

## Faraday Effect and Fermi Surfaces of the Silver-Gold Alloy System\*

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Measurements of the polar-reflection Faraday effect (PRFE) have been made in the visible and near infrared regions of the spectrum on three solid solutions of gold and silver, of 22.5, 47.0, and 71.5 at. % gold concentration. The PRFE measures bulk properties, is quite sensitive to contact of the Fermi surface with the zone faces, and gives a quantitative estimate of the extent of such contact. Further, since measurements are made at optical frequencies, the PRFE is not subject to the usual limitation of long electron lifetime, and is therefore applicable to nondilute solid solutions. These measurements yield the first direct information on the Fermi-surface geometry in nondilute disordered alloys. Because both silver and gold are monovalent, have the same atomic size, and are miscible in all proportions, the changes in the Fermi surface can be related to changes in the effective lattice potential alone. The results indicate that Fermi surface contact area and shape vary linearly from pure silver to pure gold. This result confirms the assumption that such an alloy can be treated by averaging the potentials of the pure constituents, and indicates that the symmetries of the conduction-band wave functions at the center of the  $\langle 111 \rangle$  zone faces are the same for both gold and silver.

### I. INTRODUCTION

WHEN light which is initially linearly polarized either perpendicular or parallel to the plane of incidence is reflected from a metal with a magnetic field normal to the surface, the reflected light is found to be slightly elliptically polarized, with the major axis of the ellipse rotated slightly from the initial direction of polarization. This effect is known as the polar-reflection Faraday effect (PRFE) in nonferromagnetic metals, and should be distinguished from the magneto-optic Kerr effect which occurs in ferromagnetic metals. Recent work on pure silver and gold<sup>1</sup> has demonstrated that the PRFE is a true measure of bulk properties, is sensitive to contact of the Fermi surface with the zone faces, and yields a quantitative measure of the extent of such contact. Further, since measurements are made at optical frequencies, the usual restriction of long electron lifetime is removed, and investigation of the Fermi surfaces of nondilute alloys is possible.

The present work is the first application of the PRFE to an alloy system. Measurements were made on three gold-silver alloys, of 22.5, 47.0, and 71.5 at. % gold. This system was chosen for several reasons. The Fermi surfaces of pure gold and silver have been extensively studied by many techniques, including the PRFE.<sup>1</sup> The alloy system is particularly simple; silver and gold are both monovalent and have nearly the same atomic radii, they form solid solutions with each other in all proportions, and the lattice constant varies negligibly from silver to gold. Hence, Fermi surface

changes upon alloying should be due exclusively to changes in the effective lattice potential. Further, it has been suggested<sup>2</sup> that the conduction-band wave functions at the point  $L$  (center of the  $\langle 111 \rangle$  zone faces) are of opposite symmetry. If so, for some alloy composition, the band gap at the  $\langle 111 \rangle$  zone face should be zero, eliminating the necks and causing a large increase in the PRFE.

In the next section, the theory of the PRFE is briefly summarized. Section III gives the experimental results, which are interpreted in Sec. IV. Conclusions are summarized in Sec. V.

### II. THEORY

The detailed theory of the PRFE has been discussed elsewhere.<sup>1,3</sup> For convenience, the main results are summarized here.

In the case of cubic symmetry and weak magnetic field, the only new piece of information obtained from PRFE measurements is  $\sigma_1$ , the off-diagonal element of the complex conductivity tensor. Experimentally, the PRFE rotation  $\chi$  and the ellipticity  $Q$  are measured, and for the case of initially  $s$ -polarized light,  $\sigma_1$  is determined by the relation

$$\chi + iQ = 4\pi i \sigma_1 / \{ \omega(\epsilon_0 - 1) [\sin^2\theta / \cos\theta + (\epsilon_0 - \sin^2\theta)^{1/2}] \}, \quad (1)$$

where  $\epsilon_0$  is the optical dielectric constant and  $\theta$  is the angle of incidence. In a region of the spectrum for which there are no interband absorptions and for which  $\omega\tau \gg 1$ ,  $\sigma_1$  can be written

$$\sigma_1 = (e^3 H / 6\pi \hbar^2 c \omega^2) I_{\text{FS}}, \quad (2)$$

where  $I_{\text{FS}}$  is an integral over the Fermi surface which can be written in several forms. The most convenient

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<sup>1</sup> J. C. McGroddy, A. J. McAlister, and E. A. Stern, Phys. Rev. **139**, A1844 (1965).

