

Studies of the Semiconducting Properties of the Compound CsAu

W. E. SPICER, A. H. SOMMER, AND J. G. WHITE
RCA Laboratories, Princeton, New Jersey

(Received February 5, 1959)

Data are presented showing CsAu to be a semiconductor. The optical absorption curve is typical of a semiconductor with a threshold for direct optical excitation across the gap between 2.6 and 3.3 eV and exciton peaks at about 2.6, 3.0, and 3.3 eV. A relatively high optical absorption at smaller photon energies may indicate an indirect absorption process. Additional information has been obtained by measuring the spectral response curve of the photoemission from CsAu. The resistivity of the material is approximately 0.01 ohm-cm over the range from 410°K to 4.2°K, indicating either degeneracy or impurity banding. X-ray studies show that CsAu has a CsCl structure and a lattice constant of 4.263 ± 0.001 Å. Finally, some preliminary results obtained with other alkali metal-gold compounds are described.

I. INTRODUCTION

THE existence of a stoichiometric compound CsAu with nonmetallic optical properties was first reported by Sommer in 1943.¹ This finding was confirmed in 1952 by Borzyak² who described quantitative measurements of photoemission and light absorption of this compound. He found a threshold of photoemission at about 7200 Å and an absorption edge at about 5000 Å. The present work is concerned with a more detailed study of light absorption and photoemission of CsAu; in addition, the crystal structure of the material, as well as the change of resistivity with temperature, has been established. The principal aims have been to verify that CsAu is a semiconductor, to investigate its semiconducting properties, to indicate possible band models for CsAu, and to suggest the nature of the chemical bonding involved.

II. EXPERIMENTAL TECHNIQUES

A. Preparation of CsAu

CsAu is chemically unstable in air and must therefore be prepared and studied in vacuum. For the x-ray structure determination, finely divided gold powder was exposed to Cs vapor at 200°C in an evacuated thin-wall quartz capillary suitable for Debye-Scherrer powder diagrams. For electrical and optical measurements, thin films were used which were formed on the wall of cylindrical glass (or quartz) vacuum tubes. The CsAu films were prepared by exposing an evaporated Au layer, several hundred Å thick, to Cs vapor at 150–200°C until the reaction was completed. Excess Cs was removed by continuing the baking process. Electrical contact to the film was made by means of two strips of Pt, fused into the glass. These films decomposed at about 250°C.

¹ A. H. Sommer, *Nature* **152**, 215 (1943).

² P. G. Borzyak, *Trudy Inst. Fiz. Akad. Nauk Ukr.S.S.R.* **2**, 1924 (1952).

B. Measurements of Optical Absorption and Photoemission

The apparatus³ and experimental methods⁴ used in this work have been described previously and are, therefore, not discussed in detail. All optical measurements were made with a Model 12B Perkin-Elmer monochromator. The bandwidth of this instrument, expressed in $h\nu$ per mm slit width, has been determined by DeVore³ and is given below for several values of photon energy.

Photon energy (eV)	Bandwidth (eV/mm)
1.2 to 2.0	0.1
3.0	0.07
4.0	0.05

The actual slit widths used in obtaining various optical absorption curves are indicated on the respective curves shown in the figures. A 0.3-mm slit width was used for the photoemissive measurements. The monochromator was equipped with a motor drive and the output signal was recorded. This made it possible to record the incident, transmitted, or reflected light intensity continuously as the spectrum was swept out.

Most of the experimental tubes were cylindrical with a diameter of $1\frac{3}{4}$ inches. In making the optical absorption measurements, the experimental tube was positioned so that the intensity of the reflected light and of the transmitted light could be measured without moving the tube. For the photoemissive measurements, the Au evaporator was used as the collector.

To obtain the absorption coefficients, the equation

$$e^{-\alpha d} = \frac{I}{I_0} \left[\frac{1}{1 - I_R/I_0} \right] \quad (1)$$

was used. In this equation, I is the intensity of the transmitted radiation, I_0 is the intensity of the incident radiation, I_R is the intensity of the reflected radiation, d is the thickness of the film, and α is the absorption coefficient. The use of Eq. (1) to correct for the reflec-

³ H. B. DeVore, *RCA Rev.* **13**, 453 (1952); H. B. DeVore and J. W. Dewdney, *Phys. Rev.* **83**, 805 (1951).

