

Formation of Cesium Antimonide. I. Electrical Resistivity of the Film of Cesium-Antimony System

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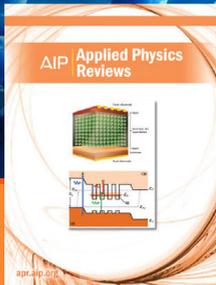
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Any static two-dimensional solenoidal solution can be written

$$\phi = aG_1 + bG_2 + cG_3 + \sum h_n C_n + \sum k_n S_n.$$

We now ask what is the nature of $\nabla^2(\nabla\phi \cdot \nabla\phi)$. It will be seen from the relations of Appendix I that the only combinations for which the Laplacian either vanishes or is constant are those involving C_1, S_1, C_2, S_2 . (Cross products of, for example C_n and S_n may vanish, but the diagonal terms do not for $n > 2$.) Furthermore, since this functional relation is clearly a positive definite one, there is no possibility of the higher functional relations cancelling out. Consequently, the most general form

of the first type of solution in two dimensions is that given by (22).

For the second type of solution, we note, by similar arguments, although the form becomes much more elaborate, that ϕ cannot contain any C_n or S_n with $n > 2$.

A similar argument applies if ϕ contains G_2 or G_3 . So ϕ can contain only G_1, S_1, C_1, S_2 , and C_2 . But we also see that the cross terms of the G 's and S_n or C_n involve factors in $(n-1)r^{-4}$ which do not vanish unless $n=1$. Hence ϕ can contain only G_1, S_1 and C_1 , which is the solution indicated.

Hence the given solutions are, in fact, the only two-dimensional static solenoidal solutions possible.

Formation of Cesium Antimonide. I. Electrical Resistivity of the Film of Cesium-Antimony System

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The films of Cs-Sb alloys whose compositions were determined by the weighing method, were prepared at the temperature ranged from 70°C to 100°C. The electrical resistance and its temperature dependency of the samples, of which atomic ratio of Cs to Sb was ranged from 0.91 to 4.86, were measured. The reproducibility of electrical resistance was obtained for all the samples, except for $Cs_{3.30}Sb$, and the temperature coefficients of resistance of the samples, except for $Cs_{0.91}Sb$, were all negative. It was found that three compounds, $CsSb$, Cs_3Sb_2 , and Cs_2Sb in addition to Cs_3Sb , having a remarkably high resistance, could be formed. The observed values of the electrical resistivity at 0°C and the thermal activation energy associated with conductivity were 1.84×10^3 ohm-cm, 0.61 eV for $Cs_{1.02}Sb$; 1.82×10^3 ohm-cm, 0.76 eV for $Cs_{2.02}Sb_2$; 2.85×10^3 ohm-cm, 0.62 eV for $Cs_{2.02}Sb$; and 1.95×10^3 ohm-cm, 0.77 eV for $Cs_{3.33}Sb$. The alloys with atomic ratio above 4 looked gold in reflected light, and those with atomic ratio above 5 were not formed.

INTRODUCTION

MANY investigations of the cesium-antimony film with a remarkable photosensitivity have been carried on since Görlich's development¹; it was found by several investigators, Lukýanov and Mazover,² Zaitsev,³ Sommer,⁴ Khlebnikov,⁵ and Miyazawa,⁶ that the composition of the material with the highest photoelectric response corresponded to the formula Cs_3Sb . However, there are some discrepancies in the reported values of its electrical conductivity and thermal activation energy associated with conductivity, even in the values reported recently by Harper and Choyke⁷ and Wallis.⁸ Indeed, it is very difficult to prepare the samples of Cs_3Sb having definite character, and the reasons why they do not exhibit definite character in

the measurements of their electrical properties are supposed to be as follows. (i) The reaction rate of cesium on antimony is too fast because of high preparation temperature (usually 150°C); (ii) the photoreponse of a cathode with thick film shows a round maximum in the final stage of its formation process, consequently, the films prepared by usual method have not always a definite composition; (iii) a material containing a larger amount of cesium than Cs_3Sb may be formed; (iv) when a film of Cs_3Sb is exposed to light, the magnitude of resistance is changed^{7,9}; (v) the resistance of the films with a composition near Cs_3Sb depends on the current passing through them; (vi) the inhomogeneity in the composition of film in the direction normal to its surface, which is caused by the incomplete reaction of cesium on a thick antimony film; (vii) the nonuniformity of film thickness, which gives rise to the nonuniform composition of the film.