<sup>2</sup> M. H. Cohen and V. Heine, Advan. Phys. **7**, 28 (1958).

<sup>3</sup> E. A. Stern, J. C. McGroddy, and W. E. Hart, Phys. Rev. **135**, A1306 (1964).

for our purposes is

$$I_{\text{FS}} = \int_{\text{FS}} V^2 \left( \frac{1}{\rho_1} + \frac{1}{\rho_2} \right) dS. \quad (3)$$

The integral is over the Fermi surface;  $V$  is the Fermi velocity at a point on the surface, and  $\rho_1$  and  $\rho_2$  are the principle radii of curvature at that point. Clearly,  $I_{\text{FS}}$  is independent of crystal orientation. Where necking of the Fermi surface occurs, as it does in the noble metals, the curvature of the surface at the base of the necks becomes negative. These regions then make negative contributions to  $I_{\text{FS}}$  and decrease its value. This is the source of the PRFE's sensitivity to contact with the zone faces.

However, velocity changes by, say, a constant scaling factor also cause  $I_{\text{FS}}$  to vary. A quantity sensitive only to Fermi surface geometry is the ratio of  $I_{\text{FS}}$  to the square of the integral  $\int_{\text{FS}} \mathbf{V} \cdot d\mathbf{S}$ , which can be determined from the intraband dielectric constant,<sup>4</sup>

$$R = 6\pi^3 n I_{\text{FS}} / \left[ \int_{\text{FS}} \mathbf{V} \cdot d\mathbf{S} \right]^2, \quad (4)$$

where  $n$  is the conduction-electron density. In spectral regions free of intraband absorptions, well below the plasma frequency, with  $\omega\tau \gg 1$  and near normal incidence,  $\chi$  is a constant independent of  $\omega$ , denoted by  $\chi_i$ , and  $Q$  is zero. In this same region, the ordinary optical dielectric constant in zero magnetic field is real, varies as  $\omega^{-2}$ , and will be denoted by  $\epsilon_i$ . From a knowledge of  $\chi_i$  and  $\epsilon_i$  in this region, it is possible to calculate  $R$  by

$$R = (4\pi n m_0)^{1/2} \chi_i / H, \quad (5)$$

where  $m_0$  is given by

$$\epsilon_i = -4\pi n e^2 / m_0 \omega^2.$$

It is easy to verify that the parameter  $R$  has the value unity for the free electron Fermi sphere, and, as follows from the argument given above, will be less than unity when the Fermi surface contacts the zone faces. Quantitative estimates of the sensitivity of  $R$  to the extent of such contact are reported in Ref. 1. Calculations were based on a model of the noble metal Fermi surface consisting of a spherical belly and eight cylindrical necks touching the  $\langle 111 \rangle$  zone faces and joined to the belly by a surface which is a portion of a toroid and tangent to both the cylinders and the sphere. For this model,  $R$  was calculated as a function of the ratio of the neck radius to the radius of the equivalent free-electron sphere. Some of the results from Ref. 1 are shown in Fig. 1.

In curve A, the length of the cylindrical portion of the neck is zero; that is, the neck consists entirely of the joint section. For curve B, the neck consists entirely of the cylindrical portion, and though the joint radius is

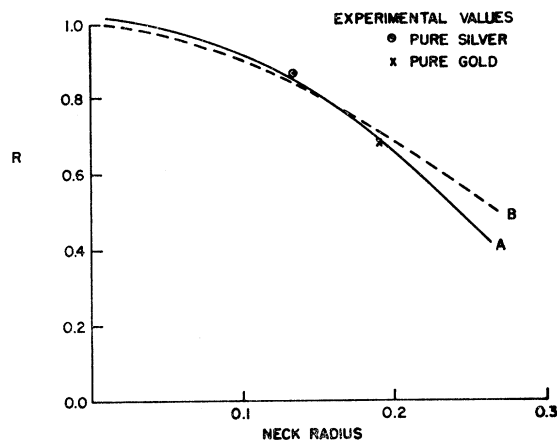


Fig. 1. Theoretical variations of  $R$  as a function of the neck radius in units of the free-electron sphere. Curve A is for the case where the neck consists entirely of the joint section; curve B is for a neck consisting entirely of the cylindrical section. The ratio of the velocity on the cylindrical portion is taken to be proportional to the ratio of the neck radius to the belly radius, and is set equal to one for  $r_n/r_b = 0.3$ . The joint velocity is always taken to be the average of the cylinder and belly velocities. The experimental values for silver and gold are plotted. This information is taken from Ref. 1. Note that the parameters of the model were chosen only to show the trends in  $R$ , and not to fit the gold and silver data.

