cifically, the strength of the *quadratic* dependence on wave vector, which we infer for each metal, is essentially identical in magnitude with those obtained by independent experiments of a completely different nature.

At the same time, the term *quartic* in the wave vector is considerably greater than can be explained by coupling among only nearest-neighboring sites, at least for nickel. This result is in contrast with the Zener-Vonsovsky model of *s-d* exchange between the localized unfilled inner shell electrons and conduction electrons, for Kasuya[36] has shown that this model leads to a negative $T^{5/2}$ term with magnitude considerably smaller than is observed in this experiment. We have also seen that a comparison of our measured quartic dependence with inelastic neutron scattering results leads to inconsistency with the model of Heisenberg coupling with arbitrary range. This is not too surprising in view of the fact that recent calculations[37] of direct exchange yield exchange integrals which are too small and of the wrong sign. On the other hand, it has been shown[38] that the itinerant or collective electron model does exhibit spin waves in the transition metals when electron-electron interactions are included. A quantitative test of this model, such as we have presented for the Heisenberg and *s-d* exchange models, must await further development of the theory. It is hoped that our work will stimulate efforts in this direction.

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Reflectivity of Silver-Gold Alloys in the Spectral Region 1.8–5.0 eV

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Experimental data for the absolute reflectivity of pure silver, pure gold, and Ag-Au alloys containing 5, 10, 20, and 50 at.% gold are presented for the spectral region 1.8–5.0 eV. Measurements were made on electropolished bulk samples and the results are discussed in terms of interband transitions. The effects of polishing and surface contamination on the reflectivity are also discussed. Sample preparation and polishing methods are described.

1. INTRODUCTION

THE optical properties of the noble metals have recently been studied in detail by several investigators.[1–5] In addition, the band structure underlying the optical properties has also been investigated.[2,6–8] From the results contained in Refs. 1–8 it seems reasonable to interpret the least energetic optical absorption in the noble metals as being due to an electron transition from the *d* band to levels near the Fermi surface.

This paper presents experimental data for the optical reflectivity of silver, gold, and silver-gold alloys in the energy range 1.8–5.0 eV. The experimental results are discussed in terms of the band structure and optical transitions. Some attention has been given to the problems of surface preparation and contamination and their effect on the reflectivity.

Section 2 describes the sample preparation, electrolytic polishing, and the apparatus employed in making the reflectivity measurements. Experimental results showing the effect of polishing and surface contamination on the reflectivity are given in Sec. 3. The reflectivity data are presented and discussed briefly in Sec. 4.

2. EXPERIMENTAL PROCEDURES

Slugs of the desired composition were obtained by melting silver and gold together in a fused silica crucible. The crucible was seated on a resistance heated tantalum strip in vacuum at a pressure of less than 10^{-4} Torr. Each slug was flattened on one face by hand lapping on standard metallographic silicon carbide papers. A mirror surface was then obtained by lapping on a metallographic polishing wheel with 6-μ and 1-μ diamond pastes.

The final surface was then produced by using a

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modification of the electrolytic slide polishing technique described by Nagai and Mano[9] and by Reinacher.[10] Very bright mirror surfaces were obtained on all samples except for the 20 and 50% gold alloys which were slightly etched during the electrolytic polishing process.

The apparatus employed in making the reflectivity measurements is shown pictorially in Fig. 1. The detector, an EMI thirteen-stage photomultiplier tube, was mounted rigidly on a brass table which could be rotated in the horizontal plane. The sample holder was mounted in the center of the table and positioned to give an incident angle of 10°. It could be rotated in the vertical plane. With a sample in position behind one of the six identical apertures in the sample holder, all measurements were made using the following sequence: The sample holder is rotated so that the beam from the exit slit of the monochromator passes through an open aperture and impinges on the face of the phototube. The table and sample holder are then both rotated so that the beam strikes the sample and is reflected into the detector. The transmission measurement is then repeated to ensure that conditions had not changed while the measurement was being made. In this manner results were reproducible at a later time to within one percent of the first measured value.

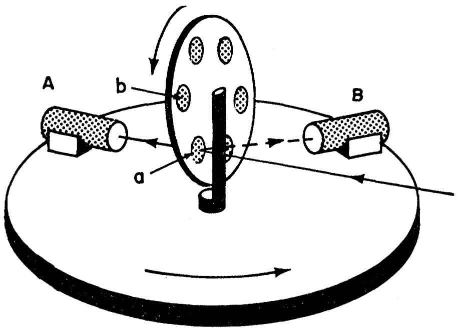

FIG. 1. Pictorial representation of the experimental apparatus. With the sample mounted behind aperature (b) the detector is placed in position (A) to receive the radiation transmitted through the open aperature at (a). The sample holder and detector table are then rotated so that the sample is moved to position (a) and reflects the beam into the detector at (B).

A Perkin-Elmer double-pass monochromator with a quartz prism was used for all measurements. A tungsten filament source was used from 1.8 to 3.4 eV and a hydrogen lamp at higher energies.

3. POLISHING AND SURFACE CONTAMINATION EFFECTS

Prior to measuring the reflectivity, certain measurements were carried out to determine the effect of various amounts of electrolytic polishing on the reflectivity. Other measurements were made to determine what changes occurred in the reflectivity when the sample was exposed to the room atmosphere for a period of several days.