Schaetti and Baumgartner¹⁰ investigated the spectral

¹ P. Görlich, *Z. Physik* **101**, 335 (1936).

² S. Y. Lukýanov and I. S. Mazover, *Zhur. Eksptl. i Teoret. Fiz.* **9**, 1459 (1939).

³ N. S. Zaitsev, *Zhur. Tekh. Fiz.* **9**, 661 (1939).

⁴ A. Sommer, *Proc. Phys. Soc. (London)* **55**, 145 (1943).

⁵ N. S. Khlebnikov, *Zhur. Tech. Fiz.* **17**, 333 (1947).

⁶ H. Miyazawa *et al.*, *J. Phys. Soc. Japan* **7**, 647 (1952).

⁷ W. J. Harper and W. J. Choyke, *J. Appl. Phys.* **27**, 1358 (1957).

⁸ G. Wallis, *Ann. Physik* **17**, 401 (1956).

⁹ W. Widmaier and R. W. Engstrom, *RCA Rev.* **16**, 109 (1955).

¹⁰ N. Schaetti and W. Baumgartner, *Helv. Phys. Acta* **24**, 614 (1951).

photoresponse, electrical resistance, and those temperature dependencies of cesium antimony photocathode, and they classified the cathodes in four groups according to their characters. The fact that even the photocathodes, prepared by the same procedure, had different characters, has shown the difficulty of preparation of Cs_3Sb . We have experimented on the formation of Cs_3Sb under low constant cesium vapor pressure in order to obtain films having nearly stoichiometric composition, and found that the film with definite character could be obtained by stopping the reaction of cesium on sputtered antimony film when their electrical resistances attained to second maximum on the formation curve.¹¹

At that time, however, we had no available data to interpret the phenomena mentioned above, and no information on the possibility of formation of the materials with the atomic ratio of cesium to antimony larger than three, except for Sommer's experiment. This work, therefore, was carried out in connection with the experiment of the formation of Cs_3Sb . It is the purpose of this paper to obtain information on the electrical resistivity and the thermal activation energy associated with conductivity of the cesium antimony system over an extended range of composition. Thus, in this work we adopted the simplest type of tube to avoid the inaccuracy mentioned previously in the composition of samples, and measured only their electrical properties.

EXPERIMENTAL ARRANGEMENTS

(a) Experimental Tube

It was necessary for maintaining the uniformity in the composition of sample during its formation process that the sputtered antimony film be uniform in thickness. Then, the sample used was prepared on a small square glass plate which corresponded to a very small part of spherical surface. Figure 1 (a) shows the used test tube. Antimony was evaporated with a tungsten filament W in the center of the spherical borosilicate glass envelope (5 cm or 7 cm in diam), and the electrical resistance of the film deposited on a square plate A was measured. Glass plate A [Fig. 1 (b)] has platinum foil leads P burned-in its two opposite edges, which were platinized over to obtain a good contact with the film to be deposited.

Preliminary tests were carried out, using four tubes with an opening of different type [cf., N in Fig. 1 (a)], in order to check whether a simultaneous reaction of cesium on antimony film takes place on all its surface. Then, the best result was obtained with a tube having the most simple type opening as shown in Fig. 1 (a). The tubes of large diameter were used for the samples whose atomic ratio was less than three to diminish the error in the thickness of the film due to the geometrical

¹¹ To be published in J. Appl. Phys.