⁴ W. E. Spicer, *Phys. Rev.* **112**, 114 (1958).

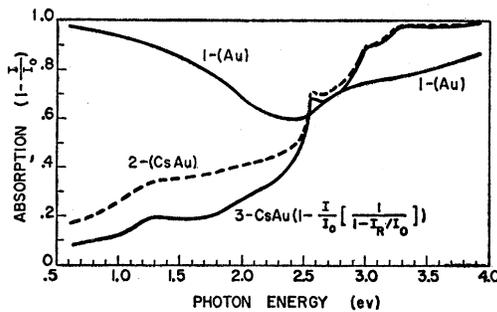


Fig. 1. Absorption of a Au layer before and after reaction with Cs. Curve 1 is the absorption $(1-I/I_0)$ of the Au layer before reaction with Cs, curve 2 is the absorption $(1-I/I_0)$ of the CsAu layer formed from the Au layer of curve 1, curve 3 contains the data of curve 2 corrected for the reflection of the CsAu layer $[1-(I/I_0)/(1-I_R/I_0)]$. The CsAu curves show structure at about 2.6, 3.0, and 3.3 ev.

tion of the film gives, of course, only an approximation since the effects of multiple reflections are not considered; however, the error involved in this approximation is estimated to be less than 10% in the region of highest absorption and not much higher elsewhere. It should be mentioned that in the absorption data there was no evidence of interference effects.

To determine the absorption coefficient, the sample thickness was determined as follows. The thickness of the original Au layer was found by comparing the Au transmission (curve 1, Fig. 1) with published curves for Au layers of known thickness. The transmission of thin evaporated Au layers depends on the manner of evaporation and on the subsequent annealing treatment.⁵ Fortunately, curves have been published for layers prepared like ours⁶ as well as for well-annealed layers.⁷ Since the characteristic transmission window of Au in these two types of layer differs by about 700 Å in spectral position, the position of the window may be used to identify the type of layer. The position of the transmission window in curve 1, Fig. 1, was identical with that of Krautkramer⁶ who formed his layers in a similar manner. The only difference between the spectral distribution of transmission of the two Au layers was slightly lower transmission of Krautkramer's layer on the long-wavelength side of the transmission window. By comparing the absolute values of transmission curve 1, Fig. 1, with the curves of Krautkramer for thicknesses of 208 Å and 281 Å, a thickness of about 220 Å was estimated.⁸ Because of the similarity between our and Krautkramer's transmission curve, it seems unlikely that the estimate of the film thickness can be off by much more than 10% or 20%. Since the thickness of the original gold layer was known, the

⁵ O. S. Heavens, *Optical Properties of Thin Solid Films* (Butterworths Scientific Publications, London, 1955).

⁶ J. Krautkramer, *Ann. Physik* 32, 537 (1938).

⁷ Gillham, Preston, and Williams, *Phil. Mag.* 46, 1051 (1955).

⁸ It should be noted that the thickness of Krautkramer's layers, and hence that of our layers, was obtained by assuming the bulk density of gold.

thickness of the final CsAu layer was calculated to be 1000 Å by using the densities of Au and CsAu (as obtained from the x-ray study, Sec. VI).

III. OPTICAL ABSORPTION

A number of CsAu samples were studied and the spectral distribution and temperature dependence of the optical absorption reported here was found to be reproducible. Because of the difficulties in determining the sample thickness, the absolute value of the absorption coefficient was determined for only one sample.

Figure 1 contains typical absorption curves for CsAu as well as an absorption curve of the Au layer taken before its reaction with Cs. Curve 1 is the absorption of the gold layer before reaction with Cs; these data are presented in the form $(1-I/I_0)$ where I_0 is the intensity of the incident radiation and I is the intensity of the transmitted radiation. Curve 2 is the absorption after reaction with Cs, again in the form $(1-I/I_0)$; and curve 3 is the absorption after reaction with Cs, corrected for the reflected light, I_R . These latter data are presented in the form $1-(I/I_0)/(1-I_R/I_0)$. Curve 1 shows the characteristic transmission window of Au near 2.4 ev. The formation of CsAu is accompanied by a very marked decrease in absorption at photon energies below 2.5 ev and a rise above 2.5 ev. This is just the change one would expect if Au combined with Cs to form a semiconductor. The CsAu curves also show peaks at about 2.6, 3.0, and perhaps 3.3 ev.

