

Resistivity, Hall Constant, and Seebeck Coefficient of CsAu*†

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Measurements of resistivity, Hall constant, and Seebeck coefficient have established that CsAu is an n -type semiconductor with carrier concentrations 10^{18} – 10^{19} cm^{-3} . The carrier concentration is essentially independent of temperature over the range 4.2–300°K and the mobility is 30–60 $\text{cm}^2\text{V}^{-1}\text{sec}^{-1}$. It is suggested that excess cesium introduces an impurity band which overlaps the conduction band. The Seebeck coefficient (-0.023 $\text{mV}/^\circ\text{K}$ at 300°K) indicates that the Fermi level lies about 0.02 eV above the conduction band based on optical lattice scattering.

I. INTRODUCTION

PREVIOUS measurements of resistivity, optical absorption, and photoemission have established that CsAu is a semiconductor.^{1,2} On the basis of optical, photoemission, and resistivity measurements, it has been deduced that CsAu is n type with carrier concentrations of 10^{19} – 10^{20} cm^{-3} and that it probably contains excess cesium.¹ Photoemission and optical studies have indicated that the minimum energy gap is 2.6 ± 0.2 eV,² which is in good agreement with a calculated minimum band gap of 2.3 eV based on a completely ionic model.³ Measurements of resistivity gave values of about 0.01 $\Omega\text{-cm}$ over the range 4.2–410°K, indicating either degeneracy or impurity banding.¹

In the present paper, measurements of resistivity and Hall constant are reported for the temperature range 4.2–300°K, and measurements of the Seebeck coefficient for the range 77–300°K. These measurements, which are the first direct measurements of carrier type and concentration, definitely establish the semiconducting properties of CsAu.

II. EXPERIMENTAL METHODS AND RESULTS

A. Preparation of CsAu

Because CsAu is chemically reactive in air, it is most conveniently prepared and studied in vacuum.¹ In the present studies, the compound was prepared in the form of a thin semitransparent film⁴ in an evacuated tube (Fig. 1). The tube was first evacuated and baked at 350°C for 4 h. Then a thin film of gold was evaporated onto one face of the tube while the template on the movable mask was held against the tube face. By this means a rectangular film of gold (1 $\text{cm} \times 4$ cm) was formed having small probes for electrical connections. These probes overlap the aluminum strips which connect to the Kovar pins in the glass envelope.

The thickness of the gold film was determined from

† Work done under auspices of the U. S. Atomic Energy Commission.

¹ W. E. Spicer, A. H. Sommer, and J. G. White, *Phys. Rev.* **115**, 57 (1959).

² W. E. Spicer, *Phys. Rev.* **125**, 1297 (1962).

³ V. E. Wood and J. R. Reitz, *Bull. Am. Phys. Soc.* **6**, 108 (1961); *J. Phys. Chem. Solids* **23**, 229 (1962).

⁴ G. A. Condas, *Rev. Sci. Instr.* **33**, 987 (1962).

transmission measurements.^{1,5} Then the gold was exposed to cesium vapor at 150°C until reaction was complete. Excess cesium was removed by continuing the baking process while vacuum pumping the tube. The thickness of the final CsAu film was calculated from the known densities of Au and CsAu.¹ Three samples of CsAu films were prepared, each having a thickness of about 1300 Å.

B. Hall Effect, Resistivity, and Mobility

Hall voltage measurements were made with a high-input-impedance differential amplifier operating at 140 cps. Provision was made for canceling probe imbalance signals. Measurements were made at field strengths up to 7 kG after first calibrating the magnet with the sample in place. Results for the Hall constant as a function of temperature are presented in Fig. 2. The sign of the Hall constant (determined from a dc Hall measurement) established the fact that CsAu is n type. The carrier concentration (10^{18} – 10^{19} cm^{-3}) is in substantial agreement with the deduction of Spicer *et al.*,¹ but it should be mentioned that their work did not permit a direct measurement of carrier concentration or type.¹

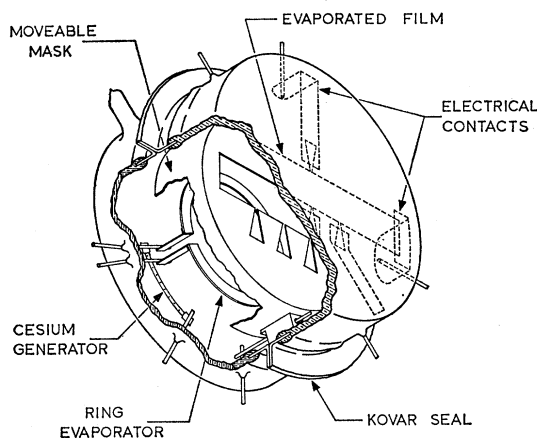


FIG. 1. Vacuum tube designed for Hall measurements. Gold is evaporated from gold foil wrapped around the ring evaporator thus producing a film of uniform thickness (Ref. 4). Cesium is generated by electrical heating of a mixture of Cs_2CrO_4 and Si in a perforated nickel channel.