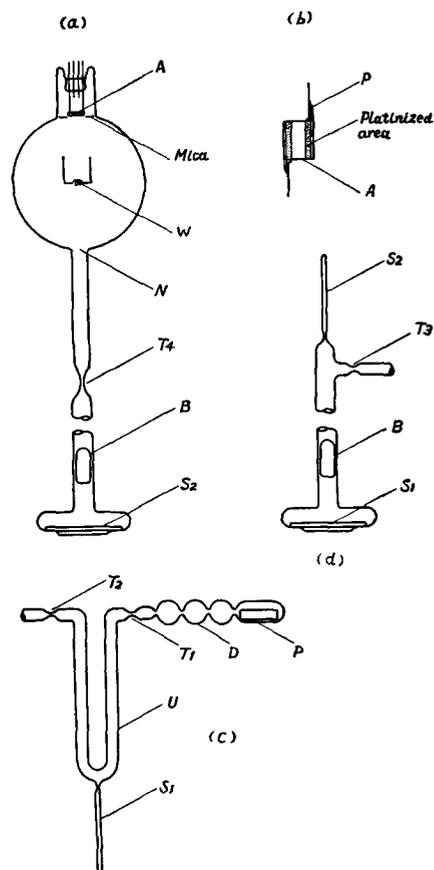


Fig. 1. Tubes used to prepare the samples and metallic cesium. (a) Test tube. (b) Glass plate on which the sample is prepared. (c) U-shaped trap used to prepare a glass ampoule containing metallic cesium. (d) T-shaped tube with a glass ampoule to be tipped off. The ampoule is shielded in the bottom of side tube of the test tube.

inaccuracy of spherical envelope and position of filament.

(b) Preparation of Metallic Cesium

Metallic cesium was made by reducing cesium chromate (guaranteed grade made by Kanto Chemical Company) with 99.99% silicon powder. Figure 1 (c) shows a U-shaped trap tube with an appendage, which is used to prepare a metallic cesium glass ampoule. The whole tube was evacuated and baked at 400°C for two hours, and trap U with ampoule was heated again by gas flame to secure outgassing. Reduced metallic cesium was distilled through condensing chambers D and trapped into U cooled by liquid nitrogen; then the appendage and the tube U containing metallic cesium were tipped off at T_1 and T_2 separately. The cesium in the U tube was evaporated by heating with gas flame and stored in ampoule S_1 , and then it was tipped off at the bottom of U tube. The ampoule S_1 containing metallic cesium was weighed by a micro-balance and sealed into the end of T tube as shown in Fig. 1(d). The T tube was evacuated and baked at 350°C for three hours in an electric oven; then it was heated again by

TABLE I. Impurity contents in used antimony.

As	0.0007%
Cu	0.0002%
Fe	0.0004%
Pb	0.0003%

gas flame, except for its bottom end containing S_1 , which was held at a somewhat lower temperature to avoid the attack of cesium on the glass.¹² The tube was tipped off at T_3 from evacuation system. Ampoule S_1 located in the bottom of T tube, was broken by dropping a glass-encased iron weight on it; released cesium was evaporated and stored in ampoule S_2 , and S_2 was tipped off at its neck. Ampoule S_2 containing metallic cesium and the tips of ampoule S_1 (about 250 mg) were weighed; S_2 was sealed into the bottom of side tube of the test tube shown in Fig. 1 (a). The total amount of metallic cesium contained in S_2 was calculated as the difference of two weighing values of ampoule S_1 with cesium and without cesium.

(c) Preparation of Samples

A weighed fragment of antimony (about 5 mg) was fixed in the filament in the center of spherical envelope. The purity of antimony used was 99.99%, and its impurities were tabulated in Table I. The tube with its side arm was evacuated and baked at the temperature ranged from 300°C to 350°C for three hours, after which the side arm was heated again by gas flame. Then, antimony was evaporated from the filament; its evaporation rate was ranged from 0.01 to 0.002 mg per cm² per min to obtain a film of uniform thickness.¹³ The structure of evaporated film of antimony has been studied by many investigators and it has been reported that the films thinner than 200 Å are amorphous, and the films thicker than 200 Å are recrystallized at room temperature.¹⁴⁻¹⁷ We used, therefore, the films with about 500 Å in thickness.

The initial resistance between two leads on glass plate was about ten ohms; the effective dimension of films was 10 mm in width and 4 mm in length. The film thickness of each sample was calculated from the weight of evaporated antimony and the dimension of spherical envelope, assuming that the resistivity of antimony in bulk is the same as that of an evaporated film.

After antimony was evaporated, the tube was tipped off from the evacuation system in a vacuum better than 3×10^{-8} mm Hg. Then, glass ampoule S_2 was

¹² J. B. Taylor and I. Langmuir, *Phys. Rev.* **51**, 753 (1937).

¹³ R. B. Jones and A. M. Glover (to RCA) U. S. 2,401,735, June 11, 1946. The evaporation rate adopted by us was very much slower than that adopted by Jones and Glover.

¹⁴ W. Latmer, *Helv. Phys. Acta* **18**, 232 (1945).

¹⁵ A. I. Frimer, *Doklady Akad. Nauk. (S.S.S.R.)* **63**, 255 (1948).

¹⁶ A. Götzberger, *Z. Physik* **142**, 182 (1955).