An absorption curve was also measured before the reaction of Au with Cs was completed. Although this curve was practically identical with curve 2 for photon

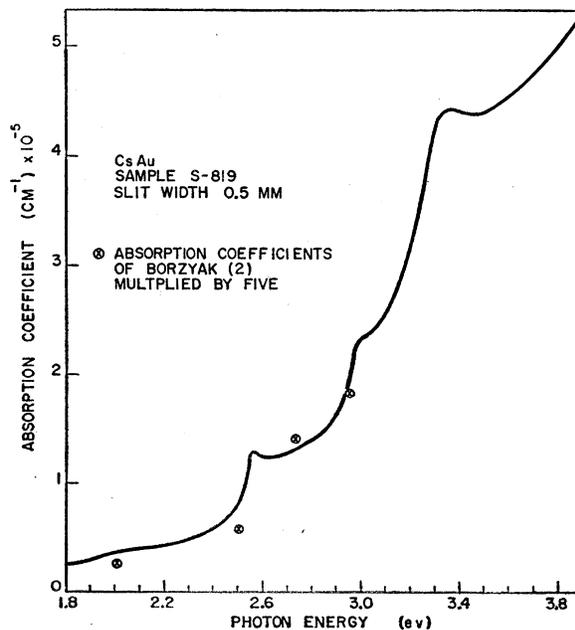


Fig. 2. Optical absorption coefficients of CsAu. The experimental points of Borzyak multiplied by five are also shown.

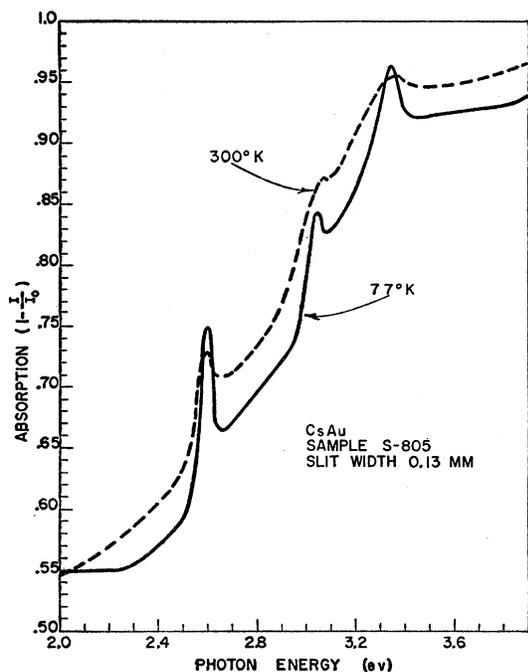


FIG. 3. The temperature dependence of the CsAu absorption. Note that the peaks at about 2.6, 3.0, and 3.3 eV become much sharper on cooling.

energies above 2.5 eV (including the structure at about 2.6, 3.0, and 3.3 eV), increased absorption was observed below 2.5 eV. Visually, the layer showed some golden color in reflection which is absent in the final CsAu layer. These observations indicate that in the intermediate stages a mixture of Au and CsAu is formed, rather than a compound with lower Cs content. Thus the existence of a reported⁹ compound $Cs_{0.77}Au$ seems to be doubtful.

Using the thickness of 1000 Å, determined as described in Sec. II-B, the absorption coefficients of Fig. 2 are obtained from the data of curve 3, Fig. 1. Note that the structure at about 2.6, 3.0, and 3.3 eV is associated with coefficients of $10^5/cm$ and larger. Qualitatively the curve agrees with the experimental points of Borzyak,² but the absolute values in this work are about a factor of five higher. We do not believe it likely that our data are in error by such a large factor. Borzyak had only three values for photon energies above 2.5 eV; hence it was impossible for him to observe the structure between 2.5 and 3.3 eV. However, both our and Borzyak's² data indicate a relatively high absorption on the long-wavelength side of the fundamental absorption. This is discussed in Sec. VII.

Figure 3 shows the effect of cooling to liquid nitrogen temperature on the absorption curve. The peak at about 2.6 eV becomes much sharper and quite pro-

⁹ W. Biltz and F. Weibke, *Z. anorg. Chem.* **236**, 12 (1938).

nounced peaks appear at about 3.0 and 3.3 eV. As indicated on the curves, the resolution is almost four times higher than for the curves in Fig. 1.

