

Infrared optical properties of amorphous nickel-phosphorus alloys

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We have measured the room-temperature reflectivity in the spectral range 0.02–2.5 eV of electro-deposited Ni-P amorphous alloys containing 15–26 at. % phosphorus. The data are well fit in the low-frequency region by the Drude model and the optical conductivities determined from the fit are in agreement with the published dc conductivities for these materials. Alloys with greater than 20 at. % P appear Drude-like to frequencies as high as 1.5 eV while those alloys with less than 20 at. % P begin to deviate from free-electron behavior at frequencies around 0.7 eV. Crystalline samples examined for comparison show structure at even lower frequencies. Values of the plasma frequency ω_p and the inverse scattering time $1/\tau$ have been extracted for the amorphous alloys and both are found to decrease with increasing phosphorus content. Such a result is consistent with the gradual filling of the Ni *d* band, causing the density of states to decrease. This would imply that the *d*- and *s*-electron density of states enter additively into a single Drude term—possibly as a result of strong *s-d* scattering.

I. INTRODUCTION

The low-frequency optical properties of metals are generally dominated by free-carrier conductivity. In amorphous metallic alloys, the effects of band structure are reduced, and free-electron theory would seem to be an even better approximation, but these materials have not been extensively studied in the infrared. Hauser *et al.*¹ have made detailed Drude fits to Au-Si amorphous alloys and have found several interesting results: (1) They find that the reflectivity can be adequately fitted to a very high frequency ($\hbar\omega < 4$ eV) by a free-electron Drude form, (2) these fits suggest an ω^2 dependence of the scattering time τ and the plasma frequency ω_p , and (3) they find large (~50%) discrepancies between the low-frequency infrared conductivity and the dc conductivities of their samples. An ω^2 dependence of the scattering rate can result from electron-electron or electron-phonon scattering processes,² while a discrepancy between dc and infrared conductivities suggests the presence of low-frequency absorption mechanisms. Information about these effects would be very useful to differentiate between the present competing theories of dc transport in amorphous metals.³

Ni-P is an especially useful system in which to extend these measurements. Amorphous Ni-P is easily prepared by electro-deposition,⁴ chemical deposition,⁵ vapor deposition,⁶ or melt quenching⁷ in the alloy range from 12–26 at. % P, and has been studied by a variety of means for over 30 years. At concentrations below 17 at. % P, the material is ferromagnetic, while above this concentration it is nonmagnetic.⁸ In addition, the temperature coefficient of the resistivity is found to be negative above 23 at. % P and positive at concentrations below 23 at. % P.⁹ Varying P content thus makes it possible to study magnetic and nonmagnetic samples in which the temperature coefficient of resistance is either positive or negative. Finally, it has been suggested from Knight-shift data that this material is polymorphous in the (15–20)-at. % P

range and can be found in one of two states depending on the preparation method.¹⁰ One of these states, formed by pulse-chemical deposition or sput-quench techniques, is characterized by a large electron density of states which decreases with increasing P content, while in the other state, the characteristic of some dc-deposited samples, the density of states is smaller and essentially constant with P content.

Optical properties of Ni-P alloys have been studied by two groups.^{11,12} A limited phosphorus-concentration range was investigated on flash-evaporated¹¹ and melt-spun¹² samples. Drude-like behavior was observed at low frequencies, but no detailed fits were reported. In order to investigate the contribution of the electron conductivity to the optical properties we have measured the infrared reflectivity of samples of amorphous Ni-P electro-deposited alloys over the readily-glass-forming range of 15–26 at. % P.