⁵ J. Krautkramer, *Ann. Physik* **32**, 537 (1938).

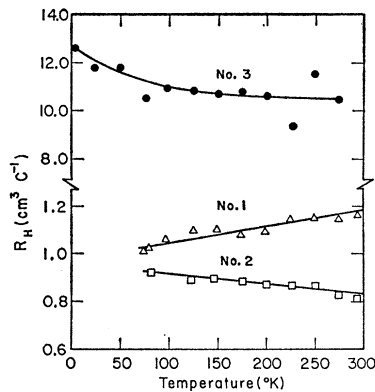


FIG. 2. Hall constant as a function of temperature.

Resistivity was determined by measuring the voltage between two probes with an electrometer while passing a known dc current through the sample. The results are given in Fig. 3. The resistivity as determined in the above manner always agreed, within 5%, with the resistivity (ac or dc) obtained from a voltage applied across the entire sample and the current through the sample. This indicates the presence of ohmic contacts and a sample of uniform thickness. Also, the values of resistivity reported here are in agreement with those reported by Spicer *et al.*,¹ which supports the view that CsAu tends to form a stable compound.

At room temperature, the mean free path of a carrier is found from the mobility by the relation

$$l = 10^{-8} (m^*/m)^{1/2} \mu\text{cm},$$

which yields $l \approx 35 \text{ \AA}$ assuming the effective mass to equal the free-electron mass and using the average mobility (Fig. 4) at 300°K. Thus, it is seen that the mobility is not limited by particle size, since the crystallite dimensions are believed to be of the order of the film thickness ($\sim 1300 \text{ \AA}$).

The mobility is seen to vary only slightly over the entire temperature range, although it always decreases with increasing temperature near room temperature. It is not possible from the data to unscramble the contributions of the various scattering mechanisms to the

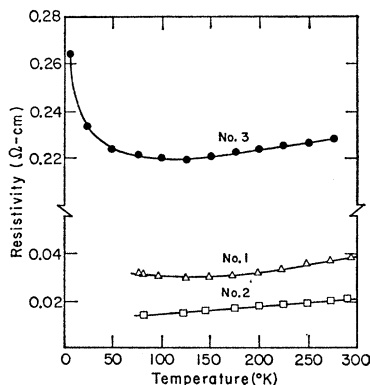


FIG. 3. Resistivity as a function of temperature.

mobility. However, at room temperature the mobility appears to be determined primarily by optical lattice scattering. The temperature dependence of mobility ($\mu \approx T^{-1/2}$) for optical lattice scattering above the Debye temperature⁶ agrees reasonably well with experiment at room temperature. Further, as will be discussed later, only optical lattice scattering gives a reasonable value for the Fermi level obtained from thermoelectric measurements.

Measurements were made on one sample (No. 3) at temperatures down to 4.2°K. The results obtained are in agreement with earlier work,¹ namely, there is essentially no change in electrical properties at temperatures down to 4.2°K.

C. Seebeck Coefficient

The Seebeck coefficient was determined over the temperature range 77–300°K. Differential temperature measurements were made by means of thermocouples (not shown in Fig. 1) embedded in the glass at each end

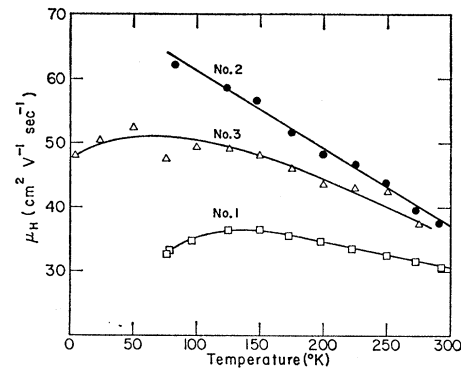


FIG. 4. Hall mobility as a function of temperature.

of the CsAu film. Voltage measurements were made with an electrometer.

The Seebeck coefficient was found to be proportional to temperature, reaching a value of $-0.023 \text{ mV/}^\circ\text{K}$ at 300°K. Because of experimental difficulties (primarily in preventing heat losses through the thermocouples) the Seebeck coefficient is believed to be accurate to only $\pm 0.003 \text{ mV}$ at 300°K. Nonetheless, it does permit an estimate of the Fermi level and it indicates *n*-type conductivity. If one assumes that optical lattice scattering is predominant at 300°K, the Seebeck coefficient is given by⁷

$$S = \frac{V_F}{T} - 3 \frac{k \mathcal{F}_2}{e \mathcal{F}_1},$$

⁶ D. J. Howarth and E. H. Sondheimer, Proc. Roy. Soc. A219, 53 (1953).

