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other materials, clearly shows the dispersion of the elastic waves. The deviation of some of the frequency curves from the sinusoidal dispersion law may be interpreted as neighbor interactions more distant than the first. A more accurate frequency spectrum could be obtained by interpreting the dispersion curves by the Born²² theory. This would yield the atomic force constants which would permit the solution of the secular equation of frequency *versus* wave vector,

²² M. Born, Repts. Progr. in Phys. 9, 356 (1942-1943).

thereby permitting the computation of a complete vibrational spectrum.

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n-Type and *p*-Type Conduction in Alkali-Antimonide Photoemitters

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Conductivity measurements were made during the formation of alkali antimonides to deduce whether these materials are *p*-type or *n*-type conductors. Reproducible results were obtained, indicating that K_3Sb and Na_3Sb are *n* type while Cs_3Sb and the multialkali antimonides are *p* type. A correlation between high-quantum efficiency of photoemission and *p*-type conduction is suggested.

INTRODUCTION

IT is well known that thin layers of evaporated Sb react with alkali metals to form semiconducting compounds of the formula M_3Sb where M represents an alkali metal. These materials are all photoemissive with quantum efficiencies approaching 0.3 electron/photon in the case of the Cs compound. Unexpectedly high efficiency has recently been obtained with antimonides containing more than one alkali metal ("multi-alkali" photocathodes).¹

The large optical absorption coefficient and the high-quantum efficiency of the antimonides are evidence for the intrinsic nature of the photoeffect, i.e., in the spectral range of high efficiency the photoelectrons must be produced by transitions from the valence band and cannot be due to a surface effect or to the presence of impurities. It has been observed in the past that the photosensitive layers, at least in the case of Cs_3Sb , are not accurately stoichiometric. Hall measurements² and thermoelectric studies³ have indicated that Cs_3Sb is a *p*-type conductor. In the work reported here, the study of the polarity of conduction was extended to other single alkali as well as to several multialkali antimonides. The main purpose of the experiments was to investigate the relationship between polarity and photoemission.

EXPERIMENTAL METHOD AND RESULTS

The antimonides were produced in the following way. An Sb layer corresponding to 20 to 50 atomic layers was evaporated onto the wall of a glass envelope. Two Pt contacts were provided to permit conductivity measurements. The Sb layer was exposed to alkali metal vapor at temperatures around 150°C at which rapid reaction takes place. During this activation process the photoemission, as well as the dark conductivity, were monitored. Three or more tubes were activated with each antimonide and results were reproducible throughout.

In all cases the photoemission reaches a peak when the alkali to Sb ratio is in the 3:1 range and drops sharply if exposure to alkali metal vapor is continued. If, while the temperature is maintained, the supply of alkali metal is stopped, the photoresponse quickly returns to a value close to the peak at which it stabilizes. This stage of peak emission can thus be considered to represent an equilibrium condition.

While the photoemission increases during the activation process, the conductivity drops by several orders of magnitude, in accordance with the transition from metallic Sb to semiconducting M_3Sb . However, in the range of the above-defined equilibrium, two groups of materials can be distinguished by their different behavior with regard to conductivity. In group I, the conductivity reaches a minimum just before peak sensitivity is obtained and then increases steadily to and beyond the stage of peak sensitivity if more alkali metal is added. If the exposure to alkali metal is

¹ A. H. Sommer, Rev. Sci. Instr. 26, 725 (1955).

² T. Sakata, J. Phys. Soc. Japan 9, 1030 (1954).

³ T. Sakata, J. Phys. Soc. Japan 8, 125, 272 (1953).

TABLE I. K₃Sb (group I).

Process	P.E.	Resistance	Remarks
Sb evaporated	...	4 × 10 ⁸ ohms	Metallic
Exposed to K vapor	0.3	10 ⁸	
Exposed to K vapor	0.7	10 ⁸	
Exposed to K vapor	1.3	10 ⁷	
Exposed to K vapor	3.3	3 × 10 ⁷	Closest to 3:1 ratio; peak sensitivity not yet reached.
Exposed to K vapor	3.6	4 × 10 ⁶	Peak sensitivity; conductivity past minimum; ratio >3:1.
Exposed to K vapor	2.5	5 × 10 ⁸	Ratio >> 3:1.
Baked to equilibrium	3.0	5 × 10 ⁴	Close to peak sensitivity; ratio >3:1.
Sb evaporated	0.4	1.5 × 10 ⁶	Minimum conductivity; ratio close to 3:1.
Exposed to K vapor	3.6	2 × 10 ⁵	Back to peak sensitivity; ratio >3:1.
Exposed to K vapor	3.0	10 ⁴	Ratio >> 3:1.
Baked to equilibrium	3.2	2 × 10 ⁴	Close to peak sensitivity; ratio >3:1.