zero, it still contributes to the integral. The velocities are allowed to vary in the following way: The ratio of the velocity on the cylinder to the belly velocity is assumed proportional to the ratio of the neck and belly radii, and is chosen to equal unity when the neck-to-belly radius ratio is 0.3. The joint velocity is always the average of the cylinder and belly velocities. Note that between these two cases, there is very little difference. Calculating  $R$  using the geometry of the model A and B, but using experimental values of the neck and belly velocities, and the neck radius, excellent agreement is found with the experimental values of  $R$ . No adjustable parameters were used in these calculations. Clearly  $R$  is sensitive to zone face contact and is independent of the fine details of velocity distribution over the Fermi surface for any reasonable distribution. The parameter  $R$  is always a monotonically decreasing function of the radius of the contact area, and is a measure of the extent of such contact. The agreement between theoretical and experimental values of  $R$  for pure Ag and Au gives added proof that the PRFE measures bulk properties. However, note that the velocities used in calculating curves A and B were not chosen to fit the data for pure silver and gold, but only to show the trend of  $R$  with increasing neck radius.

### III. EXPERIMENTAL

The experimental apparatus has been described elsewhere.<sup>1,3</sup> The samples were films vacuum evaporated on polished Pyrex plates, and were prepared from metal powders of stated purity 99.995%. Because of the disparate evaporation rates of silver and gold, the

<sup>4</sup> M. H. Cohen, *Phil. Mag.* 3, 762 (1958).

disordered alloy films were prepared in the following way, first used by Hilsch and co-workers.<sup>5</sup> Powders were mixed in the desired atomic ratios, then spread and packed into an array of small holes drilled into a graphite block. The powder mixture was then fused into small spherical pellets by heating the block with a radio frequency induction heater, the 22.5 and 47.0% gold samples in an argon atmosphere, and the 71.5% gold sample in a vacuum of  $4 \times 10^{-4}$  Torr. Finally, the films were prepared by flash evaporating the pellets one by one, each contributing about 10 Å to the total film thickness of about 2000 Å. Pressures ranged from about  $1 \times 10^{-6}$  Torr immediately before evaporation to about  $1 \times 10^{-5}$  Torr immediately after. Between evaporation and the start of the PRFE measurements, samples were exposed to the atmosphere from 2 to 4 h. In the apparatus, samples were stored at a pressure of about 0.05 Torr. Within experimental error, no change in the PRFE of the samples was observed during the usual period in the apparatus of about three weeks. Detailed studies on pure silver and gold have shown that the PRFE reliably measures bulk properties.<sup>1</sup>

At 10 500 Å, the parameter  $\omega\tau$  was estimated to be in the range of 10 to 20 for the three alloy samples. Two other samples were rejected because of excessively low lifetimes. The composition of the 22.5 and 71.5% gold samples was determined to an accuracy of better than 1% by a fire assay technique.<sup>6</sup> From this, the composition of the 47.0% gold sample was estimated to about 1% accuracy.

As further evidence of the reliability of this alloy film data, the absorption edge frequency for bulk samples,

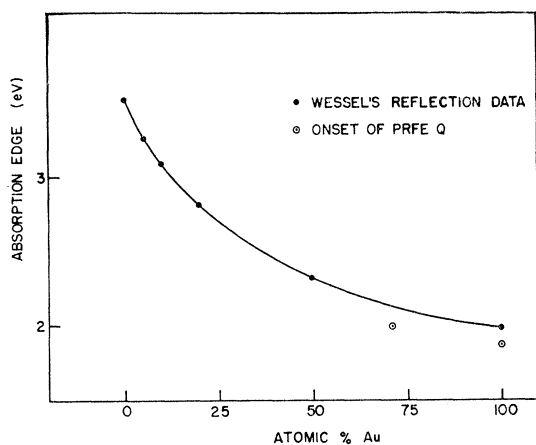


FIG. 2. The interband absorption edge of bulk silver-gold alloys, estimated from the knee of Wessel's reflectivity curves (see Ref. 7) is plotted against alloy concentration. The circled points at 71.5 and 100% gold were estimated from the onset of the polar-reflection Faraday effect (PRFE)  $Q$ . The onset of  $Q$  occurs above 2.4 eV for the alloys of lower gold content.

