

NMR and Structural Properties of CsAu and RbAu

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NMR and X-ray diffraction studies of granular samples of the intermetallic compounds, CsAu and RbAu, are reported. Studies of X-ray line intensities indicate that the CsCl lattice structure is well ordered for both materials. For the semiconducting compound CsAu, excess Cs in the lattice is shown to be the primary source of conduction electrons. X-ray studies show an expansion of lattice constant with addition of excess Cs. Measurements of NMR line shapes, Knight shifts, and relaxation times for CsAu confirm that the excess Cs is atomically dispersed in the samples. NMR measurements show our RbAu samples to have a metallic nature. However, the metallic characteristics may well derive from excess Rb known to be present in the samples.

I. Introduction

In 1943, Sommer (1) reported the existence of a stoichiometric compound, with the formula CsAu which exhibited nonmetallic optical properties. Since then, several investigators (2-5) have confirmed the existence of this compound, determined its crystal structure and optical properties, and measured the electrical properties. The band gap has been measured (5) to be 2.6 eV. The lattice constant of its CsCl-type structure is reported (2) to be 4.263 ± 0.001 Å. The band structure has been calculated (6-8) and the results of those calculations are consistent with the experimental conclusion that the material is a semiconductor.

The existence of other alkali-gold compounds of the same stoichiometry, $M_{1.0}Au_{1.0}$, has also been reported. Spicer, Sommer, and White (2) (hereafter labeled SSW) investigated RbAu, KAu, and NaAu films prepared in a fashion similar to their CsAu samples. Kienast and Verma (3) showed the existence of stable phases at the $Rb_{1.0}Au_{1.0}$ and $K_{1.0}Au_{1.0}$ stoichiometries. Alkali metal-gold com-

pounds of other stoichiometries also exist (3, 9). However, our interest lies in the properties of the 1:1 compounds, and we focus attention on these.

The motivation for the work reported here lies in the question of whether any of the 1:1 compounds other than CsAu is also semiconducting. In particular, we have investigated RbAu. Properties of this material have been less well explored than those of CsAu, and previous investigations have yielded an inconclusive answer to the question of whether it is a semiconductor or a metallic system. On the basis of their optical studies and some measurements of electrical properties, SSW concluded that "RbAu shows the characteristics of a semiconductor with bonds of an ionic nature, similar to CsAu, but less pronounced." (SSW concluded that KAu and NaAu show metallic behavior.) Norris and Walldén (10), on the other hand, concluded from photoemission studies that "the photoelectron energy distribution curves from RbAu show a Fermi edge indicating that RbAu is metallic".

Our work is organized around comparison

of properties of CsAu and RbAu. The work reported in this paper deals entirely with powder materials. However, we have profited by interchange of information with W. J. Phillips of our laboratory, who has been conducting parallel studies of electrical properties of CsAu and RbAu films.

In Section II, we discuss preparation and chemical characterization of these materials. In Section III, X-ray measurements are described, including an investigation of the degree of disorder due to possible Cs–Au and Rb–Au interchange in the stoichiometric materials. Section IV reports the NMR results. In Section V, we report the results of a study of the effects of the presence of excess Cs on the properties of CsAu. In Sections VI and VII, we summarize the significance of the results for CsAu and develop reasons for our provisional conclusion that the metallic properties of our RbAu samples (and perhaps also the photoemission results of Norris and Walldén) arise from the presence of excess Rb incorporated into the structure.

II. Sample Preparation and Characterization

Preparation of CsAu and RbAu Materials

The compounds of interest, CsAu and RbAu, react quickly with air or water vapor, as do the pure alkali starting materials. All steps in preparation or handling must be carried out either under high vacuum (10^{-6} Torr) or in a dry box (He atmosphere with less than 5 ppm O_2).

Conditions for preparation of CsAu and RbAu are set by the phase diagrams of these materials (3, 11). Successive steps of the typical preparation are shown in Fig. 1. These steps may be summarized as follows.

(1) After evacuation and outgassing (at a pressure of 10^{-6} Torr at 350°C for 24 hr) of the dumb-bell shaped quartz sample preparation unit which contains powdered Au (99.9%) (see Fig. 1a), liquid Cs or Rb (99.9%) is introduced into the dumb-bell and it is then sealed. Typical starting quantities were 2.7 g

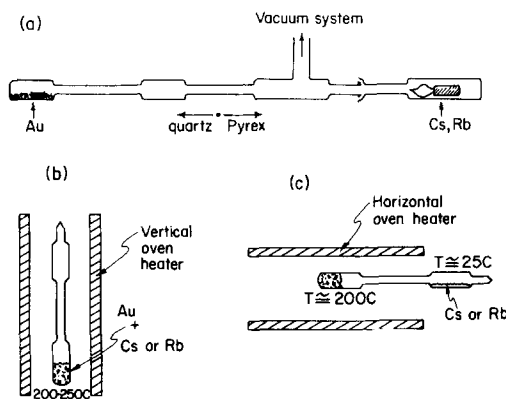


FIG. 1. Sample tube configurations used in preparing powder samples of CsAu and RbAu. (a) Arrangement of starting materials prior to preparation. (b) Configuration used during alkali-gold reaction at $200\text{--}250^\circ\text{C}$. (c) Arrangement used to remove excess alkali metal from sample.

of Au, 2 g of Cs; 4 g of Au, 2 g of Rb—quantities which correspond to a slight excess of alkali metal in both cases.

