diately suggests itself. The general decreasing strength of the first three major components in moving to shorter wavelengths is in accord with this suggestion,[11] despite the fact that the oscillator strength[12] of the main band is considerably lower than values found for the oscillator strength of the F center in NaCl-type alkali halides. Additional measurements, particularly measurements of spin resonance and the temperature dependence of photoconductivity, could check on the possibility of multiple excited F-center states and give further insight into the nature of these states.

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[1] See F. Seitz, Revs. Modern Phys. 26, 7 (1954).

[2] H. Rabin, J. H. Schulman, and R. F. Marzke, Bull. Am. Phys. Soc. 5, 48 (1960).

[3] This crystal was kindly provided by Dr. W. G. Maisch of the University of Maryland.

[4] Kindly provided by Professor A. Smakula and Dr. P. Avakian at the Massachusetts Institute of Technology who are also currently investigating color center formation in the cesium halides.

[5] This resolution is performed by assuming the chief band peaks at 642 mμ, shorter wavelength bands do not extend to wavelengths longer than 642 mμ, and the band is symmetrical on an energy scale. Similarly, it is assumed the second band which peaks at 616 mμ is not overlapped to the long-wavelength side of 616 mμ by shorter wavelength structure, namely the 580-mμ band, and it is also symmetrical. It is clear from Fig. 2 that the structure remaining does not give a simple symmetrical band at 580 mμ. However, it is to be remembered that the background absorption and errors in separating the components are lumped in this short-wavelength remainder.

[6] P. Avakian and A. Smakula, Bull. Am. Phys. Soc. 5, 48 (1960).

[7] C. J. Rauch and C. V. Heer, Phys. Rev. 105, 914 (1957).

[8] At liquid nitrogen temperature there appears to be an increased distortion in the general structure of the band, but no clearly resolved substructure appears as it does at liquid helium temperature.

[9] See, for example, W. H. Duerig and J. J. Markham, Phys. Rev. 88, 1043 (1952).

[10] The possible role of impurity atoms can not be totally ignored. H. W. Etzel and J. H. Schulman, J. Chem. Phys. 22, 1549 (1954), have shown that the same optical impurity bands produced in x-rayed NaCl doped with silver can be produced by electrolytic coloration. It is well known, of course, that the additive coloration process is quite analogous to that of electrolytic coloration. Since both Harshaw and MIT-grown CsBr crystals have been used in the present study, their impurity content would not necessarily be expected to be identical.

[11] F. Lüty has recently discussed possible excited F-band states in NaCl-type alkali halides in which the relative magnitudes of the bands are not of successively decreasing absorption strengths in passing to shorter wavelengths. This work was presented at the International Symposium on Color Centers in Alkali Halides, Oregon State College, September, 1959 (unpublished).

[12] Rauch and Heer[7] give the F-center oscillator strength as 0.26 assuming a single Gaussian band at room temperature. Since the 642-mμ band constitutes about 69% of the total area of the absorption structure of Fig. 2, the oscillator strength of the first excited state would be 0.18; similarly the second excited state (616-mμ band) would be about 0.05.

SEMICONDUCTING PROPERTIES OF CUBIC BORON PHOSPHIDE

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In recent years there has been considerable interest in group III-group V compound semiconductors as well as large band gap semiconductors. Cubic boron phosphide is such a material. It has been prepared and identified previously[1] and the present paper describes preliminary measurements of its semiconducting properties.

Cubic BP has been prepared by two basically different methods: (1) by the vapor phase reaction of boron compounds with phosphorus compounds or phosphorus vapors; and (2) by the slow cooling of a melt containing dissolved boron and phosphorus.

The BP prepared by the vapor phase reactions[2] has very small crystal size and varies from reddish tan to black in color. However, this material could be deposited in the form of films which were useful for optical absorption measurements since they could be made very thin. A variation of the vapor phase reaction resulted in small "needle" or "blade" shaped crystals. These crystals are 1 mm or 2 mm in length and reddish brown in color and transparent.

The method involving slow cooling of a melt results in crystals which are on the order of

1 mm in all dimensions and of a similar color. These crystals are also transparent and occasionally a crystal can be found with a pair of flat, parallel faces. Measurements of the displacement of an image by such a crystal give a rough value of index of refraction of between 3.0 and 3.5.