<sup>5</sup> F. Fischer, Z. Physik **139**, 328 (1954); C. Soodak (private communication).

<sup>6</sup> Kindly performed by Ledoux and Company, Teaneck, New Jersey.

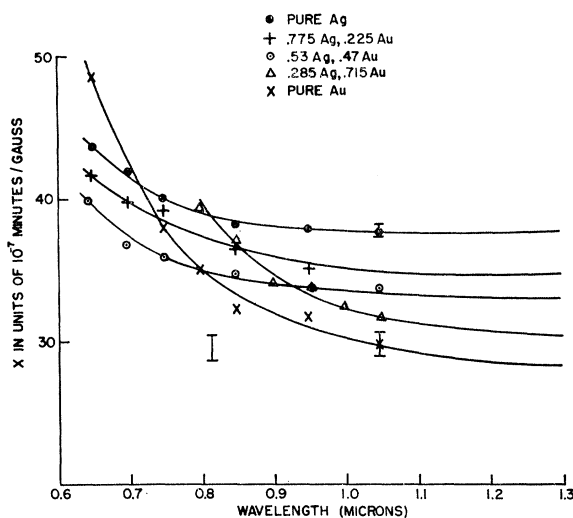


FIG. 3. The measured values of the PRFE rotation  $\chi$  as a function of wavelength. The long-wavelength extrapolation is indicated.

estimated from the knee of Wessel's curves of reflectivity versus frequency,<sup>7</sup> is plotted as a function of alloy composition in Fig. 2. The absorption-edge frequencies of pure and 71.5% gold, estimated from  $Q$  as a function of wavelength, are shown for comparison. The data for the other alloys do not extend to sufficiently short wavelengths to permit a similar determination, but their absorption edges definitely lie above 2.4 eV.

In Fig. 3, the PRFE rotation  $\chi$  is shown as a function of wavelength and the long-wavelength extrapolation to  $\chi_l$  is indicated. The error bars represent one standard deviation. Systematic errors are estimated at less than 2%. Finally, the values of  $\chi_l$  are plotted against alloy composition in Fig. 4. The error bars here are the estimated errors in the extrapolation. Theoretically, it is known that  $\chi_l$  becomes a constant at long wavelengths. With this as a boundary condition, the long-wavelength extrapolation is quite well defined by the data. The values for pure silver and gold are taken from Ref. 1.

#### IV. INTERPRETATION

As mentioned above, it is possible to obtain an estimate of the extent of contact of the Fermi surface with the zone faces from the parameter  $R$  determined by the long-wavelength extrapolation  $\chi_l$  and the optical mass. Ideally then,  $R$  should be determined for the alloys. This requires measurement of  $\chi_l$  and  $m_0$ , as indicated in Eq. (4). To determine  $m_0$ , the dielectric constants of the alloys must be measured. Such measurements were made by the Drude method on the alloys, pure silver, and pure gold. However, these measurements suffered from the usual disease of optical measurements. The values of  $k$  at long wavelengths were reproducible to only about 10% between samples of

<sup>7</sup> P. R. Wessel, Phys. Rev. **132**, 2062 (1963).

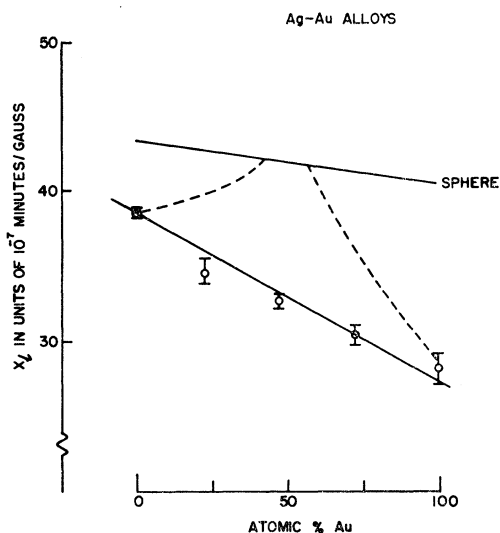


FIG. 4.  $\chi_i$  as a function of at. % gold. The dotted curve indicates the behavior which would be expected if the conduction-band wave functions in the vicinity of the necks were of opposite symmetry in pure silver and gold.

the same alloy composition. For pure silver and gold, much larger variations in the value of  $k$  have been reported in the literature.<sup>8-13</sup> Since the total variation in  $k$  between silver and gold, according to the best estimates, is only of the order of 10%, it is clear that the optical constants are not reliable enough to be of quantitative use. Qualitatively, however, the measurements indicate that  $k$  at long wavelengths decreases monotonically from pure silver to pure gold.