(2) After a quantity of liquid alkali is decanted on top of the gold powder, the sample tube is heated in a vertical position for 6 to 8 hr at a temperature in the range of 200 to 250°C , and the Au–alkali reaction proceeds to completion (Fig. 1b). (We note that quartz is required for the sample tube because of its better resistance to reaction with alkali metals.)

(3) Following step (2), excess alkali metal is removed by distillation in a temperature gradient (Fig. 1c). Completion of distillation of alkali metal is monitored visually. After completion of alkali distillation, the dumb-bell tube is separated into two sealed halves. The CsAu or RbAu material remains in the form of a sintered chunk. RbAu appears dark blue in color and CsAu appears blackish gray.

A variant on this method was used for some samples. In this alternate method, the sample dumb-bell was not initially sealed off from the main vacuum system. After reaction, the tube is turned to the horizontal position and excess alkali is again removed from the sample by condensation in a room temperature zone, as in Fig. 1c. But, because of continuous

pumping until the final sealing of the sample vial, the removal of excess alkali may progress beyond the stage reached in the sealed tube. For RbAu, this second procedure with continuous pumping was not used, because it was feared that RbAu might lose excessive amounts of alkali and decompose to give admixtures of the gold-rich phases, RbAu₂ and RbAu₅. For the more stable CsAu, this particular problem does not exist, and sample CsAu I, whose properties are described subsequently, came from material prepared by this second method. CsAu I, as prepared, was golden brown in color, rather than the blackish grey of CsAu samples prepared by the method described above. All samples on which results are reported, other than CsAu I, came from materials prepared in the sealed tubes.

Preparation of Experimental Samples

Experimental samples were prepared for three purposes—NMR measurements, X-ray analysis, and chemical analysis. All sample preparation was carried out in the dry box.

NMR Samples. The sintered material is gently ground in an agate mortar to make powder samples. Care in grinding is essential in order to avoid decomposition of the compounds. For CsAu, 2 to 4 g of powder is placed in a sealed Pyrex tube, 10 mm i.d., to form an NMR sample. An RbAu powder sample was found to be excessively lossy when placed in an NMR probe, so that the powder had to be mixed with paraffin oil (previously outgassed under vacuum). The mixture was introduced into the sample tube by funnel in order to keep the tube walls clean for sealing.

X-Ray samples. After gentle grinding, powder is introduced into a Lindeman capillary tube of 0.3 mm i.d. for Debye–Scherrer photography. The tube is sealed with a fast epoxy. This procedure produced a sample which lasted several weeks without degeneration.

Chemical analysis. A portion of a sample of interest is weighed in the dry box. Typical weights were in the range of 40 to 400 mg.

TABLE I
CHEMICAL AND X-RAY CHARACTERIZATION OF
SAMPLES

Sample	Composition	Lattice parameter (Å)
CsAu I	Cs _{1.03 ± 0.02} Au	4.262 ± 0.001
CsAu V-1	Cs _{1.08 ± 0.02} Au	4.2645 ± 0.001
CsAu V-2	No reliable result	4.263 ± 0.001
CsAu V-3	Cs _{1.06 ± 0.02} Au	4.263 ± 0.001
CsAu V-4		4.262 ± 0.001
CsAu V-5	Cs _{1.015 ± 0.03} Au Cs _{0.99 ± 0.03} Au	4.262 ± 0.001
RbAu IV		4.106 [less precise- error undetermined]
RbAu VI	Rb _{1.046 ± 0.02} Au	4.107 ± 0.001
RbAu VII	No reliable result	4.1075 ± 0.001
RbAu VIII	Rb _{1.10 ± 0.02} Au	4.108 ± 0.001

Precision of weighing is about 0.2 mg. This weighed portion is dissolved in 1 to 2 cm³ of water containing two to four drops of concentrated HCl. The compound decomposes quickly upon heating in the liquid, leaving gold particles. The gold particles are dissolved in aqua regia (typically 10 cm³). The final solution is diluted and Cs, Rb, and Au are assayed by atomic absorption spectroscopy.

Table I lists all samples upon which experimental results are reported in this paper. Results of chemical analysis are given in that table. For various reasons, not all samples were subjected to chemical analysis.

