Optical properties of RbAu and CsAu

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The dielectric constant, the refractive index, the reflectivity, and the absorption coefficient are calculated from the electronic energy bands in the photon energy range from 0.01 to 0.40 Ry for CsAu and 0.05 to 0.40 Ry for RbAu. Comparison of the present work with experimental results on the absorption coefficient for CsAu shows reasonable agreement. No other experimental results are available to make immediate comparison with. The results obtained in this work show that CsAu is very much a semiconductor, but RbAu is more like a metallic alloy with similar optical properties as pure gold in the visible region.

I. INTRODUCTION

The series of alloys formed by gold and alkali metals show gradually decreasing conducting properties as the alkali metal in the compound becomes heavier.[1,2] This problem has also been analyzed from the electronic-structure point of view, and it is found[3] that the alloys with constituent alkali metals lighter than and including potassium show metallic behavior and alloys with alkali metals heavier than and, including rubidium, show semiconducting behavior. In other words, although the constituent elements have similar electronic properties, the final compounds are different in their electrical conducting behavior. Further, it is of interest to see, from the calculated energy bands,[3,4] the optical properties of the two alloys in the series, RbAu and CsAu, which show semiconducting behaviors.

From the calculated energy bands, the density of states and the imaginary part of the dielectric constants are determined. By using the Kramers-Kronig relation, we then find the real part of the dielectric constants. The reflectivity and the absorption coefficient are thus determined from these dielectric-constant values. All these constants are evaluated over the photon energy range up to 0.4 Ry (5.44 eV). Very few experimental works on these alloys are known. Comparing the results of the present work with the only available experimental results on the absorption coefficient of CsAu by Spicer *et al.*,[2] they are found to be in reasonable agreement.

II. CALCULATIONS AND RESULTS

As defined in any elementary textbook on solid state physics, the number of states in the band with energy values between E and $E + \delta E$ can be represented by

$$N(E)\delta E = \frac{N\Omega}{8\pi^3}\delta E \int\int \frac{dS_k}{|\nabla_k E|}, \qquad (1)$$

where $N(E)$ is the density of states, and $\Omega = a^3$ for cubic structures with lattice constant a. To exactly determine the density of states actually requires a knowledge of the detailed shape of the $E(\vec{k})$ curve everywhere and performing a surface integration over complicated surfaces. The band structures[3,4] (Fig. 1) on which the present work is based are evaluated only at the center and at three high-symmetry points, with one intermediate point along each symmetry axis. Without the knowledge of the detailed structure of the bands, an alternatively approximate method is used here to figure out the density of states. One can consider the density of states as the points of k vectors represented by $E(\vec{k})$ lying in the Brillouin zone between the constant-energy surfaces E and $E + dE$, i.e., a volume in k space, $\int d^3\vec{k}$, between two constant-energy surfaces. The integration can then be evaluated by an expansion in lattice harmonics along the three principal directions, which is a method originally devised by Houston.[5] From the band profile one counts the k values in each small energy range and along each principal direction and adds the values. The results in the form of histograms are shown in Fig. 2. The imaginary part of the dielectric constant due to the interband or non-Drude effects, $\epsilon_2(\nu)$, is related to the optical density of states $N(E)$ by[6-8]

$$\epsilon_2(\nu) = \frac{A}{\nu^2}\int_{E_F}^{E_F+h\nu} N_c(E)N_v(E - h\nu)dE, \qquad (2)$$