It was felt that any quantitative use of the measured  $k$  values would produce more uncertainty than would result from ignoring them altogether. For that reason,  $\chi_i$  alone, which is more reliably known than  $m_0$ , is used as a measure of the relative variation of  $R$ . As shown in Fig. 4,  $\chi_i$ , and thus the neck radius, varies in a nearly linear fashion as a function of composition. This is again consistent with the variation of the long-wavelength values of  $k$ , and thus with monotonic variation of the optical mass from pure silver to pure gold.

The results illustrated in Fig. 2 can be cited as further evidence that the optical mass varies smoothly from pure silver to pure gold. Theoretically, the effective mass  $m_0$  and the shape of the Fermi surface are expected to depend on how far in energy the top of the  $d$  band is below the Fermi surface. It is generally accepted that the optical absorption edge plotted in Fig. 2 is produced by  $d$  electrons making transitions to just above the

Fermi energy,<sup>11</sup> and thus Fig. 2 describes how the  $d$  band is varying in relation to the Fermi energy. Again this is a monotonic variation.

Thus, all of the evidence is in favor of a smooth variation of  $m_0$  from pure silver to pure gold and thus, from the variation of  $\chi_i$ , a smooth variation of the neck radius of the Fermi surface from pure silver to pure gold. In fact, the data is consistent with a simple linear variation of the shape of all parts of the Fermi surface from pure silver to pure gold.

A possibility that must be disproved is that the films are conglomerates of silver and gold crystallites rather than disordered solid solutions of gold in silver, so that the PRFE measures just the average of the pure gold and silver values. Small crystallite size and negligible variation of the lattice constant with alloy concentration prevent the resolution of this difficulty by ordinary means, but the question is easily settled. If the sample were conglomerates of pure silver and gold crystallites, the curves of  $\chi$  as a function of wavelength would all have the silver and gold cross-over point at 7000 Å in common. Further, the absorption edge frequency determined from the onset of  $Q$  would always be that of gold. Figures 2 and 3 show that neither of these situations occur; the samples are clearly solid solutions.

It should once more be emphasized that, in view of the insensitivity of the PRFE to sample preparation and aging observed in this work and that of Refs. 1 and 3, these measurements can be confidently assumed to be representative of bulk properties.

One conclusion which may be drawn from the monotonic variation of neck radius with alloy concentration is that conduction-band wave functions of silver and gold have the same symmetry in the vicinity of the necks. Cohen and Heine<sup>2</sup> suggested the possibility of opposite symmetries for silver and gold. If true, and if the valence-band wave functions can be calculated from a weighted average of the pure metal potentials, then the band gap at the  $\langle 111 \rangle$  faces must be zero at some alloy concentration determined by the pure metal band gaps. Between the composition at this zero and the pure metals, the gap will be a slowly varying monotonic function of alloy concentration, always smaller than that of the metal in question. The neck radius will behave in a like manner. Hence, upon adding gold to silver,  $\chi_i$  will start to rise, increasing monotonically until the necks disappear and the spherical Fermi-surface limit is reached. As still more gold is added, necks will reappear, and  $\chi_i$  will smoothly drop to the value for pure gold. One would expect from the nearly equal necks that the  $\langle 111 \rangle$  gaps have roughly the same size for silver and gold. Hence a behavior similar to the dotted curve in Fig. 4 should occur, with the peak in the vicinity of 50% gold. No such behavior is observed, and so the symmetries must be the same.

Low-temperature specific-heat measurements on silver-gold alloys for the range 0 to 40 at. % gold indicate

<sup>8</sup> L. G. Schulz, *Advan. Phys.* **6**, 102 (1957).

<sup>9</sup> D. Beaglehole (to be published).

<sup>10</sup> H. Ehrenreich and H. R. Philipp, *Phys. Rev.* **128**, 1622 (1962).

<sup>11</sup> B. R. Cooper, H. Ehrenreich, and H. R. Philipp, *Phys. Rev.* **138**, A494 (1965).

<sup>12</sup> J. N. Hodgson, *Proc. Phys. Soc. (London)* **B68**, 593 (1955).