IV. PHOTOEMISSION

Typical curves of the spectral distribution of photoemission are presented in Fig. 4. Included are curves obtained from three different layers studied in this work and also data from the article by Borzyak.² Since Borzyak did not give the absolute sensitivities, his curve has been fitted vertically to our curves. As is apparent, the shape of these curves is similar.

The absolute magnitudes of the photoemission measured here were found to vary as much as a factor of five from layer to layer. Thus, the photoemission seemed to be the least reproducible of the quantities studied here. However, the threshold of response and over-all shape of the curves were generally reproducible from layer to layer. Taking the threshold as the photon energy where the yield is 10^{-7} electron/photon, we see that these curves all have a value of about 1.6 eV. Since the optical absorption measurements may indicate that fundamental absorption occurs only for photon energies greater than 2.0 eV, it is possible that this photoemission may be due to the excitation of extrinsic carriers. The low value of the yield (of the order of 10^{-3} electron/photon) is consistent with this interpretation.¹⁰ The variation in yield may be associated with the variation in "defect" levels.

It is interesting to note that the curves tend to flatten out between 2.4 and 2.6 eV and then rise more steeply for higher photon energies. This rise begins at the edge of fundamental absorption and may indicate a change from a direct excitation of photoelectrons to

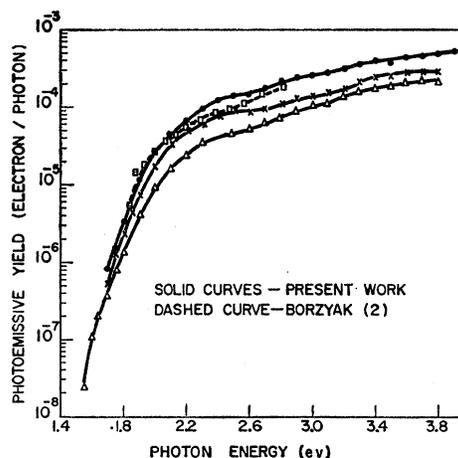


FIG. 4. The spectral distribution of the photoemissive yield from four CsAu layers. The dashed curve is that of Borzyak which has been fitted vertically to our data since Borzyak does not give absolute values for his yield curve.

¹⁰ W. E. Spicer, *RCA Rev.* **19**, 555 (1958).

a process in which excitons are first produced and then give up their energy to bound electrons.¹¹

V. RESISTIVITY

The conversion of the Au layer into a CsAu layer is accompanied by a rise in resistivity by a factor of approximately 5000. The final resistivity of these thin films of CsAu, derived from sample dimensions and resistance, is in the range of 0.01 ohm-cm. This value is too high for a metallic conductor and more compatible with the conductivity to be expected for a degenerate semiconductor. Assuming a carrier mobility between 100 and 10 cm²/v sec, a carrier density in the range 10¹⁹ to 10²⁰ is indicated.

The resistance of CsAu samples was measured at 410°K, 300°K, 77°K, and 4°K and monitored during the cooling or heating to these temperatures. Over the whole range from 4°K to 410°K, the resistance was found to be constant within about 50%. The temperature coefficient of resistance is positive, with an increase in resistance of about 20% between 77°K and 300°K and an increase of about 10% between 300°K and 410°K.

With the alkali-antimony compounds, it has been found possible¹² to vary the conductivity of the material by orders of magnitude by incorporating small amounts of additional alkali or antimony into the films. With CsAu, it was found that addition of Cs tended to decrease the resistivity, whereas the addition of Au tended to increase it. These results suggest that excess Cs is the doping agent in this material. However, the changes which could be produced were within a factor of only about two, in contrast to the very large changes obtained in the alkali-antimony compounds.

