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Virtual-Bound-State—Induced Optical Absorptivity in CuNi Alloys*

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The optical absorptivity of dilute CuNi alloys at 4°K has been measured for photon energies between 0.1 and 3 eV and Ni concentrations between 0.5 and 4 at.%. The data are interpreted in terms of the Anderson model of magnetic impurities. A virtual bound state is found 0.75 ±0.02 eV below the Fermi energy with a half-width of 0.27 ±0.02 eV. The extra absorptivity of the alloy is found to arise predominantly from the scattering of the host conduction electrons in the presence of the virtual bound state.

In describing the electronic properties of metals containing transition element impurities, the concept of a virtual bound state[1] (VBS) has been useful. In the Friedel-Anderson[2] model, the VBS results from the mixing of the d levels of the impurity with the conduction electrons of the host producing a broadened peak in the electronic density of states of the alloy at energy E_d. The interpretation of certain physical properties[3] such as resistivity, specific heat, and thermopower in terms of the VBS theory allow estimates of the VBS energy E_d and half-width Δ. Yet these properties do not provide the best probe of the VBS because they are sensitive to the electronic structure only in the immediate vicinity of the Fermi energy. In principle, optical and photoemission studies can probe an energy range large enough to examine the detailed structure of the VBS, but there has been a notable scarcity of spectroscopic studies of metal alloys. Those experiments which have been performed were generally on high concentration samples (> 10 at.%) which do not really apply to the Friedel-Anderson model because of impurity-impurity interactions; moreover, because of difficulties in interpretation, only qualitative features of the VBS theory have been confirmed. Photoemission measurements,[4,5] however, have shown the appearance of an approximately Lorenzian density of states in the alloy, and recent calculations[6] of the alloy density of states using the coherent-potential approximation seem to be in remarkable agreement with the experimental results.

In this Letter we report an optical experiment on dilute CuNi alloys which can be quantitatively interpreted in terms of the VBS theory and provides an accurate measurement of the VBS parameters. We also show that the infrared absorptivity of CuNi alloys can be interpreted in terms of the Drude response of the free electrons of the host with a frequency-dependent relaxation rate due to the VBS.

The samples were prepared by simultaneous vacuum evaporation of the constituents onto a fused quartz substrate, 0.010 in. thick by 1 in. diam. Half the sample surface was pure Cu and the other half was the CuNi alloy. The deposition rates were typically 100 Å/sec (monitored with a quartz oscillator) and the total thickness was about 3000 Å. During the deposition the pressure was about 2×10^{-6} Torr and during the subsequent annealing (500°C for 15 min) about 5×10^{-7} Torr.

We use a low-temperature (4°K) calorimetric technique described by Hunderi[7] to measure the ratio of the alloy absorptivity to that of the pure metal (A_A/A_P). The quantity of interest in the experiment, however, is the differential absorptivity $\Delta A = A_A - A_P$. We therefore separately measured the absorptivity of our pure Cu films by comparison with gold black samples, finding good agreement with the results of Biondi and Rayne[8] on electropolished bulk samples.

The measured differential absorptivity for samples with nickel concentrations between 0.5 and
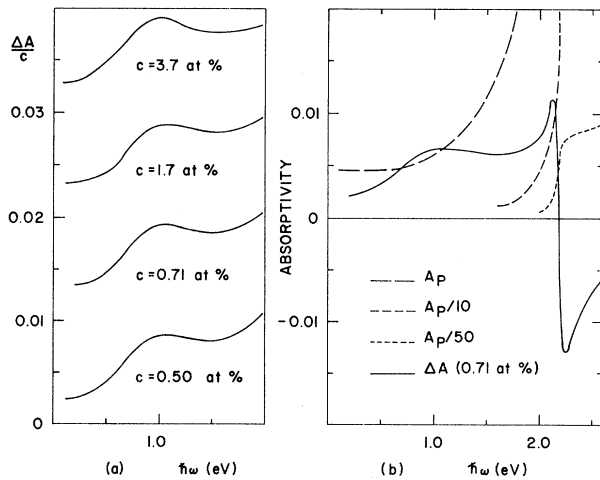
FIG. 1. Differential absorptivity of CuNi versus photon energy. (a) $\Delta A/c$ for four selected concentrations. Each curve is shifted up 0.01 with respect to the next lower alloy concentration. (b) ΔA for the 0.71-at.% sample compared with the absorptivity in a pure Cu sample.

4 at.% are shown in Fig. 1. Also shown for comparison is the absorptivity of pure Cu. The Ni concentrations were determined from resistivity ratios of the samples between room temperature and 4°K using the resistivity data of Linde.[9] Concentrations determined this way are accurate to about 10%. In the spectral region below the copper interband edge, where A_P is small and slowly varying with wavelength, the precision of the optical measurements is typically about 10%. However, above 1.8 eV the results are less accurate and are sensitive to sample preparation.

Usually in optical experiments on metals, one performs a Kramers-Kronig analysis of reflectivity data and obtains the complex dielectric constant $\epsilon = \epsilon_1 + i\epsilon_2$. In the present experiment, however, a far clearer and pleasingly simple interpretation results from a direct analysis of the differential absorptivity data itself. This is because the structure in the absorptivity due to the VBS in the CuNi system falls below the interband edge where the absorptivity in the host is small and nearly constant except for some interband tailing.

