voted to other properties and characteristics.

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Test of the Virtual-Level Model of Dilute Alloys[*]

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Measurements of the optical properties of dilute Ag : Pd alloys are described. The results are fitted to a calculation on the Friedel–Anderson model of the alloy. The agreement is sufficiently good that all of the free parameters of the model can be determined. Using these parameter values, other properties of the alloy are evaluated and compared with measurements, providing a test of the validity of the model. The result is generally favorable, and further work, both experimental and theoretical, can be done to make the test even more quantitative.

I. INTRODUCTION

The electronic structure of dilute transition-metal–noble-metal alloys has for many years been described by the Friedel–Anderson model.[1] This model has been used as a basis both for comparison with experimental results and for further theoretical work.[2]

In spite of the extensive use of the model, it has never been directly tested. That is, no experiment or experiments have been performed at low concentration which overdetermine the free parameters of the model to serve as a self-consistency check. The fundamental reason for this is that the usual quantities measured, such as resistivity, specific heat, and thermoelectric power, are each determined by the electronic properties at only one energy, the Fermi energy. The model, on the other hand, describes the electronic properties over a range of several eV and one would like to probe the electronic properties over an energy range of this size to provide a test of the model.

Optical measurements can do precisely this. Knowing the relation between the optical response of the alloy and the virtual-level parameters, these parameters ought to be deducible from optical data. Armed with values of the parameters, one can then calculate the expected values of various transport coefficients and compare these with measurements.

Caroli, Kjollerstrom, and Wolff have each calculated the optical properties of an alloy using the Friedel–Anderson model.[3] The result for the nonmagnetic case is

$$\frac{\Delta\epsilon_2(\omega)}{C}\,\frac{5}{\omega^2}\left(\frac{\omega_p^2 V^2}{\omega^2}+\omega_d^2\right)\left(\tan^{-1}\frac{E_d+\omega}{\Gamma}+\tan^{-1}\frac{E_d-\omega}{\Gamma}\right), \tag{1}$$

where $\Delta\epsilon_2(\omega)$ is the difference in the imaginary part of the dielectric function between the dilute alloy and the pure metal at frequency ω, C the concentration in at.%, ω_p the plasma frequency of the metal, V^2 the mean-square scattering potential of the conduction electrons from the impurity, ω_d an oscillator strength for interband transitions from the impurity, E_d the impurity-state energy measured from the Fermi energy, and 2Γ the halfwidth of the impurity d state. The shape of $\Delta\epsilon_2$ is essentially determined by the virtual-level shape parameters E_d and Γ, while the amplitude contains two terms, one due to conduction-electron resonant scattering proportional to V^2 and the other due to interband transitions proportional to ω_d^2.

The electronic specific heat of the alloy is increased over that of the pure metal due to the increase in density of states at the Fermi energy. Writing $C_{el}=\gamma T$, the calculated result is[4]

$$\frac{\Delta\gamma}{C}=\frac{10\pi k_B}{3}\,\frac{\Gamma}{E_d^2+\Gamma^2}\,. \tag{2}$$

The thermoelectric power difference between alloy and metal is[4]

$$\Delta Q=-LeT\,\frac{2E_d}{E_d^2+\Gamma^2} \tag{3}$$

and the resistivity difference is[4]

$$\frac{\Delta\rho}{C}=\frac{4\pi}{Ze^2k_F}\sum_l (l+1)\sin^2(\delta_l-\delta_{l+1})\,, \tag{4}$$

where δ_l are the conduction-electron phase shifts evaluated at the Fermi energy, and the coefficient $4\pi/Ze^2k_F$ is, for silver, 4.35 $\mu\Omega$ cm/at.%. Using the above model parameters, only δ_2 is determined,[4]

$$\delta_2=\tan^{-1}\frac{\Gamma}{-E_d}\,. \tag{5}$$

II. EXPERIMENTAL METHODS

Ag : Pd was chosen because of the freedom from interband absorption over a wide energy range (4 eV), the relative inertness of the constituents, and the simplicity of the alloy system. In addition, other similar measurements have been carried out on the Ag : Pd system which demonstrate the existence of a virtual level near 2 eV, which is a good energy range for our optical system. Myers *et al.*[5] have measured $\Delta\epsilon_2$ for relatively concentrated alloys (5% and up) and Kjollerstrom[3] found he could fit the results reasonably well with Eq. (1). Norris and co-workers[6] and Hufner *et al.*[6] have measured the photoemission from Ag : Pd, again for concentrations above 5 at.%, and also saw evidence of a virtual level in the density of states.