III. X-Ray Diffraction Studies

The Debye–Scherrer method was used for all X-ray measurements, with a 11.45-cm-diameter camera. Previous X-ray measurements (SSW) showed that both compounds have the CsCl structure, with lattice parameter $a = 4.263 \pm 0.001$ Å for CsAu and $a = 4.105 \pm 0.001$ Å for RbAu. Our results for lattice constants in our samples are given in Table I. These values were obtained using the procedure of Nelson and Riley (12).

We note several features of the X-ray photographs.

(1) A special feature of the CsCl structure is the set of lines corresponding to an odd value of the Miller index sum, $(h + k + l)$ whose presence results from the difference in scattering from the *A* and *B* atoms. Their presence and intensity gives information concerning the degree of ordering of the *A* and *B* sublattices. An analysis of degree of order in samples was made and is described subsequently.

(2) The powder pattern of RbAu VIII shows some faint lines not in the CsCl array. Only about four of these extra lines could be seen. They may be lines of RbAu₂. No reference pattern for RbAu₂ was available, so we did not pursue their identification.

In Table I, we note that the two CsAu samples, CsAu I and CsAu V-1, prepared under active pumping and in a sealed tube, res-

pectively, show a small difference in lattice parameter. This difference is part of a rather full story of differences in these two samples, and this story is told in detail in Section V. Properties of samples CsAu V-2, 3, 4, and 5 are part of that story and will be discussed in that section.

The lattice parameters of CsAu I and CsAu V-5, which we believe to be the samples nearest to 1:1 stoichiometry for reasons to be elaborated in Section V, agree with the value given by SSW. For the RbAu samples, our lattice parameter values show a difference from that of SSW by 0.002 Å, just outside the span of uncertainties in the two measurements. We do not know whether or not that difference represents actual difference in the materials. Table II displays the detailed X-ray data for RbAu.

TABLE II

DEBYE-SCHERRER X-RAY DATA FOR RbAu INDEXED ON THE BASIS OF A CsCl-TYPE STRUCTURE^a

<i>hkl</i>	<i>d</i> _{obsd} (Å)	<i>A</i> _{calcd} (Å)	Densitometer peak density ^b
1 0 0	4.0789	4.0789	14
1 1 0	2.8906	4.0880	107
1 1 1	2.3619	4.0910	7
2 0 0	2.0494	4.0987	24
2 1 0	1.8321	4.0967	7
2 1 1	1.6736	4.0995	49
2 2 0	1.4487	4.0975	12
3 0 0, 2 2 1	1.3646	4.0938	3
3 1 0	1.2964	4.0995	14
3 1 1	1.2357	4.0984	(1)
2 2 2	1.1833	4.0990	5
3 2 1	1.0955	4.0991	15
4 0 0	1.0245	4.0981	
3 3 0	0.9669	4.1022	
4 2 0	0.9176	4.1035	
3 3 2	0.8751	4.1044	
4 2 2	0.8381	4.1057	
4 3 1, 5 1 0	0.8052	4.1059	
Extrapolated to $\sin \theta = 1$		4.108 ± 0.001 Å	

^a Data is from sample RbAu VI, using a 11.45-cm-diameter camera, CuK α radiation, with relative line intensities determined from a densitometer recording.

^b Uncorrected for angular dependence of line width.

X-Ray Analysis of Degree of Lattice Disorder

In pursuit of our interest in the electronic properties of CsAu and RbAu, we were concerned to know whether there was significant Cs–Au or Rb–Au interchange in the CsCl lattice of these materials. Such interchange might, in particular, change the electrical properties from those of the perfectly ordered materials. The intensities of the powder pattern lines for odd values of $(h + k + l)$ can be used to estimate the degree of order in the structure.

We used a Fortran IV program (13) to predict the X-ray diffraction line intensities for CsAu and RbAu. The simulated pattern generated by the program accounts for Lorentz polarization effects but no temperature correction is made. In generating the simulated patterns, occupation factors in the CsCl lattice were altered to obtain relative X-ray intensities for 100%, 90%, 80%, 70%, 60% and 50% ordered lattices. (The ordering fraction is defined as the ratio of number of atoms of type *A* in one sublattice to the total number of atoms of that type.) The analytic constants for atomic scattering factors used were those given by Moore (14). The Au⁻¹ ion

TABLE III
ALKALI-GOLD ORDERING FACTORS IN THE CsCl
LATTICE BY X-RAY DIFFRACTION ANALYSIS

Sample	Ordering
CsAu I	Between 90% and 100%
CsAu V-1	Between 90% and 100%, but nearer 90%
CsAu V-2	Between 80% and 90%
RbAu VII	Almost 100%
RbAu VIII	Almost 100%

was assumed to be similar to Hg^o, and values given for Hg^o were used.

Densitometer traces of the experimental films were made, and values of the ratio (intensity of 100 line/intensity of 222 line) were compared with the computer predictions.

