

## Electrical and Optical Properties of Intermetallic Compounds. III. Aluminum Antimonide\*

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Measurements of resistivity, Hall coefficient, and optical absorption of AlSb are reported. The width of the forbidden energy band, derived from electrical and optical data, is 1.6 ev at absolute zero. Absorption bands are observed at 0.75 ev in *p*-type samples and at 0.31 ev in tellurium-doped *n*-type specimens. An energy level diagram with several acceptor and donor levels in the forbidden energy band is suggested to explain these observations.

### INTRODUCTION

ALUMINUM antimonide is one of a series of semiconducting compounds formed between elements from the columns IIIB and VB of the periodic table. The lattice has the zincblende structure, which is equivalent to the diamond structure when the two components are the same.

This paper presents measurements of Hall effect and resistivity as well as optical absorption of AlSb. The values obtained for the width of the forbidden energy gap and mobility agree reasonably well with those reported previously in the literature.<sup>1-3</sup> Activation energies related to defects in the crystal are also observed. It seems possible to interpret the optical and electrical data with several acceptor and donor levels in the forbidden band.

### SAMPLE PREPARATION

The compound (melting point<sup>1</sup> 1060°C) is prepared by melting the components together in stoichiometric proportions. The aluminum is the standard metal used for melting point calibrations supplied by the Chemistry

Division of the National Bureau of Standards. The purity of this material is 99.98 percent, the major impurities being As, Fe, Mn, P, Si, and traces of Cu and Mg. The antimony (purchased from Bradley Mining Company) is 99.95 percent pure and contains small amounts of Pb, As, Cu, and Fe. For details of the melting process, crystal pulling and sample preparation we refer to a paper on InSb.<sup>4</sup> The ingots obtained always contained several crystals, but it was usually possible to cut out single-crystal samples of sufficient size for electrical and optical measurements. Zone melting does not seem to improve the resistivity of this compound. The reason might be that defects are more effective than chemical impurities in AlSb as a source of carriers.

We have noticed that the compound decomposes in a humid atmosphere. Ingots become covered with a black film in a very short time, ultimately crumbling into a black powder. A desiccator affords ample protection from moisture. Pure samples are more corrosion-resistant than samples of higher impurity content. Justi<sup>3</sup> has made these same observations; he has shown that the aluminum reacts with water forming the hydroxide.

X-ray analysis of an AlSb sample indicated a lattice of the zincblende type with a lattice constant<sup>5</sup> of 6.0959 Å at 26°C and a nearest neighbor distance of 2.64 Å.

### ELECTRICAL PROPERTIES

The apparatus used for measurements of Hall coefficient and resistivity has been described previously.<sup>6</sup> The sample holder for the high-temperature range was made of stainless steel; the leads were in pressure contact with the crystal.

Two samples have been investigated. One is a *p*-type single crystal (C-7); the other was cut from an ingot doped with  $9 \times 10^{-3}$  atomic percent of Te and shows *n*-type conductivity (C-10). The temperature dependence of resistivity and Hall coefficient is given in Fig. 1.

The intrinsic range for these samples lies above 750°C.

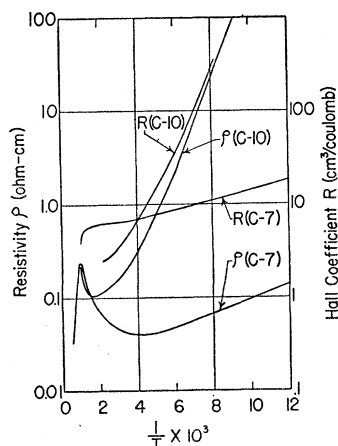


FIG. 1. Resistivity and Hall coefficients of AlSb.

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<sup>1</sup> H. Welker, Z. Naturforsch. **7a**, 744 (1952); **8a**, 248 (1953).

<sup>2</sup> Willardson, Beer, and Middleton, Phys. Rev. **91**, 243 (1953).

<sup>3</sup> E. Justi and G. Lautz, Abhandl. Braunschweig. wiss. Ges. **5**, 36 (1953).

<sup>4</sup> Breckenridge, Blunt, Hosler, Frederikse, Becker, and Ashinsky, this issue [Phys. Rev. **96**, 571 (1954)].

<sup>5</sup> These measurements were carried out by the Microstructure Section of the National Bureau of Standards.

<sup>6</sup> R. G. Breckenridge and W. R. Hosler, Phys. Rev. **91**, 793 (1953).

The Hall coefficient could not be measured at the highest temperatures due to contact difficulties. At 750°C and above we expect nearly all scattering to be due to lattice vibrations, so that the slope of  $\ln \rho$  vs  $1/T$  determines the width of the forbidden gap; this value is 1.6 eV. The carrier concentration of sample C-7 at exhaustion is  $10^{18} \text{ cm}^{-3}$ ; that of sample C-10,  $3 \times 10^{18} \text{ cm}^{-3}$ .