We decided to measure $\Delta\epsilon_2(\omega)$ as precisely as possible for sufficiently low concentrations so as to determine the intrinsic values of the model parameters. In order to measure the small difference in ϵ_2 between pure metal and dilute alloy, a sensitive differential technique is needed. Reflectivity or absorption measurements alone, combined with Kramers–Kronig analysis, are not sufficient, since the errors introduced by low- and high-frequency cutoffs influence the over-all amplitude and slope of $\Delta\epsilon_2$, both of which are important. We modified the polarization modulation ellipsometry method of Jasperson and Schnatterly,[7] which has the required sensitivity to make differential ellipsometric measurements comparing pure metal with dilute alloy.

Samples were made by evaporation in a vacuum of 10^{-8} torr or better onto a circular disk substrate. Three evaporations were performed to make a sample: first, about 2000 Å of silver were deposited on the entire substrate, then about 20 Å of Pd were deposited on the disk through a mask which covered every other octant of the substrate, and, finally, 2000 Å of silver were again deposited over the entire disk. This sandwich structure was then annealed to produce a zoned mirror, with alternate octants being pure metal and homogeneous alloy. This sample was then mounted on a rotatable drum and ellipsometry measurements were performed on the sample as it rotated. Two phase-sensitive detectors were used, the first tuned to the frequency of polarization modulation to measure the basic ellipsometric parameters and the second tuned to the frequency of alternation between metal and alloy to measure the difference in ellipsometric parameters between metal and alloy. The results allowed a direct evaluation of $\Delta\epsilon_2(\omega)$.

III. RESULTS

Figure 1 shows some examples of such measurements. Table I shows the results of fitting the measurements with Eq. (1) using a least-squares program. The rms error is about 5% averaged over the spectral range. Note that all the parameters approach constant values at low concentrations; there seems to be no systematic variation with concentration below about 3 at.%. The low concentration values of Γ and E_d agree quite well with photoemission results at 5 at.%.[6]

Using the parameters of Table I, comparisons can be made with specific-heat, thermopower, and resistivity measurements. Equation (2) for $\Delta\gamma$ predicts

$$\Delta\gamma/C = 0.42 \pm 0.025 \text{ mJ/mole Pd } {}^\circ\text{K}^2 .$$

The measured values,[8] which were made for concentrations larger than 2 at.%, average about 0.23 ± 0.2 mJ/mole Pd $^\circ$K^2. Clearly, more accurate specific-heat data are needed for a more precise test.

The thermopower calculated from Eq. (3) is

$$\Delta Q = -(2.3 \pm 0.02) \times 10^{-8} \ (\text{V}/{}^\circ\text{K});$$

measurements give

$$\Delta Q = -1.6 \times 10^{-8} \text{ V}/{}^\circ\text{K}$$

at 1 °K.[9] This is good agreement between theory and experiment for a thermoelectric effect.

The resistivity as given by Eq. (4) depends on all partial wave phase shifts, while only δ_2 is determined by the parameters. Its value is

$$\delta_2 = \tan^{-1} \frac{\Gamma}{-E_d} = 3.02 \pm 0.006 \text{ rad.}$$

The best one can do is assume that only the lowest three phase shifts are important and use the Friedel sum rule

$$Z - 1 = 9 = (2/\pi)(\delta_0 + 3\delta_1 + 5\delta_2)$$

along with Eq. (4) and the measured value[10] of the resistivity (0.44 $\mu\Omega$cm/at.%) to determine δ_0 and δ_1. The result is

$$\delta_0 = -0.46 \text{ rad},$$

$$\delta_1 = -0.18 \text{ rad}.$$

This corresponds by the sum rule to a loss of 0.62 conduction (s and p) electrons near the impurity, leaving 9.62 d electrons. Thus the impurity potential is repulsive for conduction electrons. These numbers are uncertain by about 0.02 electrons.

TABLE I. Values of the four free parameters in Eq. (1) determined from optical measurements. A spin-orbit splitting of the impurity d state of 0.3 eV was used so that $E_{3/2} = E_{5/2} + 0.3$ eV. The uncertainty estimates define a box in parameter space within which the square error is no more than twice that at the parameter values listed.

Concentration (at.%)	V^2 (eV^2)	ω_d^2 (eV^2)	$E_{5/2}$ (eV)	Γ (eV)
0.16	0.66 ± 0.06	5.1 ± 0.9	1.93 ± 0.01	0.24 ± 0.01
0.45	0.59 ± 0.07	2.6 ± 0.3	1.91 ± 0.02	0.25 ± 0.01
0.60	0.66 ± 0.06	4.5 ± 0.6	1.97 ± 0.01	0.26 ± 0.01
2.1	0.61 ± 0.08	2.3 ± 0.8	1.96 ± 0.01	0.23 ± 0.01
3.0	0.65 ± 0.07	3.6 ± 0.8	1.91 ± 0.01	0.23 ± 0.01
7.0	0.41 ± 0.13	7.7 ± 2.4	2.04 ± 0.04	0.48 ± 0.07
12.0	0.28 ± 0.20	10.9 ± 0.6	1.90 ± 0.01	0.40 ± 0.01
14.0	0.19 ± 0.26	12.2 ± 0.8	1.86 ± 0.02	0.49 ± 0.02

