REFLECTIVITY STUDIES OF DILUTE GOLD-IRON ALLOYS

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Reflectivity measurements on dilute gold-iron alloys by a new method are reported. There is clear evidence that the band gaps change steadily on alloying. In the region 3 to 6 eV additional absorption growing nonlinearly with concentration suggests that the impurities are interacting with each other.

Iron in gold is an example of an alloy in which the impurity carries a local moment. In the Friedel picture[1] the impurity *d* states are split, one spin band filled, lying completely below the Fermi level, the other partially occupied, spanning the Fermi level. At room temperature and in concentrations below 25 at.% the alloy is paramagnetic. We have studied the reflectivity of this alloy at room temperature in concentrations between 0.45 and 4.3 at.%. Previous studies of alloys of noble metals with transition-metal solutes[2,3] have involved impurity concentrations from several percent upwards. The general trend on alloying has been a submerging of the interband absorption structure of the pure metal into the rather featureless transition-metal spectrum. Weak absorption bands growing proportionally with solute concentration have identified some impurity levels. Such small energy shifts of interband structure as do occur have only been noted by Abelès.[2] The new method which we use is sensitive to small impurity concentrations. It has allowed us to study reliably changes in absorption in the low-concentration region, and to watch effects which occur when the impurities interact with each other. We measure changes in the gold absorption edges, and find additional absorption in the region 3 to 6 eV, which grows nonlinearly with concentration. This absorption is due presumably to excitation of electrons from the filled iron *d* states to the Fermi surface. We make some comments on the iron electronic configuration which gives rise to this effect.

The technique has been described by Beaglehole.[4] Light is reflected alternately from a pure gold and an alloy sample, and the quantity $\beta = (R_{\text{pure}} - R_{\text{alloy}})/(R_{\text{pure}} + R_{\text{alloy}})$ recorded continuously as a function of wavelength. The technique is sensitive to just the difference between the samples. In practice uncertainty in the results came not from the accuracy of the measuring equipment, but from the reproducibility in preparation of the samples. Two pure-gold samples prepared as described below would differ by up to 0.002 in reflectivity. Such differences, fortunately, were only slowly wavelength dependent, and faster changes of alloy reflectivity could be measured to 0.0002.

The samples were prepared by simultaneous evaporation of the two constituents onto a quartz substrate, and were around 3000 Å thick. During the evaporation an identical substrate receiving only gold provided the pure comparison sample. Before the samples were removed from the vacuum they were annealed at 600°C for about 20 min. A longer anneal resulted in clouding of the pure-gold sample, indicating that recrystallization had reached the scale of several thousand angstroms. Lower annealing temperatures—we originally used 250°C for 8 h—were insufficient, since the results for these samples changed as days passed, as the samples continued to anneal at room temperature. The higher temperature produced stable samples. The impurity content of the samples was found by dc resistivity measurements, using the values of Domenicali and Christenson[5] for the pure-gold resistivity and its change on alloying with iron. The accuracy in determining the alloy concentration was about 10 %.

In Fig. 1, β is shown for four representative samples, normalized to 1 at.% of impurity; the reflectivity of pure gold is also shown. The close similarity between reflectivity curves of copper and gold identifies the 2.5-eV edge as that for transitions from the top of the gold *d* band to the Fermi surface, and the 3.5 edge as that for conduction-electron excitation to the next excited band. Below and around the reflectivity edge at 2.5 eV the changes in reflectivity on alloying are roughly linear in concentration —although the more dilute samples appear to give slightly larger effects per atomic percent than the others, as occurs with the dc resistivity. At higher energies the changes are clearly nonlinear.