The mobility may be evaluated from the expression

$$\mu = R\sigma/r, \quad (1)$$

where  $r$  is a factor which depends on the scattering mechanism.<sup>7</sup> From the data of sample C-7 we calculate a hole mobility of  $150 \text{ cm}^2/\text{volt-sec}$  at room temperature. The electron mobility as deduced from the results for sample C-10 is about  $35 \text{ cm}^2/\text{volt-sec}$  at 300°K. The latter figure is very low, presumably due to the high concentration of both donor and acceptor impurities.

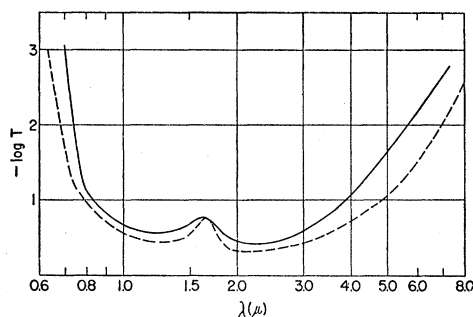


FIG. 2. Absorption spectrum of *p*-type AlSb (sample C-7).  
— 300°K, ---- 85°K, ..... 14°K.

### OPTICAL PROPERTIES

The optical absorption spectrum of small samples, ranging in thickness from 5 to 10 mils, has been investigated at wavelengths between 0.6 and  $15.0 \mu$ . The apparatus and measuring techniques have been described in an earlier publication.<sup>4</sup>

Five different specimens have been investigated. The first sample, C-7 (thickness 8 mils), is a *p*-type single crystal. Two other samples, C-8 and C-9 (both 10 mils thick), were cut from ingots doped with, respectively,  $2 \times 10^{-3}$  and  $3 \times 10^{-3}$  atomic percent of tellurium. Another two samples, C-10-1 (10 mils) and C-10-2 (5 mils), were cut from an ingot containing  $9 \times 10^{-3}$  atomic percent of tellurium and appeared to be *n*-type.

The spectrum of sample C-7 at three different temperatures is given in Fig. 2. Figure 3 compares the room temperature spectra of samples C-8, C-9, and C-10-2; the temperature dependence of the absorption of samples C-10-1 and C-10-2 is shown in Figs. 4 and 5.

The results of our measurements can be summarized as follows. For all samples a sharp absorption edge is observed at  $0.82 \mu$  corresponding to a forbidden energy

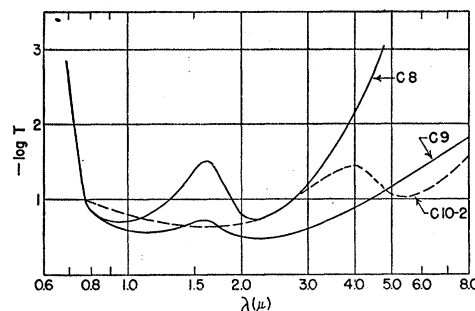


FIG. 3. Absorption spectra of three AlSb samples. Atomic percent Te added to melt

sample C-8:  $2 \times 10^{-3}$ ,  
sample C-9:  $3 \times 10^{-3}$ ,  
sample C-10-2:  $9 \times 10^{-3}$ .

gap of 1.52 eV at room temperature. This result is in good agreement with the value deduced from the conductivity measurements. The temperature dependence of the energy gap has an average value of  $-3.5 \times 10^{-4} \text{ eV/deg}$  over the temperature range studied.

In all *p*-type samples an absorption band is observed at  $1.6 \mu$  (0.75 eV). Hall effect and resistivity data show, however, no corresponding slope. Adding tellurium to the compound converts the conductivity to *n*-type. The band at  $1.6 \mu$  has then disappeared and a new band is observed at  $4.0 \mu$  (0.31 eV). Plotting  $\ln RT^{3/2}$  or  $\ln \rho T^{3/2}$  vs  $1/T$  we find, however, an activation energy of 0.14 eV.

In order to account for these observations we wish to suggest a picture which is rather similar to one proposed by James and Lark-Horovitz<sup>8</sup> to explain the behavior of bombarded Ge and Si.

The AlSb crystal will probably acquire a slight excess of aluminum over the stoichiometric amount due to the larger evaporation of the antimony from the melt. Consequently the compound will tend to contain a number of Sb vacancies. Considering the predominantly covalent character of AlSb,<sup>1</sup> such vacancies will presumably act as acceptors. The omission of an antimony atom leaves 5 unsaturated bonds at that site in the crystal. It is therefore to be expected that several

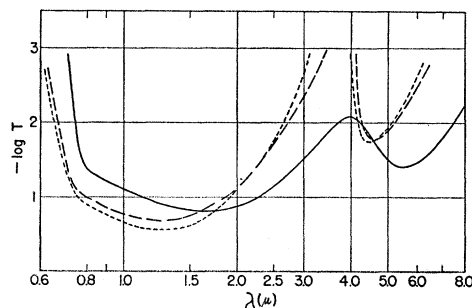


FIG. 4. Absorption spectrum of *n*-type AlSb (Sample C-10-1).  
— 300°K, ---- 85°K, ..... 14°K.