Below the edge ϵ_1,[10] which is dominated by the free-electron response, is large and negative and nearly the same for pure copper and the dilute alloy. But ϵ_2, on the other hand, while changing considerably upon alloying, remains very small compared to $|\epsilon_1|$. With these restrictions on the dielectric constant the absorptivity can be

approximated by

$$A \simeq \frac{2\epsilon_2/|\epsilon_1|^{3/2}}{1 - 1/\epsilon_1} + A_s. \tag{1}$$

A_s is the absorptivity component due to scattering of the electrons at the surface,[11] which we expect to be the same for the alloy and pure Cu and thus not to contribute to ΔA. This result is of considerable interest as it shows that $\Delta\epsilon_2$ can be obtained directly from ΔA measurements on dilute alloys once ϵ_1 for the pure metal is known.

We write the change in the dielectric constant upon alloying as $\Delta\epsilon = \epsilon^{sd} + (\epsilon^{bA} - \epsilon^{bP})$, where ϵ^{sd} is the contribution due to the VBS. The second term represents the difference of the alloy and pure interband contributions (ϵ^b) to the dielectric constant. The interband edge in copper which occurs at 2.2 eV results from transitions from the d-derived bands below the Fermi energy E_F to the s-p states above E_F. The tailing of the interband edge out to about 0.6 eV, as seen in Fig. 1(b), makes it necessary to consider the interband contribution to ΔA below the edge. Although the reason for the tailing is not understood at present, it is not appreciably affected by temperature[12] or by dilute alloying[8] ($< 5\%$) with Zn or Ge. Because the Ni impurity d electrons in Cu go into a VBS above the host d bands these host d bands contain fewer electrons than in pure Cu by the factor $1 - c$. From these considerations we expect $|\epsilon_2^{bA} - \epsilon_2^{bP}| \approx c\epsilon_2^{bP}$, and from Eq. (1) the change in absorptivity due to interband transitions for dilute alloying is $|\Delta A^b| \approx cA^{bP}$. This contribution is small below about 1.8 eV so that the change in the absorptivity in this region is determined solely by ϵ_2^{sd}.

The dielectric constant has been calculated for the VBS in the Anderson model by Kjöllerström[13] and by Caroli.[14] Their result for ϵ^{sd} contains two terms: One describes the modification of the free-electron response due to the presence of the VBS, which we refer to as the s response; the second term represents the photoexcitation of the d-like levels, which we call the d response. Each of these terms gives rise to a characteristic line shape for ΔA which depends only on the VBS energy E_d and its half-width Δ. The amplitude of the s-response structure depends on a density-of-states parameter $N(0)$, and the d-response amplitude on a parameter ω_d which is proportional to the d-s dipole matrix element. The two characteristic line shapes are shown in Fig. 2.

In making a quantitative comparison of the VBS theory to our data, we first remark that as seen
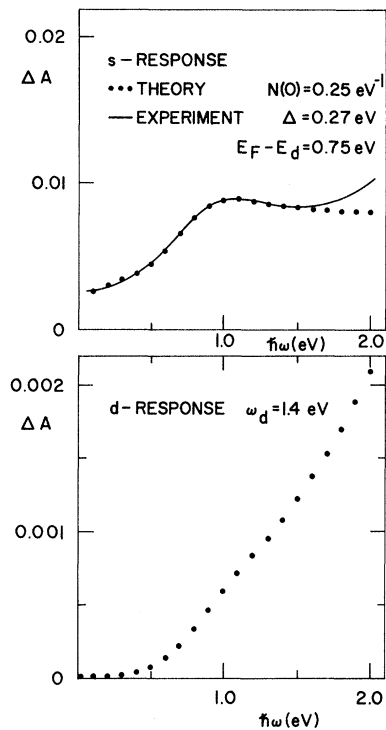
FIG. 2. Calculated s- and d-response differential absorptivity line shapes for a 1-at.% CuNi alloy. The experimental curve is a composite of the curves of Fig. 1(a).

in Fig. 2 the measured ΔA line shape is fitted very well by the theoretical line shape due only to the s-response term in ϵ^{sd}. This comes as no surprise since an estimate[15] of ω_d from the magnitude of ϵ_2 just above the interband edge in pure copper accounts for only about 10% of the ΔA at 1 eV. As a good first approximation in fitting the line shape, therefore, we assume a pure s-response line shape. We also assume that the ten d-like states in the CuNi VBS are degenerate. The assumption of spin degeneracy is justified by the absence of a magnetic moment for Ni in Cu, and an estimate by Yafet[16] indicates that the crystal-field splitting in transition-metal–noble-metal alloys is small compared with the lifetime broadening.