The approximately constant value of β below the edge results from additional Drude-like scat-

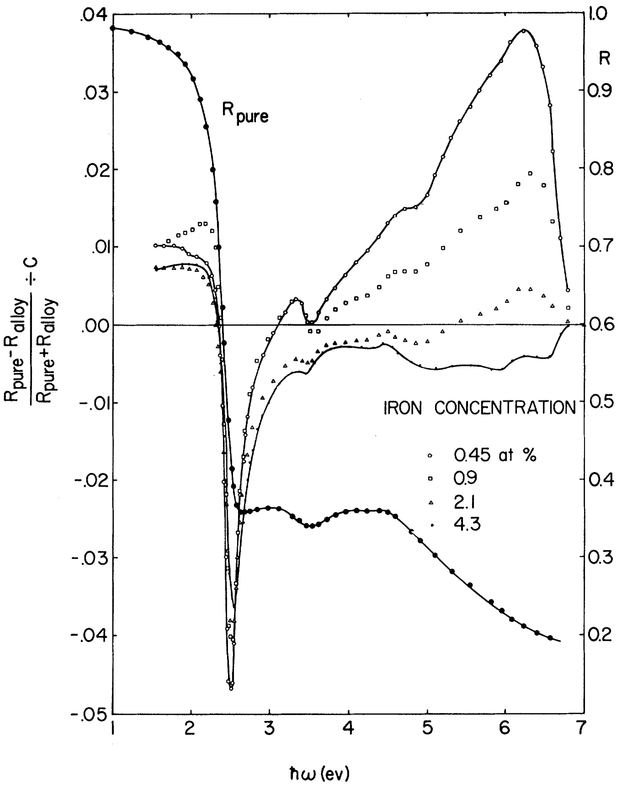

FIG. 1. The reflectivity R for pure gold and $(R_{\text{pure}} - R_{\text{alloy}})/(R_{\text{pure}}+R_{\text{alloy}})$ for gold-iron alloys. Half the points read from the continuous experimental curves are shown.

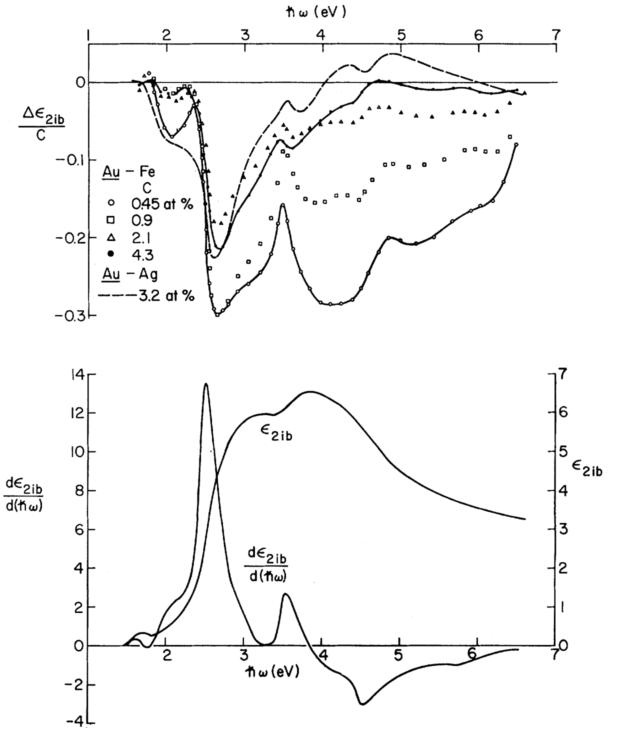

FIG. 2. $\Delta\epsilon_{2\,\text{ib}}$ as evaluated from the experimental reflectivity curves.

tering of the conduction electrons. In this region the Drude model deduces $1-R=2/\omega_p\tau$, $\Delta R=(2/\omega_p)\Delta(1/\tau)$, where $\omega_p^2=4\pi Ne^2/m^*$, N the number of conduction electrons per unit volume, m^* their effective mass, and τ their lifetime. By estimating $\Delta(1/\tau)$ from the dc resistivity, we find that the predicted ΔR per at.% is between 0.0174 and 0.016 with concentrations between $\frac{1}{2}$ and 5 at.%.[6] This compares quite well with the experimental range 0.019 to 0.014. The 0.9-at.% sample shows a rise in β below the edge. This indicates imperfect annealing. Samples annealed at low temperatures gave β values rising by a factor of 2 below the edge.