⁷ R. A. Smith, *Semiconductors* (Cambridge University Press New York, 1959).

where \mathfrak{F}_2 and \mathfrak{F}_1 are Fermi-Dirac integrals of dimensionless form.⁸ Based on this model, the Fermi level is found to lie 0.021 eV above the conduction band edge. Acoustic lattice scattering and impurity scattering yield values of V_F which are not consistent with results of resistivity and Hall measurements (a high density of carriers at temperatures down to 4.2°K), and only optical lattice scattering gives approximately the correct temperature dependence of mobility at 300°K.

III. CONCLUSION

The results of resistivity, Hall, and thermoelectric measurements conclusively show that CsAu is an *n*-type

⁸ J. S. Blakemore, *Semiconductor Statistics* (Pergamon Press Inc., New York, 1962).

semiconductor. The negligible change in resistivity at temperatures down to 4.2°K and the high density of carriers (10^{18} – 10^{19} cm⁻³) suggest that the broadening of cesium donor levels is so great as to overlap the main conduction band. The Seebeck coefficient shows that the Fermi level lies about 0.02 eV above the conduction band edge.

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Stark Effect and Hyperfine Structure of Hydrogen Fluoride*

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The nuclear hyperfine structure constants and the electric dipole moment of hydrogen fluoride, HF¹⁹, in the ground-vibration and first excited rotation state have been measured in a molecular beam electric resonance experiment. The hfs constants are: $c_F = 307.6 \pm 1.5$ kc/sec, $c_p = -70.6 \pm 1.3$ kc/sec, $\frac{2}{3}g_p g_F \mu_{nm}^2 / h \langle r^3 \rangle = 57.6 \pm 0.44$ kc/sec. The apparatus was calibrated by observing Stark transitions in the ground-vibration and first excited rotation state of carbonyl sulfide, O¹⁶C¹²S³², which gave $\mu_{HF} / \mu_{OCS} = 2.554 \pm 0.0037$, or $\mu_{HF} = 1.8195 \pm 0.0026$ D, by using $\mu_{OCS} = 0.7124 \pm 0.0002$ D. An absolute measurement of the OCS electric dipole moment gave $\mu_{OCS} = 0.7120 \pm 0.003$ D. A digitally computed solution of the Stark effect with magnetic hyperfine structure was necessary to interpret the data. The theory and experiment are in good agreement over the range of electric-field strengths used in the experiment. The hfs constants are in excellent agreement with the averaged absolute values of these constants as measured in a molecular beam magnetic resonance experiment. The agreement has significance because of discrepancies between the results from the two resonance methods, for some other molecules, in previous experiments.

INTRODUCTION

IT seemed interesting to do an electric resonance experiment on HF for the following two reasons: (1) To date, no unambiguous measurement of the electric dipole has been made even though it has been subject to extensive calculations^{1,2}; (2) Baker *et al.*³ have determined the average absolute values of the spin-spin and spin-rotation interaction constants from an almost completely resolved spectrum in a molecular beam magnetic resonance experiment. A comparison of their results with those from an electric resonance experiment might indicate if there is really something

fundamental in the discrepancies between results from the two resonance methods for some other molecules in previous experiments.⁴

THEORY

An adequate Hamiltonian for HF in an external electric field is

$$H = H_0 + H_N + H_E,$$

where

$$H_N / h = c_F \mathbf{I}_F \cdot \mathbf{J} + c_p \mathbf{I}_p \cdot \mathbf{J} + \frac{g_F g_p \mu_{nm}^2}{\langle r^3 \rangle (2J+3)(2J-1)} \\ \times [3(\mathbf{I}_F \cdot \mathbf{J})(\mathbf{I}_p \cdot \mathbf{J}) + 3(\mathbf{I}_p \cdot \mathbf{J})(\mathbf{I}_F \cdot \mathbf{J}) \\ - 2\mathbf{I}_F \cdot \mathbf{I}_p J(J+1)],$$

and

$$H_E = -\mathbf{y}(J, v) \cdot \boldsymbol{\mathcal{E}} - \frac{1}{2} \alpha_{z'z'} \mathcal{E}_z^2 - \frac{1}{2} (\alpha_{z'z'} - \alpha_{x'x'}) \mathcal{E}_z^2 \cos^2 \theta.$$

⁴ J. C. Swartz and J. W. Trischka, *Phys. Rev.* **88**, 1085 (1952).

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¹ A. M. Karo and L. C. Allen, *J. Chem. Phys.* **31**, 968 (1959).

² R. K. Nesbet, *J. Chem. Phys.* **36**, 1518 (1962).

³ M. R. Baker, M. Nelson, J. A. Leavitt, and N. F. Ramsey, *Phys. Rev.* **121**, 807 (1961).