II. THEORY OF THE OPTICAL CONDUCTIVITY OF DISORDERED METALS

The theoretical description of the optical conductivity in an amorphous metal is very difficult and a full treatment including multiple-scattering effects has not yet been worked out. It is clear that a nearly-free-electron treatment using the Born single-scattering approximation (Faber-Ziman theory) is highly successful in explaining much of the transport work on amorphous metals.³ This treatment applied to optical properties gives a result which is formally identical to the simple Drude conductivity¹³

$$\sigma(\omega) = \frac{\omega_p^2 \tau / 4\pi}{1 + i\omega\tau}. \quad (1)$$

Here τ is the carrier scattering time and ω_p is the carrier plasma frequency. The same result can be derived from the Boltzmann equation in the relaxation-time approxima-

tion,¹⁴ which gives ω_p in terms of the density of states at the Fermi level $N(E_F)$, the carrier effective mass m^* , and the electronic charge e :

$$\omega_p^2 = \frac{8\pi e^2 N(E_F) E_F}{3m^*}.$$

The scattering probability ($1/\tau$) can be found from Fermi's golden rule to be proportional to $N(E_F)$. As a result the density of states at the Fermi level drops out of the dc conductivity.¹⁵ From optical data, ω_p and $1/\tau$ can be determined independently if the Faber-Ziman approximations hold. The validity of this model will be indicated by a Drude-like frequency dependence of σ , a correspondence between dc and optical conductivities, and scattering rates proportional to the density of states.

When $\omega > 1/\tau$, structure in the density of states may appear in the optical properties, leading to deviations from the Drude form.¹³ Optical studies of Au-Si showed features that were probably due to the density-of-states structure (residual interband transitions) at frequencies above 4 eV.¹ Alloys involving transition metals might be expected to show structure at much lower energies due to the structure of the unfilled d band. Nevertheless, Rivory and Bouchet¹⁶ in their work on Co-P found that their data could be represented by a Drude form below ~ 1.0 eV. This may be because the large scattering rate broadens the sharp d -band structure and obliterates the "interband" contribution for $\omega < 1/\tau$. The onset of interband effects will be indicated by deviations from the free-electron Drude form of Eq. (1).

It has been suggested that quantum corrections to the Boltzmann equation will give rise to terms in the infrared conductivity involving virtual interband transitions.¹⁷ These terms, in contrast to direct interband absorption, are larger for large $1/\tau$, and one of these terms has a non-Drude frequency dependence. It is, however, not easy to calculate the size of these effects compared with the free-electron conductivity, and as yet they have not been experimentally verified.

Summation beyond the Born approximation of a restricted class of scattering diagrams leads to localization phenomena in dc transport theories.¹⁸ The effect of these theories on optical properties is not clear. In Ni-P, which does not undergo a metal-insulator transition in the glass-forming region, the Fermi level is most likely far from the mobility edge and localization effects can probably be neglected.

III. EXPERIMENT

Six samples of Ni-P were prepared by dc electroplating as described by Cargill.¹⁹ Samples of 2×2 cm² were plated on thick copper substrates to a thickness of about 250 μ m. The resulting material was generally flat and smooth (although not optical quality), except at the edges of the wax mask where globules of material had a tendency to form. We found it necessary to plate on thick pieces of copper because thinner substrates would be deformed by the growing Ni-P samples. This suggests that these large optical samples are under some stress as they grow. Samples with phosphorus concentrations close to the limit of

the amorphous phase—about 15 at. % P—were more difficult to prepare in amorphous form. We found, for example, that a second sample grown in a solution from which we had grown a 15-at. % P amorphous sample was invariably crystalline. We did not independently determine the P content of our samples, but we expect only small deviations from the concentrations reported by Cargill.¹⁹ Measurements of the electrical conductivities of the samples are consistent with the behavior of Cote's⁹ samples at the same nominal P-concentration range.

X-ray-diffraction scans were taken after the plating of each sample to check the amorphous state. The crystalline material was characterized by resolution-limited Laue lines and a strong Ni-Ni band at $2\theta = 23^\circ$. All of the other samples show a single broadened band, characteristic of the amorphous state. There is some variation among the sample: Those samples with less than 20 at. % P, which were harder to make in an amorphous form, show a sharply increased peak height of the first diffraction maximum. This may imply that these samples, although still amorphous, are approaching crystalline order.

The samples were cut on their copper-backing plates and then optically polished with alumina grit down to 0.05 μ m. The resulting samples had a bright smooth optical surface marked only by a few cracks that appeared during the deposition process on the thicker samples. It was not difficult to avoid these areas when taking optical measurements.