A best fit of the s-response line shape to the data is found for $E_F - E_d = 0.75$ eV and $\Delta = 0.27$ eV. The observed amplitude is then given by choosing $N(0) = 0.25$ eV^{-1}. This value of the electronic density of states is about 20% lower than that deduced from the electronic specific heat. One should not be alarmed by this difference, however, since the optical data involve $N(\epsilon)$ averaged over energies corresponding to the VBS energy,

and furthermore, the electronic specific heat involves the thermal mass of the electron, i.e., the optical mass enhanced by the electron-phonon interaction.[17] The addition of a small amount of d response, compatible with our optical data, does not unduly change the deduced VBS parameters. For $\omega_d = 1.4$ eV, as estimated earlier,[15] the theoretical line shape is nearly flat above about 1 eV, in disagreement with the data, suggesting that we have overestimated ω_d somewhat. Taking this value of ω_d as an upper bound and fitting the optical data below 1 eV we find $E_F - E_d = 0.72$ eV, $\Delta = 0.25$ eV, and $N(0) = 0.27$ eV^{-1}. The d-response line shape for this value of ω_d is the lower curve of Fig. 2.

We conclude from the above discussion that the fit of the theoretical line shape to the data is unambiguous despite the several undetermined parameters contained in the Kjöllerström theory. By fitting the amplitude as well as the line shape and by estimating the parameters $N(0)$ and ω_d from other considerations, we are able to convincingly describe the data in terms of the Anderson model with $E_F - E_d = 0.75 \pm 0.02$ eV and $\Delta = 0.27 \pm 0.02$ eV. Integrating a Lorenzian density of states characterized by these VBS parameters gives 8.9 ± 0.1 electrons in the VBS in satisfactory agreement with the prediction of 9 electrons from the Friedel sum rule (assuming no potential scattering at the impurity site).

The VBS parameters for low-concentration (< 1 at.% Ni) CuNi alloys were deduced by Folies[18] from thermoelectric power data. He found $E_F - E_d = 0.70 \pm 0.05$ eV and $\Delta = 0.25 \pm 0.1$ eV, in essential agreement with our results. Seib and Spicer,[4] on the other hand, have interpreted photoemission measurements on high-concentration CuNi alloys (13 and 23 at.% Ni) in terms of the VBS theory and found $E_F - E_d = 0.95 \pm 0.05$ eV and $\Delta = 0.42 \pm 0.05 + 0.01c$ eV, where c is the concentration in atomic percent. Attempting to explain the rather large discrepancy between these results, we have performed our experiment on a 10-at.% Ni sample. A preliminary analysis of these data shows no shift in the VBS parameters.

Finally we point out a simple interpretation[19] of the absorptivity data in terms of a frequency-dependent relaxation rate $\tau^{-1}(\omega)$ for the conduction electrons in the presence of the VBS. For constant τ, and $\tau^{-1} \ll \omega \ll \omega_p$ (ω_p is the plasma frequency), the free-electron response of a metal leads to an absorptivity $A \simeq 2/\omega_p \tau$. We can relate the inverse lifetimes of the s-like quasiparticles to the VBS density of states $\rho_d(E)$ from

the Anderson treatment[2] of the magnetic impurity problem: $\tau^{-1}(E) = [\Delta/10N(0)]\rho_d(E)$. An effective relaxation rate can be defined as an average over the allowed transitions of the sum of the electron and hole scattering rates,[20]

$$\tau^{-1}(\omega) = \omega^{-1}\int_{-\omega}^{0} dE\, [\tau^{-1}(E) + \tau^{-1}(E+\omega)]. \quad (2)$$

Using a Lorenzian for $\rho_d(E)$, this effective relaxation rate gives rise to essentially the same result for ΔA as that obtained from the Kjöllerström calculation.

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Nonanaliticity of the Magnetization Curve: Application to the Measurement of Anisotropy in Polycrystalline Samples

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We studied the second derivative of the magnetization with respect to the magnetic field, d^2M/dH^2, for polycrystalline materials having uniaxial anisotropy. Evidence is given of a singular point located at $H = H_A$, the anisotropy field. The observed sharp peak is associated with the infinity at $H = H_A$ of the d^2M/dH^2 curve for the single crystal in the hard direction. The detection of singularities is proposed as a new, and sometimes unique, method of measuring magnetic anisotropy using polycrystalline samples.

If we look at the reversible part of the magnetization curve $M(H)$ of a polycrystalline sample, we see that it is somewhat smooth, and we do not expect, in general, any kinds of sharp features. This is true if we limit ourselves to the observation of the magnetization, but we cannot be sure there will be the same behavior for the successive derivatives of M with respect to H, i.e., dM/dH, d^2M/dH^2, etc. By carrying out measurements on a sintered sample of $BaFe_{12}O_{19}$ we indeed observed a sharp peak in d^2M/dH^2 versus magnetic field H, which is very similar to a cusp

located exactly at $H = -H_A = 2(K_1 + 2K_2)/M_s$ (the anisotropy field). This result is in agreement with the curves we have obtained starting from the magnetization curve of a polycrystalline specimen of uniaxial materials computed by Stoner and Wohlfarth,[1] and merely approximating the derivatives with the incremental ratios (Fig. 1). The most interesting features of this phenomenon are its sharpness and the coincidence with the anisotropy field.

A mathematical approach starting from the usual phenomenological treatment of magnetic