

Optical properties of amorphous metallic gold-silicon alloys

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(Received 11 September 1978; revised manuscript received 12 February 1979)

The optical properties of amorphous films of Au_{1-x}Si_x alloys were studied in the spectral region from 0.01–6.2 eV as a function of composition in the range 0.13 ≤ x ≤ 0.50. The reflectivity, dielectric function, and energy-loss spectra are presented. As discussed in a previous paper, the extremely short electron relaxation times give rise to some unusual features in ε(ω). The onset of interband transitions shifts to higher energy as the silicon concentration is increased. The measured shifts are in surprisingly good agreement with those predicted by a simple rigid-band approximation.

The dielectric function ε = ε₁ + iε₂ of amorphous metallic thin films Au_{1-x}Si_x with x in the range 0.13–0.50 was determined by optical measurements in the range 0.01–6.2 eV. Its properties are of interest because the lifetimes of excited states are extremely short, considerably shorter than in crystalline alloys, and the relaxation times expressed in energy units are in some cases larger than the gap energies. A discussion of our experimental data based on an intuitive approach was recently published.¹ This paper was oriented towards obtaining information about the electron states in these amorphous alloys from the optical data. In the present paper we give additional information on the experimental method and discuss in more detail ε(ω) and related functions, as an example of a typical case of extremely short lifetimes.

We refer to Ref. 1 for a discussion of the reasons for why we chose the gold-silicon system, and for information about the preparation of the samples. The starting point for the determination of the dielectric function was the measurement of the reflectivity at near normal incidence (Fig. 1). From these curves we calculated the phase from the Kramers-Kronig relation

$$\theta(\omega_0) = -\frac{1}{2\pi} \int_0^\infty \frac{d \ln R(\omega)}{d\omega} \ln \left| \frac{\omega + \omega_0}{\omega - \omega_0} \right| d\omega. \quad (1)$$

From 6.2 eV to infinity we extrapolated the data with $R(\hbar\omega) = (6.2) (6.2/\hbar\omega)^p$, where p was chosen to make dR/dω continuous at 6.2 eV. For frequencies below 5 eV the calculated phase was insensitive to the value of p.

The greatest problem in the computations was the singularity occurring in dR/dω at ω = 0. We obtained good results only after we removed this

singularity by subtracting a term,

$$R'(\omega) = \exp[-2\omega/\pi\sigma_0]^{1/2}, \quad (2)$$

from the reflectivity. We compensated for this by

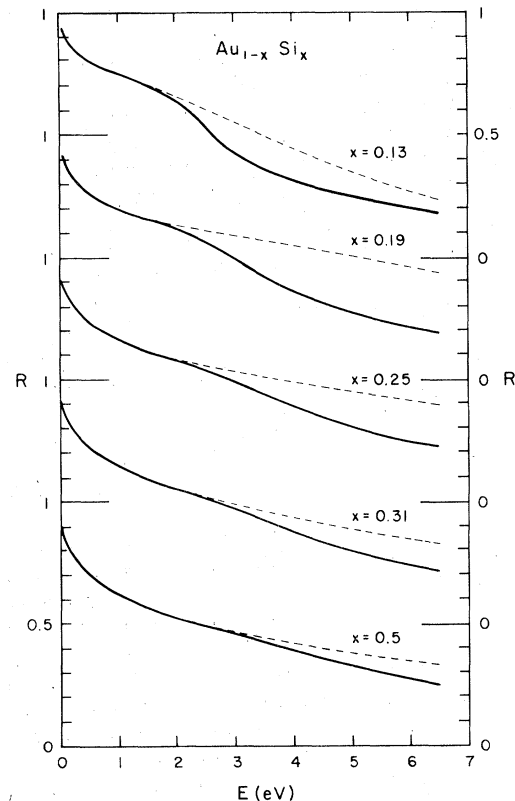


FIG. 1. Measured reflectivity (full line) and reflectivity calculated from the Drude formula (dashed line) of amorphous Au_{1-x}Si_x alloys as a function of energy and composition. Note the shifts of the zerolines of the reflectivity for different compositions.

adding a term, $\theta'(\omega_0)$, to the calculated phase,

$$\theta'(\omega_0) = (8\pi^3\sigma_0)^{-1/2} \int_0^\infty \omega^{-1/2} \ln[(\omega + \omega_0)/|\omega - \omega_0|] d\omega$$

$$= (\omega_0/2\pi\sigma_0)^{-1/2}, \quad (3)$$

where σ_0 was determined from the reflectivity data measured in the far-infrared region where Eq. (2) holds.