The samples were studied at room temperature in near-normal-incidence ($\sim 8^\circ$) reflectivity in two spectrometers. A modified Perkin-Elmer model no. 301 spectrometer was used in the near infrared from 0.45 to 2.5 eV. The drive of this instrument was controlled by a stepping motor and repeated runs were made by a computer to average the signal. Thus, the data have a statistically significant standard deviation of around 0.5%. Larger errors were recorded in regions of high atmospheric absorption. In the far infrared (0.02–0.5 eV), a Perkin-Elmer model no. 599B spectrometer was used with standard reflection attachments. Multiple runs were made and appropriate averages were taken by eye. The background in both instruments was a polished aluminum mirror. The data were corrected for the reflectivity of aluminum as derived from the literature.²⁰ Aluminum has a smooth Drude reflectivity below 1.0 eV with some structure at 1.2 eV and above.

IV. RESULTS AND DISCUSSION

The data for four amorphous and one crystalline sample are shown in Fig. 1. The spectra for the amorphous samples are compared to a fit to the nearly-free-electron Drude model which is shown by the solid lines. We note that the data deviate significantly from the Drude model at frequencies above 0.7 eV for the amorphous alloys with P concentrations less than 20 at. %, while the samples with a P concentration greater than 20 at. % appear Drude-like at frequencies as high as 1.5 eV. In contrast, the crystalline sample cannot be fit to a Drude model over any range above 0.2 eV. The behavior is similar to the behavior in Au-Si alloys observed by Hauser *et al.* These

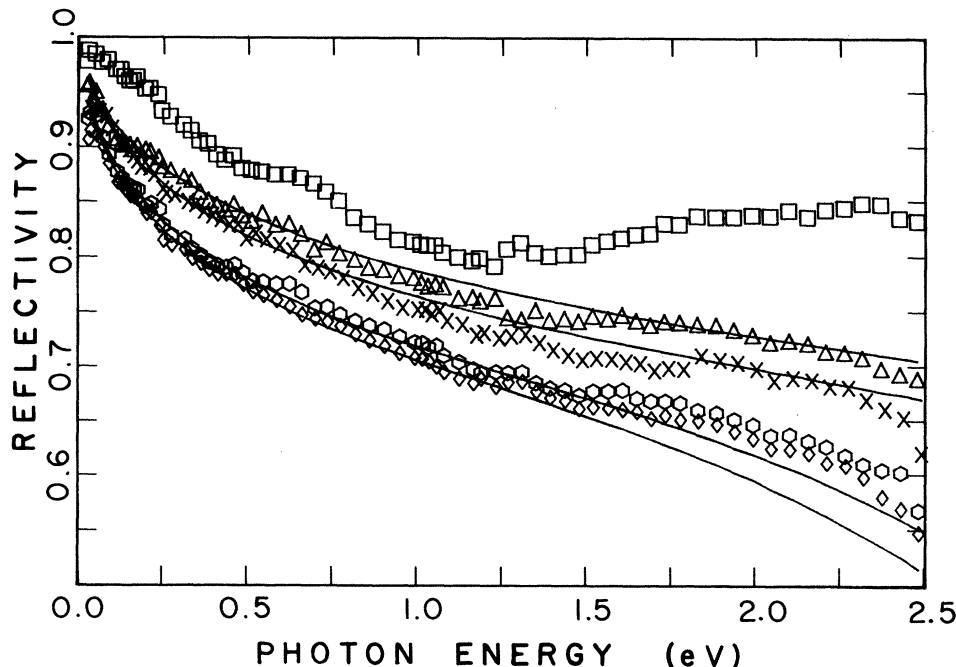


FIG. 1. Reflectivity vs $\hbar\omega$ for crystalline and amorphous $\text{Ni}_{1-x}\text{P}_x$ samples at 300 K. Key: squares represent $x=15.2$ at. % (crystalline), triangles represent $x=15.2$ at. % (amorphous), crosses represent $x=18.6$ at. % (amorphous), hexagons represent $x=21.1$ at. % (amorphous) and diamonds represent $x=26.2$ at. % (amorphous).

authors found the onset of interband features shifted to higher frequencies with the increase in the concentration of Si. The amorphous samples show a large difference between those samples below 20 at. % P and those above 20 at. % P, which corresponds with the changes observed in the x-ray diffraction in alloys of less than 20 at. % P.