where E_F is the Fermi energy, and A contains the square of the matrix element, which is assumed to be constant, and this assumption has been shown to be a good approximation in most cases.[6,9,10] The optical density of states (ODS) differs from the density of states calculated from the bands mainly in the height of the peaks.[10] The location of the structures usually remains the same. In the present work, the density of states from the bands, instead of the ODS from the photoemission measurements, is used in the evaluation of the imagi-
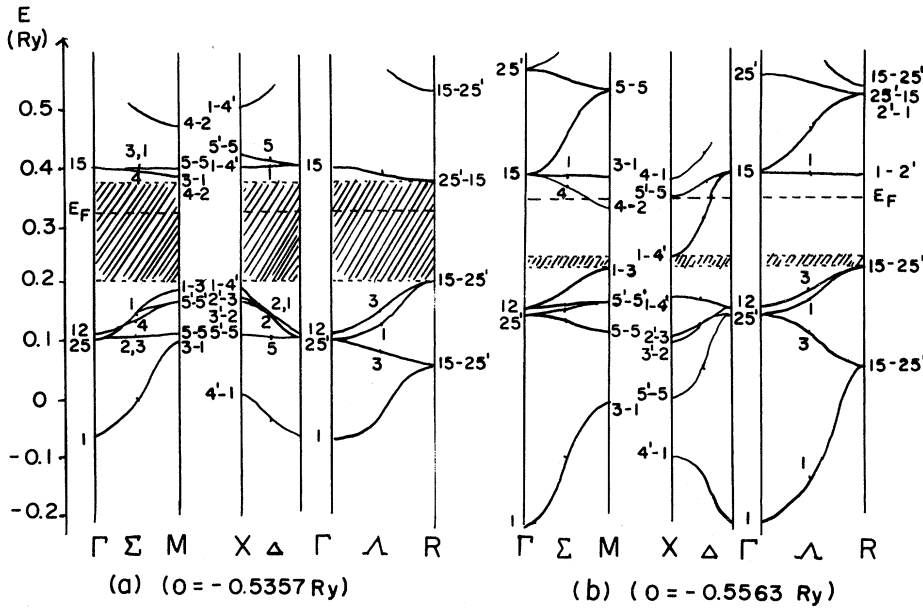
FIG. 1. Energy bands for (a) CsAu, (b) RbAu.

nary part of the dielectric constant. The real parts of the dielectric constants are calculated by a standard Kramers-Kronig transformation,

$$\epsilon_1(\nu) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\nu' \epsilon_2(\nu')}{\nu'^2 - \nu^2} d\nu' . \tag{3}$$

Since $\epsilon_2(\nu')$ is determined only up to 0.4 Ry for both alloys, a continuously decreasing tail function is

assumed to make the extrapolation into the region beyond $h\nu = 0.4$ Ry for both alloys. It looks reasonable from the extrapolation curves to assume $\epsilon_2(\nu)$ to be approximately zero at a photon energy of 8 Ry for RbAu and 10 Ry for CsAu. The principal values are used whenever singularities occur in the integration. The real and imaginary parts of the dielectric constants obtained as mentioned
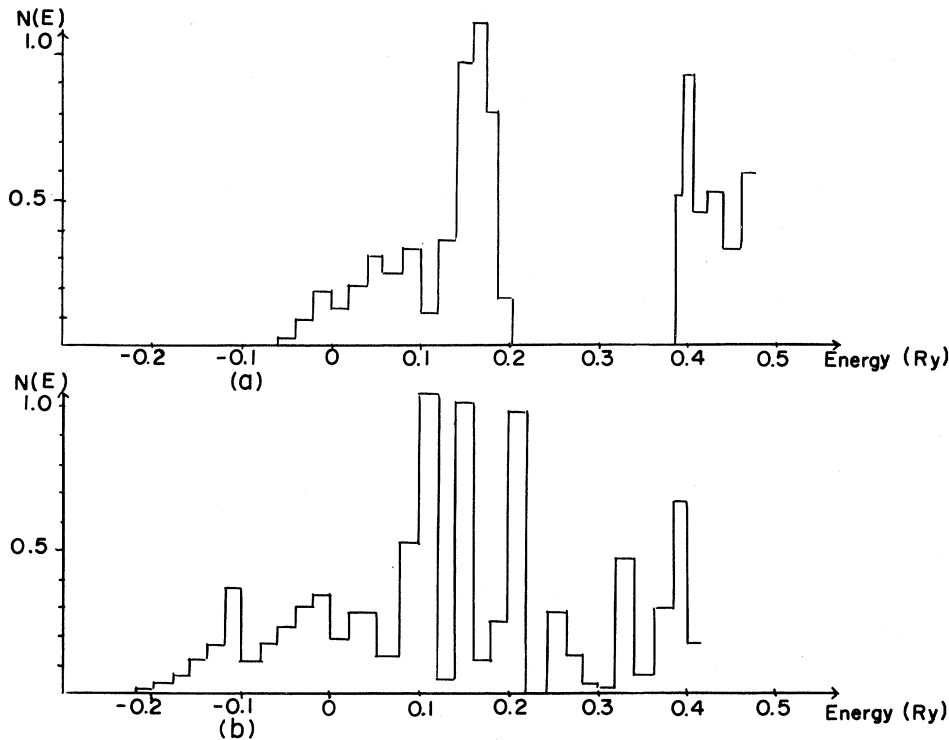