The results of this preliminary work are given graphically in Figs. 2 and 3. Figure 2 shows the reflectivity of a sample which had been electropolished for about 30 sec and the change in the reflectivity when the polishing was carried to completion. Completion is used here to denote that amount of polishing after which additional polishing gives rise to no appreciable change in the reflectivity. This usually required a polishing time of 2 to 2½ min. The most significant changes in the reflectivity occurred in the ultraviolet region and at the "knee" of the curve where the reflectivity begins to drop sharply. In addition, the minimum is slightly sharper after additional polishing and the falloff of the reflectivity is a bit steeper. These effects are probably

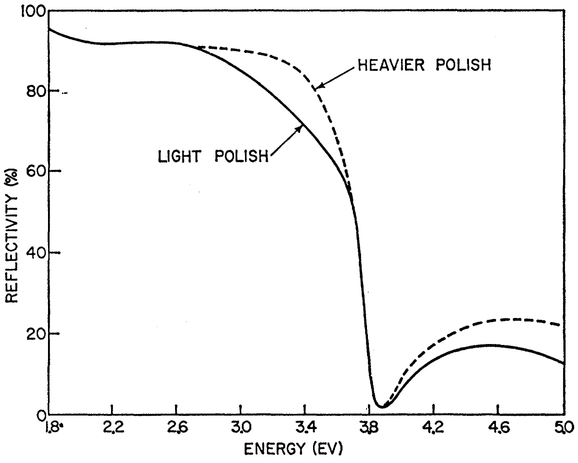

FIG. 2. Change in the reflectivity of silver with increased electrolytic polishing.

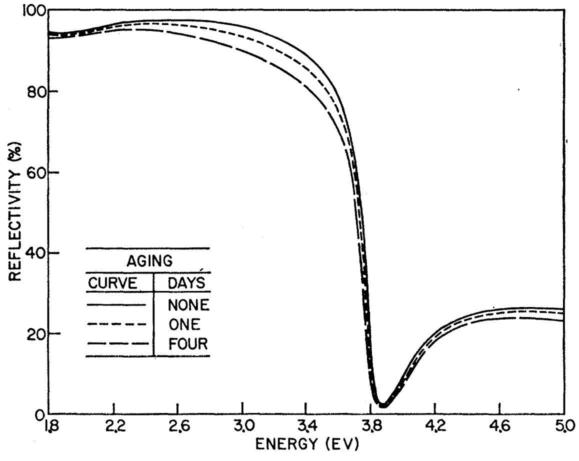

FIG. 3. Effect of aging on the reflectivity of silver.

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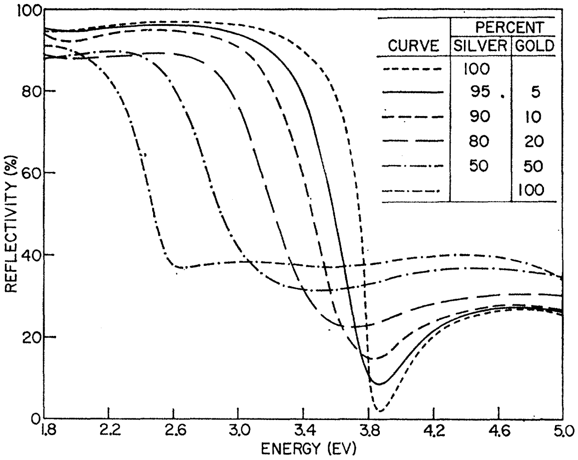

FIG. 4. Reflectivity of silver-gold alloys.

due to the removal of distorted surface material and the polishing has reached completion when all such material has been removed.

Similar results were found for the effect of surface corrosion on the reflectivity. The reflectivity of a sample of pure silver was measured immediately after polishing and then after one day and four days exposure to the room atmosphere. The results are given in Fig. 3 and again the most notable changes are the rounding of the knee and the lowering of the ultraviolet reflectivity. Also important is the fact that the minimum reflectivity drops from 1.5% to 1.1% after one day and to 0.64% after four days in the room atmosphere.

With these results firmly established it was obvious that each sample must be carefully prepared and that the reflectivity must be measured as soon as possible after the polishing was completed. Even under the best of circumstances it is difficult to assess the importance of such effects on the final results.

4. EXPERIMENTAL RESULTS AND DISCUSSION

The reflectivity data for all six samples are given in Fig. 4. As mentioned in Sec. 2, the results were reproducible at a later time to within one percent of the first measured value. The graphical results shown are based on measurements made at each one-tenth of an eV with a closer spacing taken in regions of observed structure. The lower reflectivity of the 20 and 50% gold samples in the low-energy region is due to the difficulty encountered in obtaining a smooth surface from the electrolytic polishing process. The surfaces of these samples were slightly etched in contrast to the mirror surfaces obtained on the other samples.

The reflectivity data for pure silver agree reasonably well with previously published results.[1] However, it should be pointed out that in the present results the knee is sharper, the minimum is narrower and higher, 1.5% compared to 0.7% reported in Ref. 1, and the ultraviolet reflectivity is also higher. As discussed in Sec. 3, these differences are just those which would be expected if the samples used in Ref. 1 suffered from some slight surface contamination.

The reflectivity of pure gold reported here has a sharper drop, more pronounced structure, and is somewhat higher in the ultraviolet region than has been previously reported for measurements on bulk samples. Reflectivities in the low-energy region fall slightly below those calculated from the data of Schulz.[4]

As can be seen from the whole body of the data, there is essentially a monotonic progression from the reflectivity of pure silver to that of pure gold as the gold content of the alloys is increased. The minimum moves upward and to slightly lower energies, and the region in which the reflectivity drops sharply is also shifted to lower energies.

If one assumes that the least energetic optical transition in the noble metals involves transitions from the *d* band to levels near the Fermi surface, then it would appear that the *d* band of gold lies much nearer the Fermi surface than the *d* band of silver, and that one effect of alloying is to shift their relative positions. Such an interpretation is consistent with the experimental results from the alloy samples.

Further information could be obtained from the optical constants. An attempt will be made to derive the optical constants from reflectivity experiments which are in progress at the present time.

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