We have compared our results with other optical work on Ni-P in the frequency range where the data overlap. The data of Rivory *et al.*¹¹ on flash-evaporated films are presented only after Kramers-Kronig inversion, and they do not characterize the phosphorus concentration of their samples. However, our Drude fits for the dielectric constant are the same for samples with about the same resistivity. Our results are also consistent with the data of Yang *et al.*¹² on melt-spun material. There appears to be no large differences between our results on electrodeposited samples and other work on evaporated and melt-spun material.

The Drude fit was made with a dielectric function of the form

$$\epsilon(\omega) = \epsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega + i/\tau)}, \quad (2)$$

from which the nearly-normal-incidence reflectivity is derived from

$$R = \left| \frac{\sqrt{\epsilon} - 1}{\sqrt{\epsilon} + 1} \right|^2. \quad (3)$$

We assume in this expression that the electrodynamics are local and that our reflection measurements are not influenced by surface structure or oxide layers. These assumptions are generally true in the infrared where the skin

depth greatly exceeds the carrier mean free path or the surface oxide thickness.²¹

Finally, a value needs to be assigned to ϵ_{∞} in Eq. (2), which represents the contribution to the dielectric function from the permittivity of free space (equal to 1) plus the core polarizability of the ions. The ionic core of Ni will be similar to that of copper since they differ by only one place in the Periodic Table. The value of ϵ_{∞} in copper has been determined by infrared measurements by several groups,^{22,23} and is found to be approximately 5.5. We have, therefore, used the value $\epsilon_{\infty} = 5.5$ throughout our fitting process, assuming that this value will be a good approximation for our samples that are about 80 at. % Ni. If a different value for ϵ_{∞} is selected it will slightly change the parameters extracted from our fit, but will not affect the overall conclusions.

With these assumptions, we have made a fit to our measured reflectivity with a theoretical dielectric function as given in Eq. (2). We used a nonlinear least-squares computer fitting program allowing ω_p and τ to be varied to achieve the best fit.²⁴ When it became apparent that no Drude term could account for the reflectivity over the entire frequency range, we restricted our fits to the lower frequencies. We found that below 0.5–1.0 eV, parameters returned from our fit were not very sensitive to the upper limit of the frequencies' fit. The final parameters selected are those derived from fits to all of the data below the frequency at which the spectra deviate significantly from Drude-like reflectivity—as judged by an abrupt increase in χ^2 . Since our low-frequency data did not have well-determined standard deviations, our final χ^2 is based on estimated uncertainties. Within this approximation our results indicate a good fit to the Drude form

in the low-frequency region. Attempts to improve our fit by allowing ω_p and τ to vary with frequency did not result in any appreciable improvement in the fit, and further, indicated no consistent frequency variation of these parameters within the accuracy of our data.

Values for the optical resistivity (equal to $4\pi/\omega_p^2\tau$) extracted from the fits versus P concentration are plotted in Fig. 2. Also plotted on the same figure are the resistivities from the literature.⁹ We find a good agreement between the optical and dc results, especially at higher P concentrations where we were able to make our Drude fit to higher frequencies. We believe that this correlation in the dc and optical resistivities verifies that the optical properties are dominated by the Drude free-carrier contribution. It is also evident that Ni-P shows no systematic discrepancy between the optical and dc conductivities as was observed in Au-Si by Hauser *et al.*¹

Figure 3 shows the fit values for the plasma frequency ω_p and the inverse scattering time $1/\tau$ as a function of P concentration for the five amorphous samples studied. We observe that the carrier plasma frequency and the carrier scattering both decrease with increased P concentration. It is evident that the increased resistivity of the higher-P-concentration samples is not due to an increase in scattering, but rather to the decrease in the plasma frequency. The values of plasma frequency found at low P concentrations seem rather large (≈ 15 eV). For comparison, in Au $\omega_p = 9$ eV, but plasma frequencies over 15 eV have also been observed in Au-Si amorphous alloys.¹