TABLE II. Cs₃Sb (group II).

Process	P.E.	Resistance	Remarks
Sb evaporated	...	6 × 10 ¹ ohms	Metallic
Exposed to Cs vapor	16	5 × 10 ⁶	Peak sensitivity; ratio still <3:1.
Exposed to Cs vapor	9	1.2 × 10 ⁶	Sensitivity past peak; minimum conductivity; closest to 3:1 ratio.
Baked to equilibrium	19	10 ⁴	(a) Back to peak sensitivity; ratio <3:1.
Sb evaporated	5	2 × 10 ⁴	Ratio << 3:1
Exposed to Cs vapor	12	7 × 10 ⁶	Again closest to 3:1 ratio.
Baked to equilibrium	24	5 × 10 ⁴	(b) Back to peak sensitivity; ratio <3:1.*

* The increase in sensitivity and conductivity from stage (a) to (b) is probably partly a result of the increased layer thickness.

stopped, peak sensitivity and equilibrium condition are restored, accompanied by the corresponding decrease in conductivity to a value still above the minimum and without going through the minimum. In group II, by contrast, the conductivity is still decreasing at the point of peak sensitivity and reaches a minimum only if further alkali metal is added. If the tube is held at high temperature in the absence of alkali metal vapor, the equilibrium condition of peak sensitivity can again be restored, this time accompanied by the corresponding increase in conductivity. Group I behavior was found in K₃Sb, Na₃Sb, and probably also in Rb₃Sb. In the last named, the changes in conductivity were less drastic so that the result cannot be considered definite. Group II is represented by Cs₃Sb, (KNa)₃Sb, (KCs)₃Sb, and [Cs](KNa)₃Sb.* Typical measurements during the activation process for a group I and a group II material, respectively, are shown in Tables I and II. Photoemission (P.E.) is measured in arbitrary units, using a tungsten lamp as light source.

The reversible nature of sensitivity and conductivity measurements on repeated addition of alkali metal and Sb is typical for all the investigated materials. In the group II materials, peak sensitivity and equilibrium condition are usually identical, while in group I materials peak sensitivity occurs at a slightly higher alkali to Sb ratio than that at which equilibrium is established (see Table I).

DISCUSSION OF RESULTS

As indicated in the last column of the Tables I and II, the changes of conductivity of the two groups of antimonides may be interpreted as follows. It seems reasonable to assume that the condition of lowest conductivity corresponds to the closest approach to the stoichiometric ratio M₃Sb. In group I, a stable equilibrium is reached *beyond* this stage in the activation process, i.e., at a ratio M_{>3}Sb (excess alkali metal); in group II, equilib-

rium is reached *before* the stage of minimum conductivity, i.e., at a ratio M_{<3}Sb. This interpretation is supported by the observation that on addition of Sb *beyond* the equilibrium stage, the conductivity of group I materials decreases while that of group II materials increases (see Tables I and II).

The plausible assumption that excess alkali metal produces donors and excess Sb produces acceptors, leads to the conclusion that group I and II materials are *n* type and *p* type, respectively. This agrees with previous results on Cs₃Sb^{2,3} which indicated *p*-type conduction.

There is a striking correlation between polarity of conduction and quantum efficiency of photoemission. Cs₃Sb, (KNa)₃Sb, (KCs)₃Sb, and [Cs](KNa)₃Sb, with efficiencies above 0.1 electron per photon, are all *p* type, while the low-efficiency antimonides, K₃Sb and Na₃Sb, are *n* type. The most interesting case is the contrast between the low efficiency of the *n*-type compounds of Sb with K and Na singly (K₃Sb and Na₃Sb) and the high efficiency of the *p*-type compound of Sb with both of these metals, (KNa)₃Sb. According to Spicer,⁴ all three materials have similar intrinsic band gap energies but the electron affinity of the multialkali antimonides is much smaller than that of the single-alkali antimonides. This suggests a possible connection between polarity of conduction and electron affinity.

The experiments show that in all the investigated alkali antimonides, both *n* and *p* type, the reaction of alkali metals and Sb leads to a thermally stable equilibrium ratio of the components. This ratio deviates from exact stoichiometry but, particularly in *p*-type materials, appears to be very close to the ratio corresponding to maximum photoemissive efficiency. This coincidence is most fortunate for practical purposes because, without it, stable photoemitters of high efficiency could not be made. The interesting question whether this coincidence is of physical significance still awaits a satisfactory answer.

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⁴ W. E. Spicer, Phys. Rev. (to be published).

* This symbol indicates (KNa)₃Sb material with an additional surface layer of Cs to increase the long wavelength threshold (see reference 1).