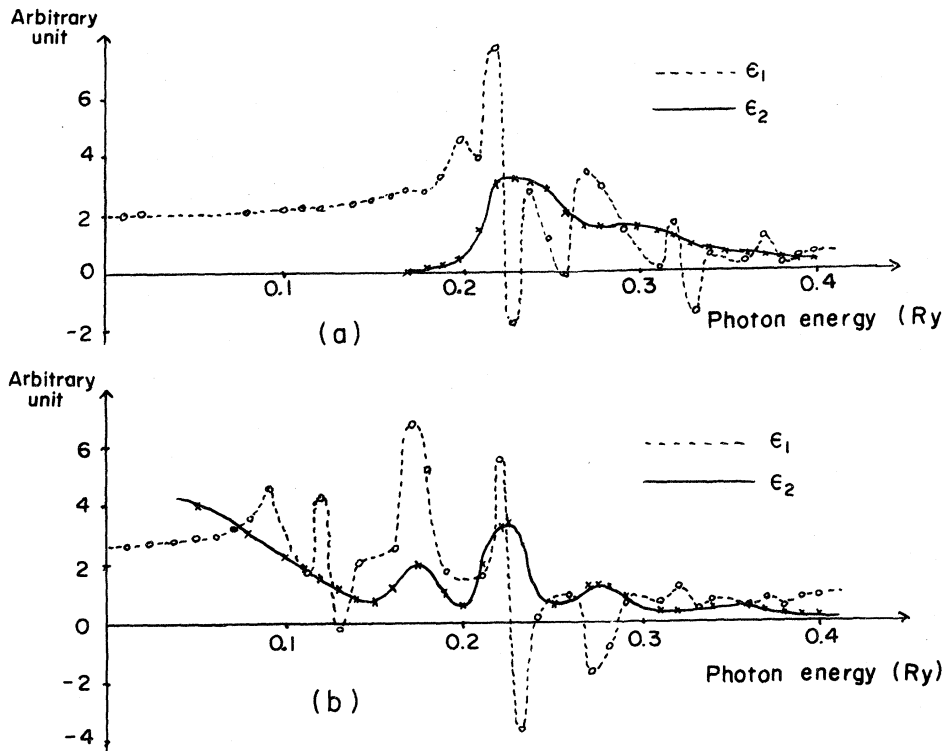FIG. 2. Density of states for (a) CsAu, (b) RbAu.

FIG. 3. Real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric constants for (a) CsAu, (b) RbAu.

above are shown in Fig. 3. The real and imaginary parts of the refractive indices for the two alloys are then obtained as functions of the photon energy by the relations

$$n^2 - k^2 = \epsilon_1, \tag{4a}$$

$$2nk = \epsilon_2, \tag{4b}$$

where n and k are the real and imaginary parts of

the refractive index. The results are plotted as functions of photon energy in Fig. 4. With these values calculated, we are then able to determine the reflectivity and absorption coefficient by the following relationship:

$$R = [(1 - n)^2 + k^2]/[(1 + n)^2 + k^2], \tag{5a}$$
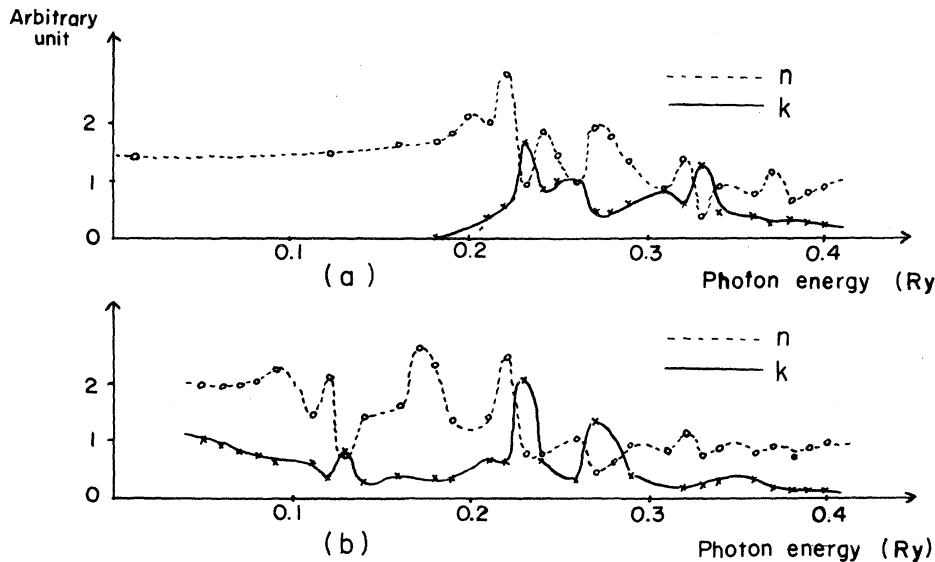
$$\alpha = 4\pi k/\lambda, \tag{5b}$$

FIG. 4. Real (n) and imaginary (k) parts of the refractive indices for (a) CsAu, (b) RbAu.

where R represents the reflectance, α is the absorption coefficient, and λ is the photon wavelength. These results are shown in Fig. 5.