The results of this comparison are shown in Table III. Although uncertainties are difficult to estimate with precision, we estimate the values of ordering percentage to be good to about 5% for CsAu and somewhat better for RbAu. (For CsAu, scattering factors of Cs and Au are more nearly equal, making the lines with odd value of $(h + k + l)$ very weak.) We conclude that disorder in the samples is not a major problem, although we cannot exclude the possibility of effects of disorder at the 1% level in RbAu, the material of prime interest in these measurements.

IV. NMR Properties of CsAu and RbAu

In this section, we report the experimental NMR results for both materials. A few more-

TABLE IV
NMR PROPERTIES OF CsAu AND RbAu POWDERS

Sample	K^a (ppm)	K_{corr}^a (ppm)	$(T_1)_K^b$	$(T_1)_{\text{exp}}$	δH (G)	T_2^* (μsec) ^c	δH^* (G) ^c	
CsAu I	298°K	360 ± 30	610	0.131 sec	7.5 ± 1.0 sec ($T_1 T = 2230 \pm 300 \text{ sec}^\circ\text{K}$)	2.1	360 ± 20	2.0
[Cs metal]			15 100					
CsAu I	77°K				37.0 ± 2.5 sec ($T_1 T = 2850 \pm 200 \text{ sec}^\circ\text{K}$)			
CsAu V-3	298°K	1425				8.99 ± 0.18		
-4.1						8.78 ± 0.16		
-4.2		1098 ± 20				8.02 ± 0.06		
-4.3		877 ± 20				6.42 ± 0.12		
-4.4		712 ± 12				5.24 ± 0.06		
-4.5		654 ± 5		0.063 sec	0.019 ± 0.001 ($T_1 T = 5.7 \pm 0.3 \text{ sec}^\circ\text{K}$)	4.00 ± 0.04		
RbAu IV	298°K	1790 ± 40	1850			6.4		
	77	1620 ± 40	1680					
	4.2	1650 ± 50	1710					
[Rb metal]			6530					
RbAu VI	298°K	1780 ± 50	1840					
		1740 ± 40 ^d	1800					
RbAu VIII	298°K	1820 ± 20 ^d	1880	2.4 msec	2.3 ± 1.0 msec	7.7 ± 0.4	48 ± 2	6.0

^a Resonance field shifts listed in the first column were measured with respect to the Cs¹³³ or Rb⁸⁷ resonances in 5.5 M solutions of CsCl and RbCl, respectively. Knight shifts are usually given in comparison with the resonant frequency of the nucleus of interest in a "salt." Baron [*J. Chem. Phys.* **38**, 173 (1963)] gives the chemical shift of Cs¹³³ in CsI, with respect to the ion in dilute solution, as -253 ± 1 ppm, and of Rb⁸⁷ in RbI as -57 ± 12 ppm. Values of K_{corr} given in the second column result from adding this diamagnetic shift to our experimental values. These values of K_{corr} are the more appropriate ones to use in determining T_1 from the Korringa relation or in comparing the Knight shift to other electronic properties.

^b These values are calculated from the Korringa relation, Eq. (1), using values of K_{corr} from the second column.

^c Values of T_2^* are obtained by making a best fit of the free induction decay to a Gaussian model. The Gaussian model is observably superior to the simple alternative of an exponential decay. δH^* is the peak-to-peak derivative width calculated from the experimental values of T_2^* and the Gaussian lineshape assumption.

^d These two values are most reliable for intersample comparison, being obtained on the same day under identical experimental conditions.

or-less obvious conclusions to be drawn from some of the experimental results will be noted in passing. The broader implications of the NMR results, together with results of other aspects of our experimental work, will be discussed in the two following sections.

Measurements on both systems are summarized in Table IV. Standard NMR properties have been measured at room temperature in several samples of both materials. Selected lower temperature measurements have also been made and the results of these are included in the table. CW measurements were made with a Varian V4210-A wide-line spectrometer unit, using standard lock-in techniques. Pulsed measurements were made with a high-power, single coil pulsed spectrometer which provides a value of H_1 , the rotating rf field, of about 90 G. When necessary, signal averaging was done by storing a single trace in a Biomation Model 610 transient recorder with subsequent averaging in a Nuclear Data Model ND-800 Digital Memory Oscilloscope ("Enhancer"). Sample volumes were typically about 1 cm³. Sample coding coincides with that given in Table I.

The NMR properties of the sample labeled CsAu I given in Table IV are consistent with the well-known semiconducting properties of this material. When inserted inside the coil of an RF tank circuit, the sample of golden-brown powder does not affect the Q of the circuit, and it has no measurable effect on the inductive balance of the Varian NMR probe. There is a positive field shift of 360 ± 30 ppm for the Cs¹³³ resonance with respect to its position in CsCl solution. The simplest explanation of this small positive shift is that it arises from free electrons contributed by excess Cs atoms acting as donors. (Investigation of the effects of excess Cs is described in the next section.) Free electrons should also contribute to nuclear relaxation. If we assume this positive shift to be a Knight shift arising from these free electrons, then we can estimate a value for the nuclear relaxation time, T_1 , determined by these electrons

through the Korringa relation (15), which follows.

$$T_1TK^2 = \frac{\hbar}{4\pi k} \gamma_e^2/\gamma_n^2. \quad (1)$$

K is the value of the fractional shift in resonance frequency determined by the paramagnetism of the free electrons, γ_e and γ_n are the electron and nuclear gyromagnetic ratios, T is the Kelvin temperature. We note that the value given in Table IV for this "Korringa T_1 " in sample CsAu I is 0.131 sec, much shorter than the experimental value of 7.5 ± 1.0 sec. We also note that the experimental value of the product, T_1T , whose constancy is a characteristic signature of relaxation by conduction electrons, is nearly but not quite constant between 298 and 77°K.