¹⁷ L. T. Tatarinova, *Trudy Inst. Krist. Akad. S.S.S.R.* **11**, 104 (1955).

broken by dropping a glass-encased iron weight on it; released cesium was evaporated and condensed near neck T_4 [Fig. 1(a)], and the lower part of side arm below T_4 was tipped off. The loss in the amount of cesium due to tip-off was estimated from repeating the weighing of glass ampoules with and without cesium; the mean loss in the weight of cesium for ten ampoules was 0.1 mg. The sensitivity of the micro-balance used was 10 micrograms.

The test tube with its side arm containing cesium, was heated and maintained at a definite temperature in an electric furnace. Although the character of samples is independent of the preparation temperature, the materials, whose atomic ratio are larger than 1.5, are decomposed by heating above 100°C.¹⁸ The preparation of samples, therefore, was carried out at the temperature range of 70°C to 100°C; in some cases

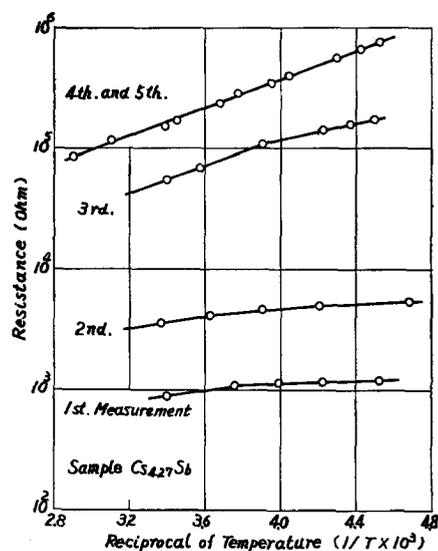


FIG. 2. Changes in the electrical resistance and its temperature dependency of the sample $Cs_{4.27}Sb$ produced by the reaction of cesium on antimony.

the temperature was risen to 130°C at the final stage of preparation in order to secure the completion of reaction. The both ends of the electric furnace used were enclosed, and so the maximum deviation in the temperature distribution along the spherical part of tube could be less than 0.5°C.

(d) Measurement of Electrical Resistivity

The electrical resistance of the specimen on glass plate A was measured by using a potentiometer, and its resistivity was calculated from the known thickness of the film. Generally the electrical resistance of most specimens is reduced by exposing them to light, remarkably for the specimens near Cs_3Sb . The measurement of resistance, therefore, was carried out after the

¹⁸ According to our investigations on the thermal dissociation of Cs_3Sb , this phenomenon occurs appreciably at temperatures above 100°C.

tube had been stored in a copper cylinder placed in a Dewar vessel for sixteen hours or more.

The resistance and its temperature dependency of specimen were observed during the formation process, because it is a measure to deduce the end of the reaction of cesium on antimony film whether by further heating the electrical properties were changed or not. Furthermore, the electrical properties of specimens that attained a definite character were measured again after several months to see whether any change in their character was produced or not (cf. Fig. 2).

The measurement of electrical resistivity was carried out at the temperature range of 70° to -70°, considering that the samples would be decomposed at higher temperatures and that it was difficult to prevent a small leakage current at lower temperatures owing to the simple structure of the experimental tube.

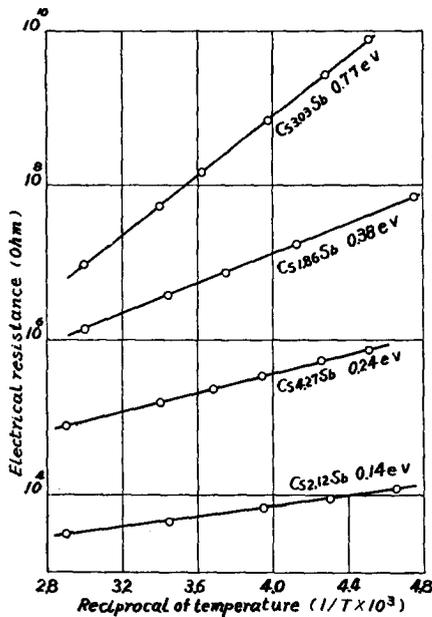


Fig. 3. Electrical resistance as a function of temperature for four samples with definite composition.