III. DISCUSSION

A. CsAu

CsAu has been more extensively studied[11-15] than RbAu; hence we start by discussing CsAu first. Compared with other calculations, the energy bands used here are in agreement with those in Refs. 14 and 15 about the position and type of the narrowest gap. Some of the energy levels [Fig. 1(a)] are different from those in the author's earlier work[14] because a better method was used to extrapolate the quantum defects in Refs. 3 and 4. However the value of the forbidden gap in Refs. 3 and 4 (2.32 eV) is closer to Reitz and Wood's result[15] (2.3 eV) than the author's earlier value[14] (2.7 eV). From Fig. 3 we see that the $\epsilon_2(\nu)$ curve for CsAu has a threshold value at about 0.17 Ry which is caused by the R_{15}-$R_{25'}$ to $R_{25'}$-R_{15} transition. The peak around 0.23 Ry, the highest peak in the whole range up to 0.4 Ry, should correspond to the transitions from the top of the valence band at M and X to the states near the bottom of the conduction band. This peak in ϵ_2 has its counterpart in the density of states (Fig. 2) at $h\nu = 0.17$ Ry. A shoulder in ϵ_2 around 0.27 to 0.32 Ry seems to correspond to the wide and flat peak in the density-of-states curve, extended from approximately 0.02 to 0.10 Ry, which seems to be caused by transitions from the group of states around 0.1 Ry in the band scale (Γ_{12}, $\Gamma_{25'}$, $X_{5'}$-X_5, M_3-M_1, and M_5-M_5) to the group of states near 0.4 Ry in the band (Γ_{15}, X_1-$X_{4'}$, $X_{5'}$-X_5, M_4-M_2, M_3-M_1, and M_5-M_5). The tail function seems to start at around 0.33 Ry.

The $\epsilon_1(\nu)$ curve has more structures than $\epsilon_2(\nu)$ in the photon-energy range from 0.16 to 0.40 Ry. At low photon energies, $\epsilon_1(\nu)$ varies slowly and allows a possible determination of $\epsilon_1(0)$ which has an approximate value of 2 units in the diagram. From Fig. 4(a), we may be able to determine the static index of refraction by extrapolating the $n(\nu)$ curve to zero photon energy, which gives a value of 1.43.

Most of the structures in the reflectance and absorption-coefficient plots [Fig. 5(a)] are in the ultraviolet region. The visible region extends from approximately 0.12 to 0.23 Ry. In this region, two small minima appear in the reflectivity curve $R(\nu)$ at 0.18 and 0.21 Ry, which correspond

to photon wavelengths 5080 and 4350 Å, respectively. The reflectivity remains essentially constant in the infrared region. The first and second small peaks immediately followed by the small minima mentioned above occur at 0.17 and 0.20 Ry. The former corresponds to the $\epsilon_2(\nu)$ threshold, and the latter seems to be caused by the indirect transitions from $M_{5'}$-$M_{5'}$ and $X_{3'}$-X_2 to $R_{25'}$-R_{15} and M_4-M_2, which is not shown on the smeared-out $\epsilon_2(\nu)$ curve. The first high peak occuring at 0.23 Ry obviously corresponds to the largest peak in ϵ_2 at 0.23 Ry. Briefly speaking, every structure in $R(\nu)$ has its counterpart in $\epsilon_2(\nu)$, while $R(\nu)$ has better resolution for the peaks. For the tallest peak in $R(\nu)$ at 0.33 Ry, it is hard to find its counterpart in the ϵ_2 curve. This is probably due to a mishandling of the principal values of $\epsilon_1(\nu)$ near this position.