The behavior of rough linearity below and near the edge, and nonlinearity above, shows up again in the $\Delta\epsilon_2$ values deduced from these curves. ϵ_2 is the imaginary part of the dielectric constant and $\Delta\epsilon_2$ its change on alloying, $\Delta\epsilon_2=\epsilon_{2\,\text{alloy}} - \epsilon_{2\,\text{pure}}$. To obtain ϵ_2 we have used the Kronig-Kramers method. For pure gold the reflectance was extrapolated to low energies with the Bennetts' values[7] (with a correction for nonspecular electron surface scattering) and at high energies with those of Canfield, Hass, and Hunter.[8] For the alloy we have assumed that the constant value of β measured at low energies continues into the infrared, while at high energies we have taken β as zero beyond 7 eV. The experimental values of $\Delta\epsilon_2$ in the infrared were indeed found to follow closely the Drude relation $\Delta\epsilon_{2\,\text{Drude}} \propto \omega^{-3}$ suggested above by the constant value of β.[9] To study the change in the interband region in more detail we have subtracted the experimental $\Delta\epsilon_{2\,\text{Drude}}$ from the experimental values of $\Delta\epsilon_2$, $\Delta\epsilon_{2\,\text{ib}}=\Delta\epsilon_2-\Delta\epsilon_{2\,\text{Drude}}$, providing $\Delta\epsilon_{2\text{ib}}$ the change in the interband part of ϵ_2. In Fig. 2 we have plotted $\Delta\epsilon_{2\,\text{ib}}/c$, showing the change per atomic percent impurity. In this figure we also plot $\epsilon_{2\,\text{ib}}$ for pure gold, its derivative with frequency, and for comparison $\Delta\epsilon_{2\,\text{ib}}$ for a gold-silver sample. (In the region from 1 eV to the interband edge the pure gold ϵ_2 departs from the Drude ω^{-3} variation, being more like ω^{-2}. This has been noticed by others,[2,7] and may be due to a variation of τ with frequency. Subtracting an ω^{-2} variation leaves a small bump in $\epsilon_{2\,\text{ib}}$ at 1.8 eV, which is as little understood as the ω^{-2} variation.)

The experimental curves show a sharp dip at 2.5 eV, whose magnitude is somewhat smaller for the stronger concentrations than for the weaker. The concentration varies by 9.5 while the dip varies by just 7. Some of this difference is probably due to uncertainties in determining the iron concentration. At higher energies the curves for the various concentrations are well separated, by much more than might be assigned to errors in the impurity concentration. $\Delta\epsilon_{2\,\mathrm{ib}}/c$ is near zero for the 4.3-at.% sample at high energies, while systematically more negative for the weaker.

To analyze the data it has been necessary to consider four contributions to $\Delta\epsilon_{2\,\mathrm{ib}}$: (1) Changes which come from shifts of the band gaps to new energies. If $\Delta(\hbar\omega)$ is an energy shift then a $\Delta\epsilon_2 = [d\epsilon_{2\,\mathrm{ib}}/d(\hbar\omega)]\Delta(\hbar\omega)$ will result. (2) Reduction in the magnitude of $\epsilon_{2\,\mathrm{ib}}$. (3) Broadening of the interband edge. (4) Additional absorption due to excitation of the electrons associated with the impurity atoms. The experimentally measured $\Delta\epsilon_{2\,\mathrm{ib}}$ is the sum of these contributions.

That the band gaps are shifting on alloying is seen by the similarity between the experimental curves and $d\epsilon_{2\,\mathrm{ib}}/d(\hbar\omega)$. The latter has sharp peaks at 2.5 and 3.5 eV, and a dip at 4.5 eV. The experimental curves show, superimposed on a background, dips at 2.5 and 4.5 eV, and a peak at 3.5 eV. This indicates that the 2.5-eV edge—it is convenient to characterize an edge by the position of maximum slope—moves to higher energy, the 3.5- and 4.5-eV to lower energies. The similarity of the gold-iron to the gold-silver curve is added confirmation, since it is known that the band gaps of gold shift smoothly on alloying with silver.

If shifts were the only effect present, then $\Delta\epsilon_{2\,\mathrm{ib}}$ would be zero at 3.3 eV, where $d\epsilon_{2\,\mathrm{ib}}/d(\hbar\omega) = 0$. The experimental curves are still quite negative. This indicates another contribution, a reduction in strength of $\epsilon_{2\,\mathrm{ib}}$—which of course is to be expected, since the number of gold states per unit volume decreases as the iron concentration increases. Such a reduction will be, at least in the first approximation, proportional to $\epsilon_{2\,\mathrm{ib}}$ for pure gold. In the analysis of these curves, the size of this component has been chosen to fit the experimental value at the point where the shift changes are zero.