We understand these results because ω_p depends not on the total number of electrons, but rather on their densities of states at the Fermi level. If we assume, as indicated by the magnetization data,⁸ that the *d*-bands are in the process of filling up in this P concentration range, we arrive at a picture of the Fermi level in the upper part of the *d*-band density of states. As electrons from the P atoms are added to the Ni bands, the Fermi level rises and the densi-

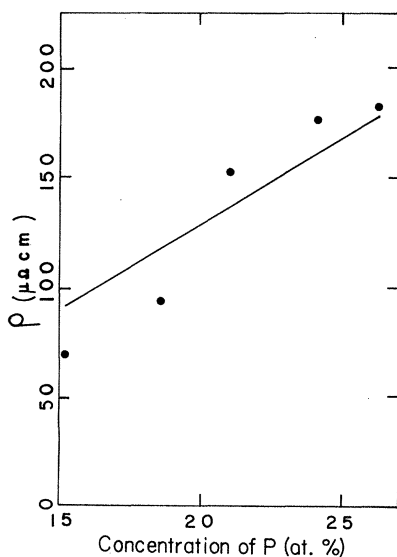


FIG. 2. Optical resistivity (equal to $4\pi/\omega_p^2\tau$) vs phosphorus concentration for amorphous Ni-P samples. Solid line is the dc resistivity from the literature.

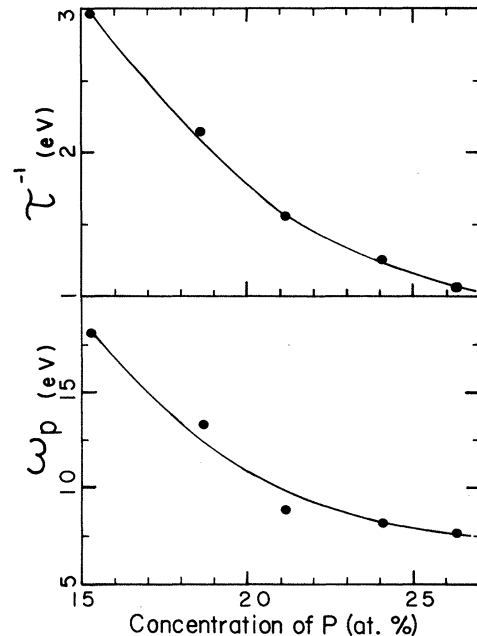


FIG. 3. Plasma frequency and inverse scattering time vs phosphorus concentration determined for amorphous Ni-P from Drude fits to the reflectivity data.

ty of states at the Fermi level (and hence ω_p) decreases.

This picture simultaneously provides an explanation for the decrease in carrier scattering. The effect of the addition of P is to decrease the density of final states at the Fermi level, thereby reducing the scattering. This effect is illustrated in Fig. 4 which plots $1/\tau$ versus ω_p^2 from our fitted parameters. Since ω_p^2 is proportional to the density of states, the near linearity of this plot is evidence that the scattering can be understood from the nearly-free-electron picture.

A decrease in the electronic density of states at the Fermi level with increasing P content is consistent with previous Knight-shift,¹⁰ specific-heat,²⁵ and thermopower mea-

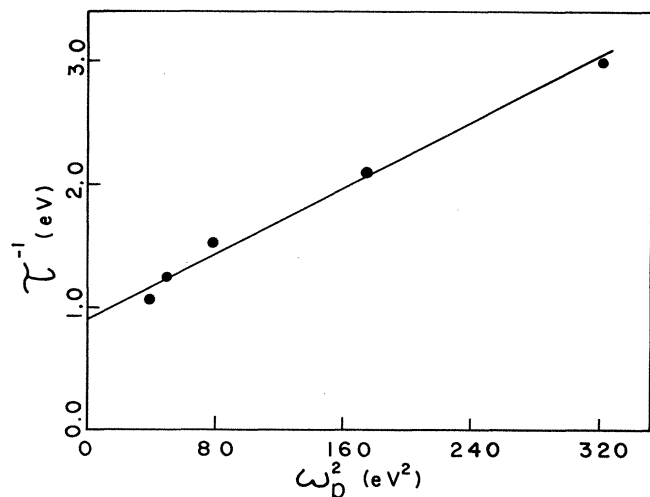


FIG. 4. Inverse scattering time vs the square of the plasma frequency for amorphous Ni-P alloys. Solid line is the least-squares fit to the data.