The absorption coefficient as a function of the photon energy $\alpha(\nu)$ has its first sharp rise near 0.20 Ry, and what seems to be a peak at around 0.21 Ry [Fig. 5(a)]. The first high peak appears at around 0.23 Ry. The second high and wide peak appears at around 0.25 to 0.26 Ry. A sharp drop and a big valley occur near 0.27 Ry, which corresponds to a wavelength of 3400 Å. The forth peak at 0.31 Ry corresponds to the shoulder in ϵ_2. The fifth peak is questionable, as mentioned before in discussing $R(\nu)$. The only direct experimental work that can be compared is the absorption-coefficient measurement by Spicer et $al.$[2] in the photon
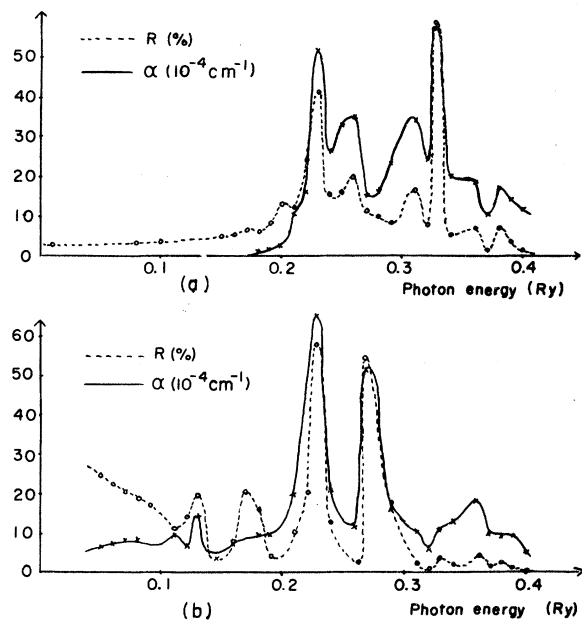

FIG. 5. Reflectivity (R) and absorption coefficients (α) for (a) CsAu, (b) RbAu.

energy range 1.8 to 3.8 eV (0.13 to 0.28 Ry). In their work, three peaks occur at around 2.6, 3.0, and 3.3 eV (0.19, 0.22, and 0.24 Ry), and the heights are approximately 1.2×10^5, 2.4×10^5, and 4.5×10^5 cm^{-1}. In the present work, the first three peaks occurring at 0.21, 0.23, and 0.26 Ry have heights 1.1×10^5, 5.2×10^5, and 3.5×10^5 cm^{-1}, respectively. The position of the peaks in the present work seems to be shifted approximately 0.02 Ry toward the high-energy end. Since the present results have not taken into account the higher bands, nor the spin-orbit splitting, such an agreement with experiment should be considered reasonable. It should be noted that all these optical constants show semiconducting behavior.[16, 17]

B. RbAu

The $\epsilon_2(\nu)$ curve for RbAu in Fig. 3(b) has no threshold. Its first peak appears at 0.175 Ry, which seems to be caused by the transitions from the peak in the density-of-states histogram near 0.2 Ry to just above Fermi level. These transitions are between the tops of the valence-band states just above the Fermi level (R_1-R_2', Γ_{15}, M_3-M_1, and X_4'-X_1). The major peak at 0.225 Ry seems to correspond to the peaks in the density of states around 0.15 Ry, and this should be caused

by transitions from Γ_{12}, $\Gamma_{25'}$ to Γ_{15}, and those from M_5'-M_5' to M_3-M_1 and X_1-X_4' in the valence band to X_4'-X_1 above the Fermi level. The other $\epsilon_2(\nu)$ peaks correspond to the flatter peaks in the density-of-states histogram near the low-energy end. The $\epsilon_1(0)$ value can be determined, by a less reliable extrapolation, to be 2.7 units. From Figs. 5(b) and 3(b), we see again the similarity between the positions of the peaks in the $R(\nu)$ and $\epsilon_2(\nu)$ curves. The peaks in $R(\nu)$ are just more exaggerated. A wide minimum of $R(\nu)$ occurs in the visible region at 0.14 Ry, which corresponds to a wavelength of 6540 Å. This is similar to the situation with pure gold which has a major minimum in its $\epsilon_2(\nu)$ plot at approximately 2.1 eV (0.15 Ry).[8] No direct experimental work on RbAu is available to make immediate comparison. However, it is interesting to see that for RbAu, the behavior of $\epsilon_2(\nu)$ near the low-energy end, as well as the position of the minimum in the $R(\nu)$ plot in the visible region, are more like those for an ordinary metal than for a semiconductor. From the energy-gap point of view,[3] RbAu was believed to be a narrow-gap semiconductor. However Norris et $al.$[13] have found by a photoemission experiment that RbAu has metallic behavior. Probably some further investigations are needed before the final decision about its conducting property can be made.

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