The x-ray powder diffraction pattern of these materials is identical to that reported for cubic BP by other workers.[1] Elemental analyses give boron to phosphorus ratios of unity within about 1% which is the accuracy of the method.

BP is quite inert chemically. It is not attacked by mineral acids or any of the usual semiconductor etches. It is attacked slightly by molten NaOH. BP has a hardness about equal to that of silicon carbide (Knoop hardness number of 3200 for 100-g load).

Ruehrwein and Williams[3] of this laboratory have found by means of optical absorption measurements on thin polycrystalline films, that the energy gap of BP is almost 6 ev. Figure 1(a) shows representative measurements[3] on films of different thicknesses. If one neglects scattering effects, the absorption coefficient at 0.3 micron is about 5×10^4 cm^{-1}. These films were deposited on quartz plates. The absorption of the quartz is negligible in this region. The value of energy gap of about 6 ev is consistent with what one would expect on the basis of lattice parameter considerations. Note the shoulder around 0.6 micron accounting for the reddish color which this material exhibits by transmission.

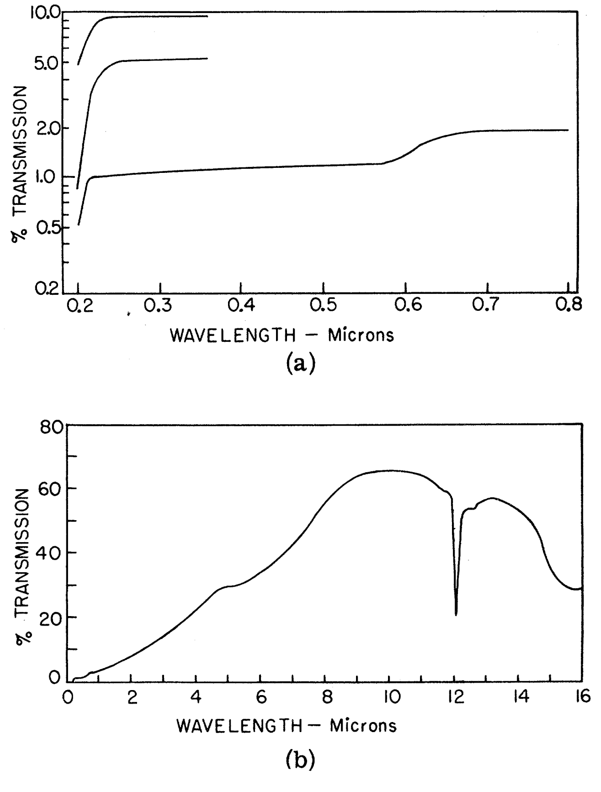

FIG. 1. (a) and (b) Percent transmission of polycrystalline films of boron phosphide.

Absorption measurements on a polycrystalline film in longer wavelength regions are shown in Fig. 1(b). For this measurement the film was stripped off its quartz backing. The gradual increase in transmission out to about 10 microns is probably due to a decrease in scattering at longer wavelengths. The sharp absorption at 12.1 microns is presumably a lattice absorption.

Optical absorption measurements of single-crystal samples are more difficult because of the small size of the crystals available and the difficulty in producing thin samples. The sensitivity is too poor to show the fundamental absorption and the only feature observed is the absorption responsible for the color of the crystals. The highest absorption coefficient measured on a single-crystal sample is 10^3 cm^{-1}.

Preliminary Hall measurements have been made on crystals grown by method 2. The sample geometry was determined by their natural crystal faces. Electrical contact was made using silver paint, tungsten, or platinum points. The lead resistance could usually be decreased considerably by the use of a capacitor discharge. The measurements show that these crystals are p-type with a carrier concentration ranging from 1 to 5×10^{18} carriers/cc. The Hall coefficient is essentially constant from about 900°K down to about 160°K. Difficulties with leads prevented Hall measurements at lower temperatures. The shape of the resistivity curve at low temperatures suggests that the material is still in the exhaustion range at 78°K. Figure 2 gives Hall mobility on such p-type BP as a function of $1000/T$. At room temperature the mobility is decreasing with decreasing temperature, characteristic of impurity scattering. Thus the room temperature lattice mobility of p-type BP must be considerably greater than the measured value, perhaps as large as 300 or 500 cm^2/volt second.