VI. X-RAY STRUCTURE DETERMINATION

X-ray diffraction powder photographs were taken of several samples of CsAu, using Cu K α radiation. As can be seen from Table I, all the x-ray lines can be indexed on the basis of a CsCl-type structure (space group O_h⁹). The weak "superlattice" lines with $h+k+l$ odd, are due to the difference in scattering power between Au and Cs and show that the structure is ordered, in agreement with the postulated stoichiometric formula CsAu. Using the Nelson-Riley¹³ method of extrapolation to $\theta=90^\circ$, the value $a_0=4.263\pm 0.001$ Å was obtained. The density calculated for one atom of Au and one atom of Cs per unit cell is 7.065. The Au-Cs interatomic separation is 3.692 Å, appreciably shorter than the sum of the metallic radii, 4.04 Å. From the value of the density, a value for the volume of the unit

TABLE I. X-ray data for CsAu indexed on the basis of a CsCl-type structure.

hkl	d (obs)	d (calc)	Intensity
100	4.1329	4.2630	VVW
110	2.9834	3.0145	VS
111	2.4409	2.4613	VVW
200	2.1142	2.1315	M
210	1.8976	1.9165	VVW
211	1.7310	1.7404	S
220	1.5000	1.5072	M
300, 221	1.4141	1.4210	VVW
310	1.3430	1.3481	M
222	1.2278	1.2321	W
321 ^a	1.1367	1.1394	S
400	1.0644	1.0658	VW
330, 411	1.0010	1.0048	W
420	0.94991	0.95326	W
332	0.90683	0.90888	W
422	0.86852	0.87020	W
431, 510	0.83486	0.83606	M
521	0.77824	0.77830	S

^a α_{112} doublet resolved from this point down. A weighted mean wavelength was used for the earlier reflections.

cell can be computed and compared with a "calculated" volume which is obtained by simply adding the atomic volumes of Au and Cs as found in the crystals of the elements. In the case of CsAu, it turns out that the "real" volume is 42% smaller than the "calculated" volume. This result will be referred to in Sec. VII.

VII. DISCUSSION OF RESULTS

A. Semiconducting Properties of CsAu

Very strong evidence for the semiconducting nature of CsAu is obtained from the optical absorption data. Whereas the transmission of the original gold layer (see Fig. 1) is relatively symmetrical and quite low on either side of the gold transmission window, the transmission of the CsAu film is much lower than that of the Au film above 3.0 eV and considerably greater below 2.5 eV. These are just the changes in absorption to be expected in the conversion of a metallic into a semiconducting material. The absorption peaks at about 2.6, 3.0, and 3.3 eV can be interpreted as exciton peaks in a semiconductor, whereas there seems to be no mechanism which could explain such peaks in a metallic alloy.

In addition to the optical evidence, the increase in resistance by orders of magnitude during the conversion of the Au film into the CsAu film indicates that CsAu is a semiconductor. Finally, the results of the x-ray studies also support the conclusion that CsAu is a semiconductor. The ordered CsCl crystal structure can be taken to indicate that the material is either a semiconductor with some degree of ionic binding or a metallic alloy with long-range order. However, it is unlikely that a material with such a low dissociation temperature (250°C) would form an ordered alloy at room temperature. Strong evidence for ionic binding is found in the contraction of the lattice during the formation of

¹¹ For a discussion of this type of emission, see E. Taft and L. Apker, Phys. Rev. **83**, 479 (1951); E. Taft and L. Apker, in *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley (John Wiley and Sons, Inc., New York, 1952), p. 246.

¹² A. H. Sommer, J. Appl. Phys. **29**, 1568 (1958).

¹³ J. B. Nelson and D. P. Riley, Proc. Phys. Soc. (London) **57**, 160 (1945).

CsAu. As pointed out in Sec. VI, the "real" volume of CsAu is 42% smaller than the "calculated" volume obtained by adding the atomic volumes of Au and Cs. By contrast, in predominantly covalent compounds between metals or metalloids, such as GaAs and InSb, the "real" volume is *larger* than the "calculated" volume by 10% to 20%, while in metallic alloys, such as Cu₂Zn, "real" and "calculated" volumes are identical within a few percent. Only a few intermetallic compounds with ionic binding are known, but in a typical example, Cs₃Sb,¹⁴ the "real" volume is 48% smaller than the "calculated" volume. Thus, there is a strong indication that contraction is associated with ionic binding. It should be noted that because of the very large difference between the metallic radius of Cs, 2.62 Å (8-coordinated), and the ionic radius of Cs⁺, 1.67 Å, an appreciable volume contraction could be achieved in compounds containing Cs with a relatively small fraction of ionic character in the bonds.