Data for sample CsAu V in various stages of a treatment which will be described in detail in the next Section, are given in Table IV, and displayed in Fig. 2. Figure 2 also displays the

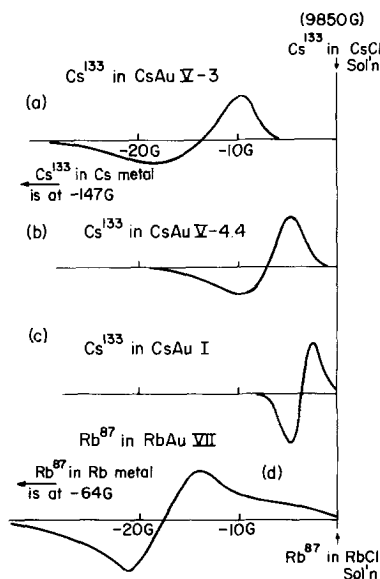


FIG. 2. Sketches of absorption derivative NMR lines in various samples (a) Cs¹³³ resonance in sample CsAu V at an intermediate stage in removal of excess Cs. (b) Cs¹³³ resonance in sample CsAu V near end of process of removal of excess Cs. (c) Cs¹³³ resonance in sample CsAu I. (d) Rb⁸⁷ resonance in RbAu VII. Rb⁸⁷ resonances in other RbAu samples show similar line width and Knight shift.

line shapes and positions for samples CsAu I and RbAu VII, in order to permit comparison of NMR line width and shift data in the various samples. We note that for sample CsAu V-4.5, the value of T_1 noted in Table IV is roughly consistent with that calculated from the Korringa relation on the basis of the measured Knight shift. This consistency contrasts with the behavior of sample CsAu I, noted previously.

The observed value of free induction decay time, T_2^* , in CsAu I is shorter than one might expect on the basis of Cs–Cs dipole–dipole interaction only. The second moment calculation for the simple cubic lattice of Cs ions gives $(\overline{\Delta H^2})^{1/2} = 0.45$ G. For a Gaussian line shape, this second moment would predict a value for T_2^* of 1.6 msec. Whether the discrepancy of this number with the measured value, $T_2^* = 360$ μ sec, arises from a large indirect dipole–dipole term, from quadrupole effects, or from a residual inhomogeneity in Knight shift values cannot be determined from our data. In principle, such a question could be resolved by a careful study of linewidth as a function of static magnetic field or by a measurement of the spin–echo value of T_2 , which would be affected by an indirect dipole–dipole interaction but not by a distribution of values of K .

For RbAu VIII, the values of K and T_1 given in Table IV are consistent with the presence of a free-carrier system. Unfortunately, we have not been able to test RbAu for one key signature of metallic relaxation, namely, a relaxation rate proportional to absolute temperature. A loss of intensity in the Rb⁸⁷ signal at low temperature has precluded measurement of values of T_1 below room temperature.

The Rb⁸⁷ linewidth in our RbAu samples is much larger than the calculated dipole–dipole width [$(\overline{\Delta H^2})_{\text{calc}}^{1/2} = 0.33$ G]. Two likely explanations of this large linewidth are (1) quadrupole broadening in field gradients generated by lattice strain and (2) a distribution of values of K from nuclear site to

nuclear site. If a distribution of values of K were the source of broadening, the inhomogeneous character of the broadening should permit observation of a spin echo at times shorter than the homogeneous dipolar free induction decay time, $T_2 = \pi^{1/2}/\gamma(2\overline{\Delta H^2})^{1/2} = 250$ μ sec. A two pulse spin–echo experiment with pulse separations of 50 to 100 μ sec was tried, but no echo was seen. Moreover, we do not observe the line asymmetry which typically results from a distribution in values of K . We conclude that quadrupole interactions are probably responsible for the broad line.