The voltage applied between the two leads of samples was usually 1.5 v. For three samples, however, with the composition, Cs_{2.67}Sb, Cs_{2.75}Sb, and Cs_{3.30}Sb, the applied voltage was lowered below 0.3 v to reduce a drift in their resistivities in the vicinity of room temperature, but it was still difficult to measure them without drift. The mean cooling rate of samples on the measurement of the temperature dependency of resistance was about 0.2°C per minute. Thus, the electrical resistance and its temperature dependency of all the samples in the experiment were reproducible except for those of Cs_{3.30}Sb.

RESULTS

Figure 3 shows the relations between the logarithm of electrical resistance and the reciprocal of absolute temperature on four samples. The electrical resistivity

TABLE II. Data for the electrical resistivity and thermal activation energy of used samples.

Composition of sample, Cs/Sb (atomic ratio)	Thickness of film (Å)	Electrical resistivity (ohm-cm)	Thermal activation energy (ev)
0.91	584	9.27×10 ⁻³	0
1.02	507	1.84×10 ³	0.61
1.46	527	9.27×10 ²	0.56
1.51	403	1.82×10 ³	0.76
1.86	517	8.27×10	0.38
1.92	443	1.16×10 ²	0.42
2.02	544	2.85×10 ³	0.62
2.05	558	9.35×10 ²	0.52
2.12	570	7.99×10 ⁻²	0.14
2.24	532	1.10×10	0.17
2.67	551	2.34×10	0.66
2.75	511	3.83×10	0.68
3.03	431	1.95×10 ³	0.77
3.14	540	2.05×10 ²	0.71
3.30	549	8.24×10	0.57
4.04	551	3.30×10	0.29
4.27	532	2.93×10	0.24
4.86	416	5.41×10 ⁻²	0.08

at 0°C and the thermal activation energy of all the samples were tabulated in Table II. Figure 4 shows the relation between the electrical resistivity at 0°C and the composition denoted with the atomic ratio of cesium to antimony. Figure 5 shows the relation of the thermal activation energy to the composition denoted with the same unit.

Samples with the atomic ratio 0.91 to 4.86 were used, and their temperature coefficients of resistance were negative, except for the sample with atomic ratio 0.91,

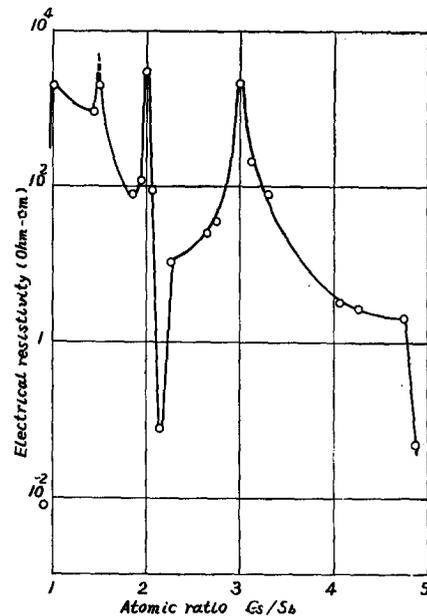


Fig. 4. Relation between the electrical resistivity at 0°C and the composition denoted by the atomic ratio of cesium to antimony. The resistivity of Cs₃Sb₂ is expected to be higher than that shown in this figure, considering the results of another experiment on the thermal decomposition of Cs₃Sb.

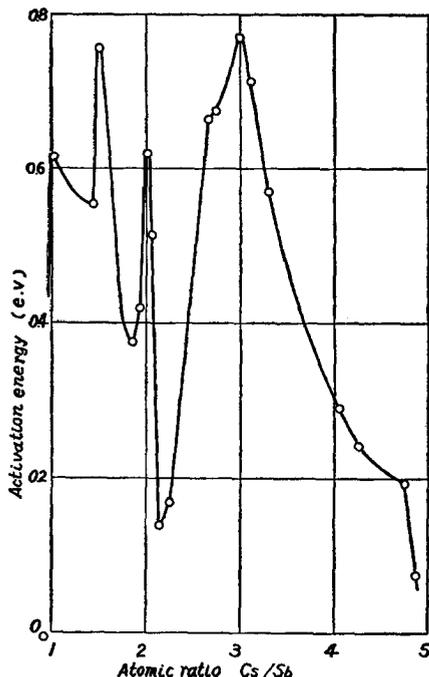


FIG. 5. Relation between the thermal activation energy associated with conductivity and the composition denoted by the atomic ratio of cesium to antimony.