B. Chemical Nature of CsAu

The presence of some degree of ionic binding in CsAu, indicated by the volume contraction and crystal structure as discussed in the previous section, seems surprising at first. In such an ionic compound, Au would have to be the negative constituent because of the highly electropositive character of Cs. The existence of Au⁻ does not seem to have been reported previously, but the electronic structure makes it, in fact, quite likely, in particular when combined with an element as electropositive as Cs. Au has the same electronic configuration as Hg, except for the presence of only *one* 6s electron instead of two. Hg has a strong tendency toward a completed 6s shell as indicated by the fact that the positive ion Hg⁺ is not known but only Hg₂⁺⁺. In view of the identical inner-core configuration of Au, it is, therefore, not surprising that Au reacts with the strongly electropositive Cs to fill its 6s shell. It is interesting to note that in a recent publication¹⁵ the existence of Au⁻ is predicted on the basis of general considerations of a similar nature.

C. Evidence for Excitons

All the experimental evidence is consistent with the identification of the absorption peaks at about 2.6, 3.0, and 3.3 eV as excitons. This evidence includes: (1) sharpening of the peaks on cooling, (2) half-widths of the absorption bands at liquid nitrogen temperature which are as small as 0.05 eV, and (3) large absolute values of the absorption coefficients associated with the absorption peaks ($10^5/\text{cm}$ to $4 \times 10^5/\text{cm}$).

The exciton peaks do not have hydrogenic spacing but are almost evenly spaced. Thus the excitons do not

seem to be of the loosely bound hydrogenic type, but of the more tightly bound type found in the alkali halides.¹⁶ It may be significant that the lowest excited states above a negative Au ion (6s² configuration) are the 6s 6p triplet states. In Hg, where the splitting should be similar to that for Au⁻, these triplet lines are separated by 0.225 eV and 0.57 eV. By comparison, the spacings of the CsAu peaks are 0.4 and 0.3 eV. This similarity between the separation of the exciton peaks and that of the triplet lines may indicate strong 6p components in the exciton wave functions.

D. Optical Absorption at Photon Energies below the Exciton Peaks

Both in the data of Borzyak and of this work, the optical absorption below 2.0 eV is surprisingly large (see Fig. 1). Although the measured absorption in this region may be affected by experimental errors, such as scattering of light from the beam and inadequate correction for the effect of multiple reflections, it seems certain that the reported absorption cannot be entirely due to these experimental errors. All, or most, of this absorption may be due to imperfections in the film and/or the large density of conduction carriers; however, there is also a possibility that it is due to a non-vertical transition across the band gap¹⁷ (i.e., an indirect absorption process). A more thorough examination will have to be made before the optical absorption can be fully understood.

E. Energy Band Model of CsAu and Conduction Type

From optical absorption, photoemission and conductivity data, tentative conclusions can be drawn concerning the band model and the conductivity type of the CsAu films. A definite model cannot be suggested until it has been definitely established whether or not indirect band to band absorption is taking place below 2.0 eV. At present, it is apparent that the direct band to band absorption is in the vicinity of the exciton bands. In the alkali halides, the band to band transition has been reported to lie between the first and second or second and third exciton peaks.¹⁸ Assuming, by analogy, that the edge for the direct band to band absorption of CsAu lies between the first and third exciton peaks, a value of between 2.6 and 3.3 eV is indicated for this process and thus for the band gap if no indirect transitions occur below 2.6 eV.

¹⁶ For example, see H. Haken, *J. Phys. Chem. Solids* **8**, 166 (1959); also, *Halbleiterprobleme*, edited by W. Schottky (F. Vieweg and Sohn, Braunschweig, 1958), Vol. 4.

¹⁷ Hall, Bardeen, and Blatt, *Phys. Rev.* **95**, 559 (1954); also, *Proceedings of the Photoconductivity Conference, Atlantic City, 1954*, edited by R. G. Breckenridge *et al.* (John Wiley & Sons, Inc., New York, 1956).

¹⁸ E. A. Taft and H. R. Philipp, *J. Phys. Chem. Solids* **3**, 1 (1957).

¹⁴ H. Miyazawa and S. Fukuhara [*J. Phys. Soc. Japan* **7**, 645 (1952)], have reported ionic transport in Cs₃Sb.

¹⁵ C. H. L. Goodman, *J. Phys. Chem. Solids* **6**, 305 (1958).