<sup>7</sup> W. Shockley, *Electrons and Holes in Semiconductors* (D. van Nostrand Company, Inc., New York, 1950), pp. 278-279.

<sup>8</sup> H. M. James and K. Lark-Horovitz, *Z. physik. Chem.* **198**, 107 (1951).

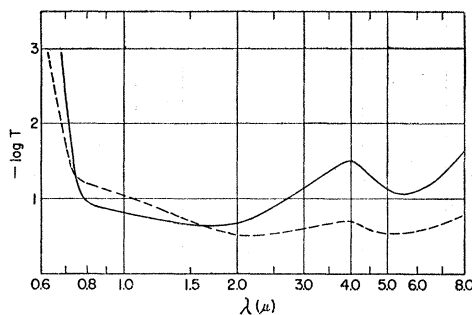


FIG. 5. Absorption spectrum of *n*-type AlSb (Sample C-10-2).  
— 300°K, --- 85°K.

localized levels will be split off from the valence band as indicated on the left of Fig. 6. The first level will lie close to the filled band, the second, third, etc. levels at a considerable distance from the band edge.

We identify the second activation energy with the value of 0.75 ev observed in the *p*-type samples. The first level will already be occupied at rather low temperatures, while the second level will be essentially empty up to temperatures much higher than 300°K.

It is possible that donor centers in a smaller number than acceptors will be present at the same time. The fact that only the 0.75-ev band has been observed in the *p*-type samples indicates that these levels are lying higher than the second acceptor level (and will therefore be empty) or lower than the edge of the filled band.

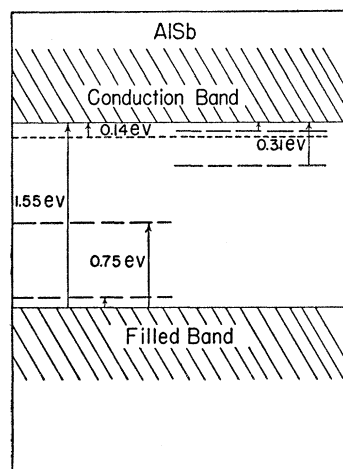


FIG. 6. Suggested energy level diagram for Te-doped AlSb.

It is now readily seen what the result of the addition of tellurium will be. The tellurium atom has approximately the same radius ( $r=1.32$  Å) as the antimony atom ( $r=1.36$  Å)<sup>9</sup>; the outer shell contains, however, one electron more. It might be expected therefore that it can replace the antimony in the crystal and act as a donor. The donor centers introduced by the addition of tellurium will then compensate the acceptors normally present. The conductivity of the *p*-type crystal will thus decrease until sufficient tellurium is added to convert the crystal to *n*-type. The activation energy of the tellurium donor levels can be estimated on the basis of the hydrogenic model. With a dielectric constant  $\epsilon'=10.8$ ,<sup>10</sup> this value is calculated to be 0.125 ev. We can identify this activation energy with the value calculated from resistivity and Hall plots.

The absorption band in the *n*-type sample at 0.3 ev is not too well understood. Since this band is only observed in the *n*-type samples, the absorption band might be due to a donor level at 0.3 ev below the conduction band. This activation energy will not show up in the resistivity and Hall plots if the number of these donors is less than the number of tellurium atoms.

There are several possible interpretations as to the origin of these donor levels. In the first place one may assume that the excess aluminum will take up interstitial sites. Kendall<sup>11</sup> has proposed such a picture to explain the properties of *n*-type SiC. These interstitial atoms will give rise to several donor levels in the forbidden band analogous to the vacancy levels. The open structure of the zincblende-type lattice and the geometrical equivalence of interstitial and lattice sites<sup>12</sup> could account for the rather small second activation energy of such donors.

Another possibility is the presence of tellurium in interstitial as well as substitutional positions. One could also explain these donor levels as being due to other chemical substitutions. From spectroscopic analyses of the Al and Sb used there is no indication of any impurity expected to produce *n*-type conductivity with such a large activation energy.

<sup>9</sup> L. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals* (Cornell University Press, Ithaca, 1945).

<sup>10</sup> Briggs, Cummings, Hrostowski, and Tanenbaum, *Phys. Rev.* **93**, 912 (1954).

<sup>11</sup> J. T. Kendall, *J. Chem. Phys.* **21**, 821 (1953).

<sup>12</sup> H. W. Leverenz, *An Introduction to Luminescence in Solids* (John Wiley and Sons, Inc., New York, 1950), p. 94.