We have observed that the intensity of the Rb⁸⁷ NMR signal decreases as soon as the sample temperature drops below about 175°K. Although we did observe the CW line at 4.2°K, its signal strength in comparison to the room temperature signal was much lower than appropriate to the Boltzmann factor of 298/4.2. It seems likely that crystal strains in the lattice are eliminating Rb⁸⁷ nuclei from the resonance through the interaction of the strain-induced electric field gradients with the rather large Rb⁸⁷ quadrupole moment. (We note that for the case of Cs¹³³ in CsAu, the anomalously small quadrupole moment of Cs¹³³ would tend to suppress any similar effect in that material.) From a cursory investigation in which we watched the amplitude and shape of the Rb⁸⁷ free induction decay while the sample temperature was cooling from 298 to 77°K, it seems likely that the effect is produced by a continuing increase of strains rather than by a phase transition to a noncubic crystal structure. A more thorough investigation of this effect would require a study of X-ray patterns as a function of temperature, a study we are not at the moment set up to carry out.

V. Effects of Excess Alkali in CsAu

We have noted that sample CsAu I, prepared under active pumping, showed a golden-brown color, while CsAu samples prepared in the sealed tube show a blackish-

gray color. When we placed sample CsAu V in an NMR coil, we found that it was quite lossy. This observation led us to pursue a rather illuminating investigation of the role of excess cesium in determining various properties of the CsAu powder samples. The sample codes CsAu V-1, V-2, V-3, V-4, and V-5 represent various stages of treatment of this sample which were initiated for the purpose of removing excess cesium from the powder. The treatment was straightforward. The tube containing the sample was placed in a temperature gradient, with the sample at about 185°C, and the other end of the tube at about 5°C. At the cold end, Cs vapor condenses, thus encouraging any excess Cs to leave the CsAu sample. This condensation was allowed to continue for a period of about 1 or 2 days between successive monitorings of the properties of the sample. As the sample progressed through its history from CsAu V-1 to CsAu V-5, a variety of properties were observed to change.

(1) The color of the sample gradually changes from blackish gray to golden brown. CsAu V-5 is only slightly darker in color than CsAu I.

(2) The loading effect on an RF coil gradually disappears.

(3) The NMR properties were monitored through stages CsAu V-3 and CsAu V-4, and, as shown in Table IV and Fig. 2, show a steady shrinking of the mean value of the Knight shift, and a steady narrowing of the NMR line as the distribution of Knight shifts narrows. We found that the linewidth is roughly proportional to applied magnetic field, and the line shape is quite asymmetric, as shown in Fig. 2.

(4) Finally, the lattice parameter is observed to decrease in the process. Fig. 3 shows data plotted according to the Nelson and Riley scheme, and the derived values of a .

It seems quite obvious that the sample is originally metallic in character as a result of the presence of excess Cs in the lattice, and gradually approaches the semiconducting pro-

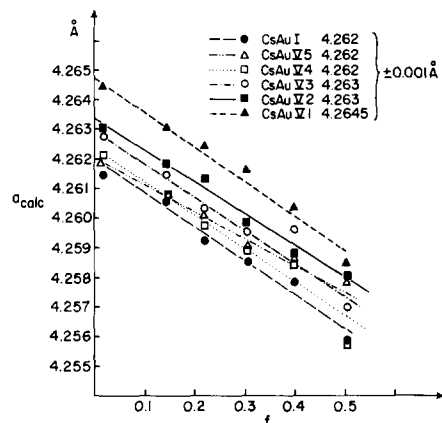


FIG. 3. Data obtained from X-ray powder patterns of various CsAu samples, plotted according to the method of Nelson and Riley. The lattice constant, a , is given by the $f = 0$ intercept of the best straight line through the data points [$f = 0.5 \cos^2 \theta (1/\sin \theta + 1/\theta)$].

erties of stoichiometric CsAu. Moreover, the data of Fig. 3 show a small but unambiguous shrinking of the mean lattice parameter as Cs is removed. The NMR and X-ray measurements suggest to us that the excess Cs is atomically dispersed in the CsAu. There is no interstice in the perfect CsAu lattice of size adequate to accommodate the Cs⁺ ion. It is possible that Cs⁺ has substituted for the Au⁻ ion to make an atomic cluster resembling Cs metal or that it is dispersed along grain boundaries in the particles.

The chemical analysis data given in Table I is of considerably lower sensitivity to small departures of stoichiometry from the 1:1 ratio than the other properties. However, the chemical analysis data for CsAu V during its history is roughly consistent with the conclusions drawn from X-ray, NMR, and the qualitative measures of color and RF electrical losses.

We should note that W. J. Phillips of our research group has studied the electrical conductivity of CsAu films produced by reaction of Au films with ambient Cs vapor (16). He finds that the electrical conductivity can be altered by a thermal treatment similar to that used in the treatment of the CsAu V powder sample. As Cs vapor is condensed in a

cold region far away from the heated CsAu film, the electrical conductivity falls toward the values found by Wooten and Condas in their better films. These results confirm the original work of SSW on the role of excess Cs is a primary donor in CsAu films, and are consistent with our interpretation of our results on sample CsAu I.