<sup>13</sup> L. G. Schulz, *J. Opt. Soc. Am.* **44**, 357 (1954).

an initial decrease in the thermal effective mass upon addition of gold to silver.<sup>14</sup> At 30% gold, the decrease amounts to about 3% of the effective mass of pure silver, and preliminary data at 40% gold indicate that the effective mass rises to the pure silver value again. However, as in the case of optical data, this difference is on the order of the spread in values reported by different authors for pure silver.<sup>15</sup>

We have described the silver-gold alloy system as disordered. Some slight short-range order has been observed in the system. For 25 and 50% gold, values of  $\alpha_1$  of  $-0.05$  and  $-0.08$ , respectively, were observed.<sup>16</sup> The values for complete disorder are zero, and for perfect order,  $-0.33$ . This amount of short-range order should not produce the additional gaps that one expects for the ordered alloy, and for our purposes we can neglect this short-range order.

Theoretically, the experimental results found for the silver-gold alloy system can be understood using a simple argument due to Cohen and Heine.<sup>2</sup> The potential in the alloy can be Fourier-analyzed and will be of the form

$$V(\mathbf{r}) = \sum_{\mathbf{K}} [\alpha G(\mathbf{K}) + (1-\alpha)S(\mathbf{K})] e^{i\mathbf{K}\cdot\mathbf{r}} + \int \sigma(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{k},$$

where  $\mathbf{K}$  is a reciprocal lattice vector,  $\alpha$  is the atomic fraction of gold in the alloy, and  $G(\mathbf{K})$  and  $S(\mathbf{K})$  are the  $K$ th expansion coefficients in the pure gold and silver lattice potentials, respectively. The last term on the right-hand side is a scattering term arising from the random distribution of solute and solvent ions at lattice sites, and giving rise to an electron relaxation time  $\tau$ . The observed lifetime of these alloys, about  $10^{-14}$  sec, indicates a smearing of the Fermi energy due to this term on the order of 1%. In any case, experimentally, the optical frequency  $\omega$  is chosen so that  $\omega\tau \gg 1$  and the scattering effects can be neglected. What remains is just the average periodic potential, and the properties of the Fermi surface of the alloy can be calculated from this average periodic potential.

<sup>14</sup> A. A. Valladares and B. A. Green Jr., *Bull. Am. Phys. Soc.* **10**, 127 (1965).

<sup>15</sup> A tabulation of specific-heat data of various authors is given by B. A. Green Jr. and H. V. Culbert, *Phys. Rev.* **137**, A1168 (1965).

<sup>16</sup> N. Norman and B. E. Warren, *J. Appl. Phys.* **22**, 483 (1951).

This concept that the Fermi surface of alloys is determined by the average potential of the constituents makes an implicit assumption that is not satisfied in general, although it is valid for silver-gold alloys. This is that the amplitude of the alloy wave function for electronic states near the Fermi energy is nearly equal on the two constituents. It has been shown<sup>17</sup> that such a case occurs only when the potentials of the two constituents are quite similar. More precisely, when the difference of the average energies of the conduction electrons in the pure metal of each constituent is small compared to the energy width of the conduction band, the alloy wave function has approximately equal amplitude on each constituent and the Fermi surface is given by a simple average potential. When, however, the average energies are quite different, the amplitude of the alloy wave functions on each constituent can be quite different, and one does not expect that the simple average potential will determine the Fermi surface, if it can be defined at all. Reasoning of this sort leads to the conclusion that, since the  $d$  bands of pure silver and gold have quite different widths, the  $d$ -band absorption edge of the alloys should not be calculable from a simple average potential. Hence the nonlinear variation of the optical absorption edge shown in Fig. 2 is not surprising.

## V. SUMMARY

The PRFE  $\chi$  and  $Q$  have been measured for the silver-gold alloy system at 22.5, 47.0, and 71.5 at.% gold. The results for these alloys indicate a well-defined Fermi surface of the noble-metal type, with the neck radius and general shape varying linearly as a function of alloy concentration from pure silver to pure gold. The insensitivity to sample preparation and aging observed in this and earlier work plus the good agreement between theoretical and experimental values of  $R$  for pure silver and gold indicate that these results are representative of bulk properties.

The results indicate that the conduction-band symmetries in the vicinity of the necks are the same for pure silver and gold. Further, the Fermi surface for these alloys can be calculated by averaging the potentials of the constituents.

<sup>17</sup> E. A. Stern, *Physics* (to be published).