Thermoelectric power and rectification measurements on the needle-shaped crystals indicate that these crystals are n-type. Crude resistivity measurements indicate that the impurity level may be around 10^{17} carriers/cc if we assume the electron mobility to be of the same order of

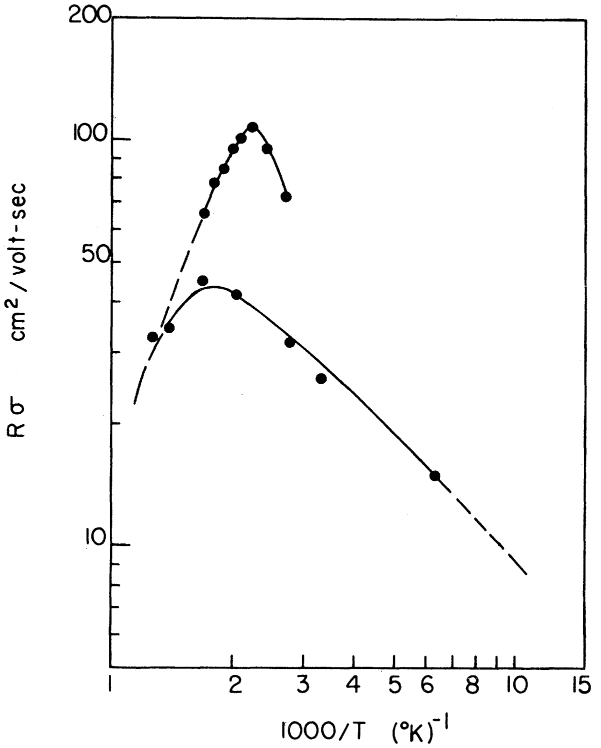

FIG. 2. Hall mobility of single-crystal p-type boron phosphide.

magnitude as the hole mobility.

The thermoelectric power of both the n- and p-type material is about 300 microvolts/°C. Point contact rectification has been observed with both n-type and p-type BP. Rectification ratios of greater than 10^3 to 1 have been observed at both room temperature and 400°C.

It is necessary to comment concerning the color of the BP obtained to date. A semiconductor with an energy gap of nearly 6 ev should be transparent and colorless, while the BP obtained has a reddish color. The optical absorption responsible for this color occurs at a wavelength corresponding to an energy of about 2 ev. Such a level would not be ionized at the temperature of the measurements, so it would not contribute carriers, even if this were possible. There are several possible explanations for this absorption but more work will be necessary before any conclusions can be reached.

In summary it has been shown that it is possible to produce single crystals of cubic BP of measurable size, and although the material prepared so far is impure, by semiconductor standards, and although the measurements just presented are preliminary in nature, the properties of BP appear to be interesting and promising.

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[1] P. Popper and T. A. Ingles, Nature 179, 1075 (1957).

[2] F. V. Williams, paper presented at American Chemical Society Meeting, Boston, Massachusetts, April, 1959 (unpublished).

[3] R. A. Ruehrwein and F. V. Williams (unpublished data).

MECHANISMS OF VOLUME SELF-DIFFUSION IN α-Fe AND γ-Fe†

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Several years ago, Kuczynski[1] introduced a method for determining self-diffusion coefficients without the aid of radioactive tracers. An expression was derived which relates the dimensions of a sintered interface between two particles to D, the coefficient of volume self-diffusion. Although this method will never supplant the tracer method for determining diffusion parameters, the importance of its use should not be overlooked in diffusion studies (*a*) where no suitable isotopes are available and (*b*) where it is desired to distinguish various diffusion phenomena which have different causes. As long as 50 to 100 measurements of separate fillets are made for each point on the $\ln D$ vs $1/T$ curve, the statistics will be favorable to enable the determination of D within a factor of 2 or 3 with about an 80% confidence limit for most metals.

An adaptation of this method has been used to determine the self-diffusion parameters in both face-centered cubic (fcc) and body-centered cubic (bcc) thorium,[2] where no suitable isotope for tracer studies is available. In this latter work, it was found that near the transition temperature, D in bcc thorium is approximately a factor of five less than D in fcc thorium. In contrast, radioactive tracer studies[3,4] show that D in bcc iron is approximately 400 times larger