VI. Discussion

Our primary motivation in this work has been to elucidate the electronic properties of RbAu. However, in order to provide a sound background for interpretation of measurements in RbAu, we conducted various parallel studies of the parallel studies of the related and better known material, CsAu. In the course of these CsAu studies, we have extended knowledge concerning this unusual semiconductor. Therefore, we shall first give a summary of the results of the CsAu studies, both for their own sake and as a preparation for interpretation of measurements in RbAu.

CsAu: Pure and Doped with Excess Cs

Our observations during sample preparation, as well as the X-ray and NMR studies, point clearly to the fact that the golden-brown powder which comprises our sample CsAu I is essentially the same material as the CsAu films studied by SSW and by Wooten and Condas (4).

The set of measurements on CsAu V, which include observation of color change, lattice parameters, eddy current, and NMR properties, show quite graphically the role of excess Cs in the sample. We note that even at the rather good stoichiometry associated with CsAu I, there is a certain concentration of free electrons, as evidenced by Knight shift and T_1 measurements. This result seems quite consistent with the observation of Wooten and Condas that the remanent conductivity in their CsAu films is typically temperature independent, as though arising from electrons in an "impurity band," with temperature-

independent impurity scattering limiting the mobility.

From Table IV, we see that while the Knight shift for sample CsAu I is only a factor of two smaller than the Knight shift of CsAu V-4.5, the relaxation time is a factor of 400 longer in CsAu I. Said in a different way, the Korringa product [Eq. (1)] has dramatically different values in the two samples. It is our judgment that in this case, the relaxation times may be a more reliable measure of the relative strengths of the electron-nucleus coupling than the Knight shift. For the Knight shift, there is always the difficulty that the correct zero for measurement is not known with certainty, and it is our suspicion that the value of K given in Table IV for sample CsAu I may be overstated. If we assume that relaxation in both CsAu samples is determined by coupling to a set of degenerate electrons and if we further assume that the strength of the hyperfine coupling is about the same as in Cs metal (an assumption which is surely not precisely true but may not be far wide of the mark), then we can test for consistency of this assumption by estimating the density of conduction electrons in the two CsAu samples.

If the effective hyperfine coupling constant has the same value in CsAu I, in CsAu V-4.5, and in Cs metal, then the relaxation rate, $1/T_1$, will be proportional to $n^{2/3}$, where n is the electron density in the sample in question (15). The value of T_1 in Cs metal at room temperature is $370 \mu\text{sec}$ (17). Using the values of T_1 from Table IV, we can obtain derived values of electron density of CsAu I and CsAu V-4.5 from the known electron density in Cs metal and the assumption, $1/T_1 \propto n^{2/3}$.

Material	T_1	n
Cs metal	$370 \mu\text{sec}$	$8 \times 10^{21} \text{cm}^{-3}$
CsAu V-4.5	19msec	2.7×10^{19}
CsAu I	7.5sec	4×10^{15}

For sample CsAu V-4.5, we do have one cross-check upon the value obtained for n . At the conclusion of a Cs exhaustion procedure

similar to that used for CsAu V, Phillips (16) found a value of electrical resistivity of $7100 \mu\Omega\text{cm}$ at room temperature. If one compares this value with those of Wooten and Condas and selects an appropriately matching Hall coefficient value from their data, an excess electron concentration of $3 \times 10^{19} \text{ cm}^{-3}$ is estimated. This number is in good agreement with the value of $2.7 \times 10^{19} \text{ cm}^{-3}$ derived from the T_1 measurement.

The relatively long value of T_1 for sample CsAu I suggests a sample remarkably near to perfect stoichiometry. Our only cross-checks on purity of that sample do not have sufficient sensitivity to give a good test of the value of n . The apparatus used by Phillips was not capable of generating a film under active pumping to match the conditions of preparation of CsAu I.

Uncertainty about the nature of the energy states of the electrons responsible for Knight shifts and relaxation times in the CsAu samples makes us hesitate in attempting to make direct contact between our NMR results for CsAu and previous calculations of band structure for this material. It is not clear whether the electrons reside in the bottom of the conduction band of CsAu, or in an "impurity band" formed somehow by clusters of excess Cs incorporated either intimately into the lattice or along the boundaries of very small grains of CsAu.

RbAu

Our discussion of RbAu focuses on what seems to us to be the central question concerning this material. With precisely 1:1 stoichiometry, in a perfectly ordered crystal structure, will the material be conducting at $T = 0^\circ\text{K}$? (For CsAu, all of the evidence supports an answer of "No" to that question.)

There is no question that all of our RbAu powder samples are conducting at room temperature. We noted in Section II that electrical isolation of the particles is necessary in order to reduce eddy current effects.

Moreover, the natural conclusion from the NMR measurements listed in Table IV is that we are observing the effects of interaction of conduction electrons with the Rb^{87} spin system. The close correspondence of the experimental value of T_1 to that calculated from the Korringa relation using the measured value of K implies that Knight shift and relaxation rate are determined by the same coupling to the conduction electrons.