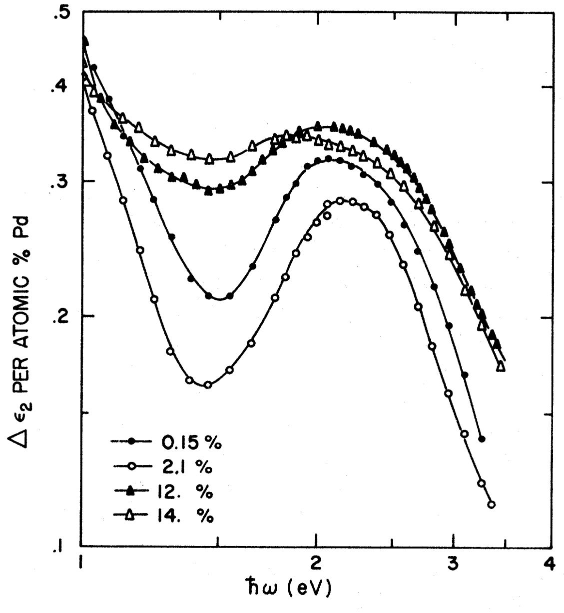

FIG. 1. Measured values of $\Delta\epsilon_2(\omega)$ per at.% Pd for concentrations between 0.15 and 14 at.%.

IV. DISCUSSION

We have shown that the Friedel–Anderson model is consistent with the optical properties of Ag : Pd with a precision of a few percent for concentrations below about 3 at.% Pd. Predictions of other properties using the optically deduced parameters of the model show agreement within the experimental uncertainties of these quantities. There is much room for further progress along two main lines: better specific-heat data, which would allow an improved comparison with this important quantity, and improvement in the calculation of $\Delta\epsilon_2$, i.e., Eq. (1). This equation is based on a free-electron gas model and ignores phase shifts other than δ_2. Without including many-body effects at all, such as the x-ray exciton correction, one could imagine a calculation including δ_0 and δ_1 as well as the deviation of ϵ_1 and ϵ_2 of pure silver from free-electron values. These corrections will probably change the amplitude parameters (V^2 and ω_d^2) more than the shape parameters (E_d and Γ) on which the above comparisons are based. The amplitude-shape connection $\Gamma = \pi D(E_d)V^2$ is not well obeyed by the above parameters. Using the low-concentration value of V^2 and an estimated value of $D(E_d) = 0.23\ \text{eV}^{-1}$, the relation predicts $\Gamma = 0.45$ eV, almost a factor of 2 too large. We expect that including $l=0$ and $l=1$ phase-shift contributions in Eq. (1) probably will reduce V^2, improving the agreement.

Further work is currently under way on magnetic alloys.[11]

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Construction of Wannier Functions and Applications to Energy Bands[*]

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This paper is a contribution to the theory of Wannier functions. The main emphasis is on practical methods for the *ab initio* construction of Wannier functions for simple and composite bands from appropriate variational principles. The cases of a simple *s* band, a hybridized *s-d* band, and the valence and conduction bands of the diamond structure are treated in detail. The calculations of Bloch waves, energy bands, and densities of states from Wannier functions is described. Questions of uniqueness and nonuniqueness and problems due to attachment to other bands are also discussed.

I. INTRODUCTION

Since their first introduction in 1937,[1] the notion of Wannier functions has played a very extensive and important role in the conceptual development of the electron theory of solids. However, while the existence of this convenient set of localized and orthonormal functions has often been invoked in theoretical discussions[2] and while their general properties have been exhibited in considerable detail,[3-10] they have, to the author's knowledge, found no significant use in quantitative calculations. While Wannier functions have lain quantitatively neglected, there has been, in the last fifteen years, a tremendous surge of calculations of their transforms, the Bloch waves, and the associated energy bands.[11] No doubt an important reason for this state of affairs has been the preoccupation, during this period, of solid-state physicists with the physical properties of relatively wide-band, pure solids such as nontransition metals and group-IV elements. These could be best analyzed in terms of extended Bloch waves which are similar, in general character, to free-electron states.

In recent years we have felt in our own work on superconductivity of narrow-band superconductors, on properties of disordered systems and on properties of solid surfaces, a strong need for a framework which highlights the atomic character of the electrons. In a series of papers of which this is the first, it is our aim to develop practical methods for the calculation of Wannier functions for simple and composite bands in perfectly periodic crystals, and of their generalizations for non-