of which the temperature coefficient of resistance is slightly positive. Comparing the sample of atomic ratio 0.91 with that of atomic ratio 1.02, the former had an extremely low resistivity, about 10^{-3} ohm-cm, while the latter had a very high resistivity, above 10^3 ohm-cm, though there was no difference in the color of films by transmitted light. It should be noted that the former, whose content of cesium was deficient in the stoichiometric quantity, had a metallic character; the latter with near stoichiometric composition exhibited a character of semiconductor. The sample with atomic ratio 4.86 was formed by heating for more than 100 hours at a temperature 70° to 100°C ; when the temperature was risen to 130°C after measuring its electrical characters, it was decomposed and a large amount of metallic cesium was released. The samples with atomic ratio above 5 could not be obtained because of melting in the course of formation. The sample with atomic ratio 2.12 showed a very low resistivity and had a small activation energy, compared with other samples.

Miyazawa prepared Cs_3Sb with the effusion method and measured the total electrical resistance of the sample of intermediate state at 150°C . Then, he found that the compounds with the composition of CsSb and Cs_3Sb were present, but the presence of Cs_3Sb_2 was not conclusive. According to his results, there is a minimum value of the electrical resistance at the composition of Cs_2Sb , but our result showed that a maximum value of the resistance was obtained at the same composition. Thus, Fig. 4 suggests the presence of the compounds of Cs_3Sb_2 and Cs_2Sb as well as CsSb and Cs_3Sb . Moreover,

it was shown that the materials with a composition of atomic ratio above 3 were formed by prolonged heating, although the presence of such materials was not confirmed in Sommer's experiment. The resistance of Cs_3Sb_2 was remarkably higher than that of the samples near Cs_3Sb_2 and the activation energy of Cs_3Sb_2 was rather large, but those of the materials between CsSb and Cs_3Sb_2 had only a small variation in the magnitude.

The values of electrical resistivity of Cs_3Sb have been reported in a few papers and those values at room temperature were generally below 100 ohm-cm, except for Wallis's values. The resistivity of our sample with $\text{Cs}_{3.03}\text{Sb}$ was about 10^3 ohm-cm, and its thermal activation energy associated with conductivity was 0.77 eV, which corresponded to the values of Morgulis and Djatlowitzkaja¹⁹ or Shuze *et al.*²⁰

Wallis showed that the compositions of the sample at the maximum and minimum points on the formation curve, which showed the relation between the electrical resistance of film and the amount of reacted cesium, corresponded to those of CsSb and Cs_3Sb , respectively. Although the values of the resistivity and the thermal activation energy of CsSb and Cs_3Sb obtained by him were dispersed over some range, the resistivity of CsSb ranged from 10^3 ohm-cm to 10^4 ohm-cm, and agreed with the value obtained by us— 1.84×10^3 ohm-cm for $\text{Cs}_{1.02}\text{Sb}$.

The color of the samples with atomic ratio above 2.67 by transmitted light was deep red. Then, as the content of cesium in the sample increased over this ratio, the color of film became deeper red. The samples with atomic ratio above 4 looked gold in reflected light.

DISCUSSION

One of the difficulties in the preparation of cesium antimony photocathode arises from the possibility of the formation of materials with atomic ratio above 3. Although Sommer concluded that no further reaction of cesium on Cs_3Sb occurred, it is evident, as shown in this experiment, that such materials can be obtained by prolonged heating even at a rather low temperature; for example, the sample with $\text{Cs}_{3.30}\text{Sb}$ was obtained by heating at 70°C for 70 hours. Therefore, it will not always be impossible that a material containing more cesium than Cs_3Sb is formed by heating for a comparatively short time at a usual preparation temperature, about 150°C .

By a usual method, there is a possibility that the samples would have a composition in a state arising from an equilibrium of the formation and decomposition of Cs_3Sb , in which case the composition of samples would not always attain Cs_3Sb , and would have a low resistivity and a small activation energy.

In all the compositions except for $\text{Cs}_{0.91}\text{Sb}$, the elec-

¹⁹ N. D. Morgulis and B. T. Djatlowitzkaja, *Izvest. Akad. Nauk. S.S.S.R.* **12**, 126 (1948).

