS$  coupling, but three in  $jj$  coupling; it was therefore natural to ask if the different spins of these two nuclei can be explained by intermediate coupling. Calculations are in progress on this subject, and the first results are very satisfactory.<sup>2</sup>

In the meantime it has been suggested by Inglis, Mayer, and Kurath<sup>3</sup> that the coupling should be extreme  $jj$  and the mixture of exchange forces should be such as to give the correct spins for Li<sup>6</sup> and B<sup>10</sup>. We wish to discuss now some consequences of this hypothesis.