Since the conductivity of CsAu cannot be explained as being due to intrinsic conduction in a semiconductor, one has to postulate conduction by extrinsic carriers. The negligible change of conductivity with temperature indicates either a degenerate semiconductor or impurity band conduction. The low value of the resistivity would support the first alternative. However, in the case of impurity band conduction, this band would have to lie relatively close to the conduction or the valence band in order for the wave functions of the impurity to overlap sufficiently. Therefore, it seems unlikely that the Fermi level is more than a few tenths eV from either the conduction or the valence band. It is hoped that Hall measurements will give more information on the conduction mechanism.

If the actual band gap lies between 2.6 and 3.3 eV, the threshold of photoemission of 1.6 eV is smaller than the band gap energy by between 1.0 and 1.7 eV and, thus, it appears that this photoemission must be associated with the excitation of extrinsic carriers. If CsAu were *p*-type, the Fermi level would have to lie at least 1.0 eV above the valence band to give the 1.6-eV threshold. However, this seems impossible since, according to the arguments of the preceding paragraph, the Fermi level must lie within a few tenths of an electron volt of either the conduction or valence band. However, this contradiction does not arise if we assume CsAu to be *n*-type. The large density of conduction carriers, estimated at 10^{19} to 10^{20} , and the extremely low quantum efficiency of 10^{-7} electron/photon at the threshold make it likely that this threshold is due to excitation of the conducting electrons from either the conduction or "defect"¹⁹ band. Thus, the value of the electron affinity would be approximately equal to the value of the photoemissive threshold, if a degenerate semiconductor is assumed, or several tenths eV below the value of the threshold if "defect" banding is assumed. These considerations lead to an estimate for the electron affinity of CsAu within the approximate limits of 1.3 to 1.7 eV. However, if the absorption on the long-wavelength side of the exciton is due to indirect absorption across the band gap, it is possible that the photoemission is due to excitation from the valence band. In this case, the electron affinity would be below the 1.3 to 1.7 eV estimate already made.

¹⁹ "Defect" band as used here means any band caused by energy levels in the forbidden band, whether they be due to impurities or lattice imperfections.

APPENDIX. COMPOUNDS OF Au WITH Rb, K, AND Na

While only the Cs-compound of Au has been studied in detail, some preliminary findings on other alkali-gold compounds deserve mention. The compounds RbAu, KAu, and NaAu have been reported.¹ Since the electropositive character of the alkali metals decreases in the series Cs-Rb-K-Na, one might anticipate a corresponding diminution in the ionic character of the gold compounds. The following facts seem to support this expectation:

(1) RbAu shows the characteristics of a semiconductor with bonds of an ionic nature, similar to CsAu, but less pronounced. The visual appearance is non-metallic. There seems to be a band edge and an indication of structure in the optical absorption. Again, the resistance increases when Au reacts with Rb, though by less than two orders of magnitude, and the x-ray study shows a CsCl structure with a 4.105 ± 0.001 Å lattice parameter. This corresponds to a volume contraction of 36%.

(2) KAu has a metallic appearance and the resistance increases only by a factor of about two during formation. Most significantly, x-ray examination showed a complex structure with a large unit cell, typical of alloys with metallic binding.

(3) NaAu has a metallic appearance and even retains some of the color of the original gold layer. The resistance of the NaAu film does not differ from that of the original Au layer. This contradicts recent reports²⁰ claiming a rise of resistance by a factor of 2000 during the conversion of Au into NaAu. However, these results may have been due to an aggregation effect which has been observed if thin Au layers are heated in the presence of excess Na. X-ray results are not yet available.

To sum up, the experimental evidence seems to point to a transition from semiconductors with partially ionic bond to predominantly metallic alloys in the series from CsAu to NaAu, with the break probably occurring between RbAu and KAu. More detailed studies are now being made.

ACKNOWLEDGMENTS

The authors wish to thank Professor H. Haken of Erlangen University, Professor S. Nikitine of Strasbourg University, and Dr. D. S. McClure, Dr. R. Williams, and other members of the RCA Laboratories for many stimulating conversations, and Mr. M. L. Kaiser for assistance in taking the photoemission data.

²⁰ I. L. Sokol'skaia, J. Tech. Phys. U.S.S.R. 27, 127 (1957) [translation: Soviet Phys. Techn. Phys. 2, 108 (1957)].