²⁰ Shuze, Motzchan, and Ryvkin, *Zhur. Tekh. Fiz.* **18**, 1494 (1948).

trical resistivity of samples was larger than that of both components and its temperature coefficient was negative. Then it was found that four compounds with stoichiometric composition— CsSb , Cs_3Sb_2 , Cs_2Sb , and Cs_3Sb —were present as in the case of the cesium bismuth system.²¹ The electrical resistivity and its activation energy associated with conductivity of the compounds having near stoichiometric composition were 1.84×10^3 ohm-cm, 0.61 ev for $\text{Cs}_{1.02}\text{Sb}$; 1.82×10^3 ohm-cm, 0.76 ev for $\text{Cs}_{3.02}\text{Sb}_2$; 2.85×10^3 ohm-cm, 0.62 ev for $\text{Cs}_{2.02}\text{Sb}$; and 1.95×10^3 ohm-cm, 0.77 ev for $\text{Cs}_{3.03}\text{Sb}$.

It is supposed that the electrical conductivity of these compounds is a result of the presence of impurity levels arising from the stoichiometric excess or deficiency of cesium atoms, and the thermal activation energy associated with conductivity represents the energy difference between the impurity level and filled band or conduction band. In fact, Wright²² and Sakata^{23,24} ascribed the conductivity of Cs_3Sb to the presence of an acceptor level, and Lukyanov and Mazover² to that of a donor level. According to our other experiments,¹¹ the photoresponse of cesium antimony film reached to a maximum just after the electrical resistance had passed through the maximum due to the formation of Cs_3Sb ; in other words, cesium antimony film containing an excess of cesium showed a maximum photoresponse.

Provided that a material in an intermediate state consists of a layer of stoichiometric compound and another layer whose content of cesium is very excessive or deficient as compared with the compound, and the latter has a high conductivity and a small activation energy associated with conductivity, the electrical conductivity of the material at low temperatures may be characterized by the latter. Then, a small activation energy of Cs_3Sb at low temperatures, observed by a

few investigators, may be a result of an impurity level produced by the presence of such a layer within specimens used by them. The activation energy of Cs_3Sb at low temperatures obtained by Suhrmann and Kangro²⁵ or Schaetti and Baumgartner¹⁰ was about 0.15 ev and agreed with that of our sample $\text{Cs}_{2.12}\text{Sb}$.

The electrical resistance of the film $\text{Cs}_{0.91}\text{Sb}$ showed a metallic character. This suggests that the film consists of a thick CsSb layer with high resistivity and a thin layer of nonreacted antimony or dilute cesium-antimony alloy. Assuming that the thickness of the metallic layer is of the order of ten percent of the film, about 50 Å, which is deduced from the atomic ratio of the sample, and neglecting the effect of CsSb layer because of its high resistivity, the calculated value of electrical resistivity of the metallic layer becomes 8×10^{-4} ohm-cm.

Thus, when the amount of cesium is insufficient to form CsSb , it seems that the reaction of cesium on antimony is stopped and a nonreacted antimony or dilute cesium-antimony alloy layer is left. This fact suggests a model for the mechanism of the reaction of cesium in vapor phase on solid antimony. In this work, it might be desirable to obtain the relation between composition and characteristics of optical absorption of the samples, and also to determine their crystal structure by x-ray crystal analysis. However, considerable changes in the shape of the glass envelope to be used were required to reduce a high background intensity in x-ray crystal analysis,^{26,27} or to measure the optical property of the samples. Therefore, we gave up such studies.

²⁵ R. Suhrmann and C. Kangro, *Naturwissenschaften* **40**, 137 (1953).

²⁶ K. H. Jack and M. M. Wachtel, *Proc. Roy. Soc. (London)* **A239**, 46 (1957).

²⁷ Private communication from M. Owaki. He has made an experiment to determine crystal structure of Cs_3Sb films by x-ray crystal analysis, and found that an extremely thin window was needed to reduce strong reflection and absorption of x-ray on and in the glass of the envelope, and a very thick film of the samples was necessary to obtain x-ray photographs with sharp diffraction pattern.

²¹ W. Klemm, *Angew. Chem.* **66**, 148 (1954).

²² D. A. Wright, *Semiconductors* (John Wiley & Sons, Inc., New York, 1955), second edition, p. 129.

²³ T. Sakata, *J. Phys. Soc. Japan* **8**, 125, 723, 793 (1953).

²⁴ T. Sakata and S. Munesue, *J. Phys. Soc. Japan* **9**, 141 (1954).