surements.²⁶ Lashmore *et al.*¹⁰ found, in their Knight-shift experiments, that the density of states decreased only for splat-quenched or pulse-deposited samples. Our dc-electrodeposited samples appear similar to those of Bakonyi *et al.*²⁷ rather than to those of Lashmore *et al.* Annealing studies, which have been shown to change from one state of amorphous Ni-P to the other, would be interesting to resolve this question.

The qualitative features of our results can be explained from a simple Ni rigid-band model where electrons from P act to fill up the Ni *d* band. It must be assumed that each P atom contributes not five but three electrons to the Ni bands. This is what might be expected from the valence of Ni₃P, the predominant compound in this part of the phase diagram, and what will also give excellent agreement with the disappearance of ferromagnetism at 17 at. % P—three electrons per P atom would just fill the 0.6-at. % Ni *d*-shell hole at 16.7 at. % P.

There is, however, good evidence that the *d* shell is not completely filled at 17 at. % P. The density of states indicated from our results for the plasma frequency, and from the specific-heat and Knight-shift measurements as well, continues to decrease to close to 25 at. % P. In addition, soft-x-ray-absorption measurements indicate the presence of *d* holes in alloys above 17 at. % P.²⁸ An alternative explanation would involve the broadening of the *d* levels, resulting in a lowering of the density of states, while the number of *d* holes is conserved.²⁹ The actual electronic structure of amorphous NiP, while undoubtedly very complex, may feature some combination of the simple rigid-band model with a P valence of 3 and a high-energy *d*-band tail with holes remaining up to a concentration of about 25 at. % P.

This interpretation in terms of the total density of states at the Fermi level describes the general features of our results well. The use of a total density of states in the Drude form [Eq. (1)], however, is difficult to justify rigorously. If *s* and *d* electrons both contribute to the conductivity, then they should enter in two separate terms. From analogy to crystalline materials, the *s*-electron term will dominate due to its smaller effective mass. A similar problem occurs in the Knight-shift experiments, which also suggest a density of states which decreases with P content, that is, *s* electrons are expected

to dominate the Knight shift since they have a larger density at the nuclear site.

The optical conductivity could be described by a single Drude term using the total density of states if all carriers in the material had similar effective masses. It is not unreasonable that such a result might occur in an amorphous material with strong scattering of the *s*-like states and a delocalization of the *d* electrons due to exchange scattering with conduction electrons. This picture would suggest, to a greater extent than previously recognized, that the distinction between *s* and *d* electrons breaks down in an amorphous metal. The contribution of the high *d*-electron density of states to the plasma frequency may explain the large values for the plasma frequency found in our low-P-concentration samples.

V. CONCLUSIONS

The low-frequency optical properties of amorphous Ni-P alloys are fitted well by a model with a single Drude term. Alloys with less than 20 at. % P begin to deviate from Drude behavior at about 0.7 eV, while those alloys with higher P concentrations appear to be free-electron-like up to 1.5 eV. Fits of the spectra to a Drude model correctly predict the dc conductivities, and indicate that both the plasma frequency and the inverse scattering time decrease with increasing P content. Both these results are consistent with a gradual filling of the Ni *d* band by electrons from P, thereby decreasing the total density of states at the Fermi level. It is, however, not possible to justify adding *d*- and *s*-electron densities of states into one Drude conductivity unless the carriers have similar masses. We suggest that the *s* and *d* states may be strongly mixed by the scattering, and that the distinction in the optical conductivity between *s* and *d* electrons may be obscured.

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