In the higher-energy region, as we pointed out above, the gold-iron curves do not fall near one another—this is so even if we were to assume that the 2.5-eV region was truly linear and scale down the weaker $\Delta\epsilon_{2\,\mathrm{ib}}$ curves. In the 3- to 6-eV region there must thus be an additional absorption growing nonlinearly with concentration. This extra absorption most likely arises from excitation of electrons from impurity *d* states 3 to 6 eV below the Fermi surface. Such absorption from impurity states has been observed in other alloy systems, as we mentioned in the introduction, but at energies below the interband region. The iron *d* states in gold apparently lie further below the Fermi surface than, for instance, the nickel *d* states in gold.[2]

In the region of 2.25 eV the gold-iron curves show an upswing as compared with the gold-silver and $[d\epsilon_{2\,\mathrm{ib}}/d(\hbar\omega)]$ curves. This may perhaps be due to a further additional absorption from impurity states, but would also result from a small broadening of the main absorption edge. Since a broadening is always to be expected from changes in lifetime, the latter seems the more likely explanation.

The experimental curves have been broken down into the various contributions in the fashion outlined here. The various components contributing to $\Delta\epsilon_{2\,\mathrm{ib}}$ are illustrated schematically in Fig. 3. We have found the following values (in eV) for the energy shift per atomic percent of the absorption edges:

Concentration (at.%)	Edge 2.5-eV	3.5-eV
0.45	+0.008	−0.04
0.9	+0.014	−0.03
2.1	+0.010	−0.009
4.3	+0.013	−0.009
Average	+0.011	

The shift in the 3.5 edge is smaller at higher concentrations, the shift in the 2.5-eV edge approximately linear. The extra width due to the broadening is estimated as approximately 0.002 eV/at.%. The shifts at 4.5 are rather obscured by the background and have not been analyzed.

In concentrations below 1 at.%, magnetic susceptibility measurements[10] find a spin $S = \frac{3}{2}$ for the local moment, suggesting the $3d^7 4s^1$ electron-

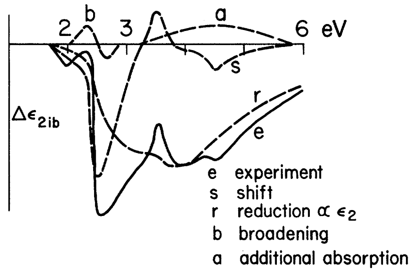

FIG. 3. Contributions to $\Delta\epsilon_{2\,\mathrm{ib}}$.

ic configuration for the iron impurity. In this case there will be no change in the conduction-electron density, although the gold energy levels will be perturbed by polarization effects of the impurity atom. In the paramagnetic region this will occur without spin splitting of the gold levels. From the experiment we see that the interaction is such as to increase the gap between d bands and the Fermi surface, and to reduce the gap between the Fermi surface and the next higher band. The charging theory of Stern[11] is relevant here, and the situation is quite similar to gold-silver alloys as far as the gold states are concerned. In the range 2 to 12 at.% the impurity spin[12] climbs to $S = 2$. Mössbauer measurements in this range by Violet and Borg[13] find that the characteristic iron line shows sidebands developing as the concentration increases. Apparently pairs of iron atoms finding themselves occasionally as nearest neighbors interact with each other. Correlation of their spins produces a higher effective spin number, and modification of the 4s electron density in their vicinity produces an isomer shift. Violet and Borg find a higher s density on the paired nearest-neighbor iron atoms. It is in this same concentration range, in which iron-iron nearest neighbors become probable, that we find the nonlinearity in optical absorption in the 3- to 6-eV region. Since the oscillator strength for the iron d-state excitation will depend upon the excited electron's configuration in the vicinity of the impurity atom, and since this will be more p-like as the s density increases, it is reasonable that the additional absorption for such excitations grows in strength as the pairing occurs more often.

Lattice-constant variations on alloying are too small to explain the energy shifts as being due to a change in the conduction-electron density. 1 at.% of iron changes the lattice constant by only 0.05%.[14]

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