The question remains, "Is that conducting state intrinsic to ordered, stoichiometric RbAu, or is it induced by structural or chemical imperfections?" Our best judgment at the present time is that the measured electronic properties in our samples are determined by excess Rb present in the samples. This judgment arises from an assortment of pieces of evidence, no one of which is of itself compelling, but which tend to point to a common conclusion.

(1) The chemical analysis given in Table I indicates excess Rb in several samples to the extent of perhaps 5%. Comparison with CsAu, about which we have much more complete information, suggests that this analysis, while quantitatively suspect, is in the right direction.

(2) CsAu samples prepared by a technique similar to that used for RbAu show metallic properties, with those metallic properties fading as excess Cs is removed.

(3) The X-ray studies described in Section III suggest that disorder in the RbAu lattice is likely not to be the cause of the metallic character.

(4) Studies by Phillips¹ with film samples

¹ We commented previously that Phillips was able to raise the resistivity of a film of CsAu to $7100 \mu\Omega\text{cm}$ by condensation of excess Cs in a temperature gradient. He informs us that a similar attempt to extract excess Rb from RbAu films also raised the resistivity, but less dramatically. A typical value of ρ for RbAu films as prepared was measured at room temperature to be $35 \mu\Omega\text{cm}$. Extensive attempts to condense Rb from the film led to values of ρ as high as $400 \mu\Omega\text{cm}$. Phillips informs us that measurements of R_H strongly suggested that remaining excess Rb may not be uniformly distributed through the film. He noted that the film color changed

of RbAu suggest that excess Rb is more difficult to remove from RbAu than is Cs from CsAu.

(5) The crystal structures of RbAu and CsAu differ only in that the Rb–Au distance 3.50 Å (2) is 0.14 Å shorter than the Cs–Au distance in CsAu. This shortening is very close to the difference in covalent or single bond radii of the two atoms, a fact which suggests similar mechanisms of binding in the two materials. This implication, in turn, suggests that pure RbAu is, by analogy with CsAu, a semiconductor.

Using the same chain of inference for RbAu which was applied to CsAu earlier in this section, we can estimate the conduction electron density in the sample for which we have measured the value of T_1 given in Table IV. The results are given below.

Material	T_1 (μsec)	n (cm^{-3})
Rb metal	260 (17)	1.1×10^{22}
RbAu VIII	2300	4.2×10^{20}

One electron per formula unit in RbAu would give an electron concentration of $1.4 \times 10^{22} \text{ cm}^{-3}$. Therefore the derived value of n for RbAu VIII, if excess Rb is the source, would imply 3.0% excess Rb, a number roughly consistent with the chemical determination.

VII. Summary and Conclusions

Our study of the properties of powders of CsAu and RbAu at or near the 1:1 stoichiometry leads us to the following conclusions.

(1) Carefully prepared CsAu powders, golden brown in color, exhibit crystal structure and NMR properties consistent with the conclusion from previous studies that this material is a semiconductor with a large band gap. The NMR properties suggest the exist-

tence of a small concentration of delocalized electrons, a result consistent with the temperature dependence of σ in the films studied by Wootton and Condas.

(2) We have excellent direct evidence that the primary source of conduction electrons in CsAu is excess Cs in the structure. The NMR studies of sample CsAu V as Cs is extracted in a temperature gradient seem quite conclusive on this point. The measurements of lattice parameter as Cs is removed, shown in Fig. 3, suggest rather strongly that the excess Cs is well dispersed in the lattice.

(3) While the NMR results on CsAu I are not inconsistent with the wave function composition of the bottom of the conduction band given in the calculation of Liu and Amar (6), a combination of puzzles about the data and concern about possible residual effects of excess Cs lead us to conclude that our NMR data cannot be used for firm testing of the nature of the wave functions in the conduction band.

(4) Metallic properties of our RbAu powders probably arise from excess Rb incorporated into the crystallites. We suspect that the observations of Norris and Walldén (10) and of SSW were also determined by excess Rb (the SSW films were probably somewhat closer to 1:1 stoichiometry than our samples or those of Norris and Walldén.) Thus, we are not able to resolve the underlying question of whether stoichiometric, ordered RbAu is semiconducting or semi-metallic. Further experiments along the lines of those used with sample CsAu V, but more carefully controlled may finally resolve the question.

In a closing note, we call attention to a rule of thumb given by Goodman (18) for classifying intermetallic compounds into those which are semiconductors and those which are conducting. He comments, "it is usually found that a semiconductor is a material with a maximum in the melting point curve as a function of composition." The Cs–Au phase diagram does show such a melting point

reversibly from a deep blue color in its original state to a golden-brown color at maximum Rb exhaustion, but there was no evidence that the final state of the film corresponded to intrinsic RbAu.

maximum, whereas for Rb–Au, none appears to exist (3, 11). If RbAu is finally shown unambiguously to be a semiconductor, either Goodman's rule of thumb is violated or the phase diagram for RbAu has some small kinks not uncovered in the studies to date.

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