From R and θ we determined $\epsilon = \epsilon_1 + i\epsilon_2 = (n + ik)^2$ using the relation

$$\sqrt{R} \exp(i\theta) = (n - 1 + ik)/(n + 1 + ik).$$

$\epsilon_1(\omega)$ and $\epsilon_2(\omega)/\lambda$ obtained in this way are shown in Figs. 2 and 3. We found that they can be described as a superposition of intraband and interband transitions,

$$\epsilon = \epsilon^D + \epsilon^i - 1, \quad (4)$$

where the first term can be represented by the Drude formula

$$\epsilon^D = \epsilon_0 - \omega_p^2/\omega(\omega + i/\tau), \quad (5)$$

where $\omega_p^2 = 4\pi n e^2/m^* = 4\pi n_{\text{eff}} e^2/m$, n is electron

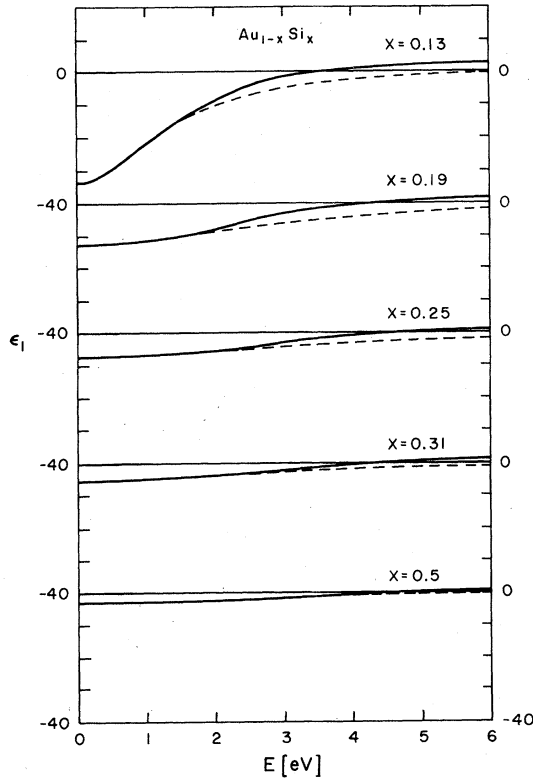


FIG. 2. Real part of the dielectric constant ϵ_1 calculated from Kramers-Kronig analysis (full line) and from the Drude formula (dashed line) of amorphous $\text{Au}_{1-x}\text{Si}_x$ alloys as a function of energy and composition.

concentration, m^* is the electron effective mass, τ is the relaxation time, and ϵ_0 is the core polarizability. We can calculate the two parameters that characterize the intraband transitions from

$$1/\tau = \omega\epsilon_2/(\epsilon_0 - \epsilon_1), \quad (6)$$

$$\omega_p^2 = \omega\tau(\omega^2 + \tau^{-2})\epsilon_2 = (\epsilon_0 - \epsilon_1)(\omega^2 + \tau^{-2}). \quad (7)$$

The best agreement with the data was obtained with a weakly frequency dependent τ and ω_p^2 :

$$1/\tau = 1/\tau_0 + a(\hbar\omega)^2, \quad (8)$$

$$\omega_p^2 = \omega_{p0}^2 + b(\hbar\omega)^2. \quad (9)$$

The frequency dependence of ω_p^2 is a consequence of the frequency dependence of τ and the dispersion relation for ϵ_1 and ϵ_2 .^{2,3} In Fig. 4 the frequency dependence of τ and ω_p^2 is shown for $x=0.13$ and 0.25 . The values of $1/\tau$ and ω_p^2 at very low energy are subject to large errors because n and k are very sensitive in this region to small errors in R and θ . The extrapolated straight lines drawn in Fig. 4 give excellent agreement with the measured

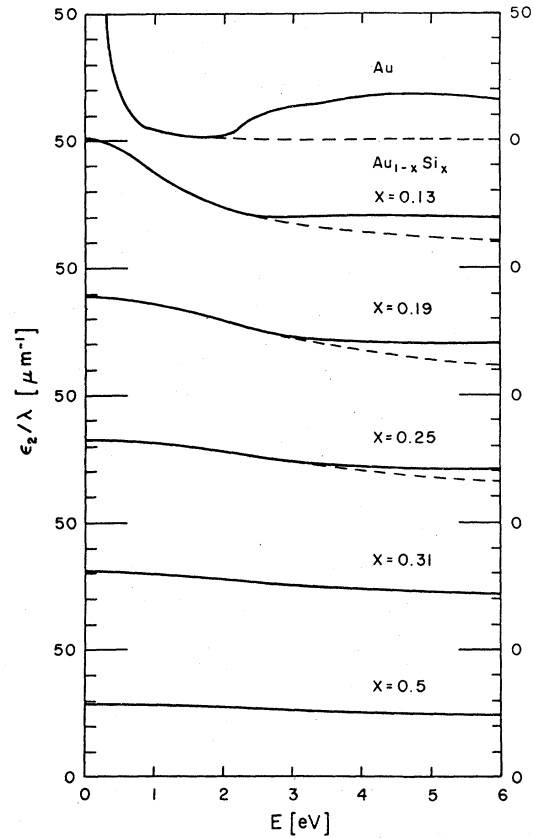


FIG. 3. Optical absorption ϵ_2/λ calculated from Kramers-Kronig analysis (full line) and from the Drude formula (dashed line) of Au (after Thèye, Ref. 8) and amorphous $\text{Au}_{1-x}\text{Si}_x$ alloys as a function of energy and composition.

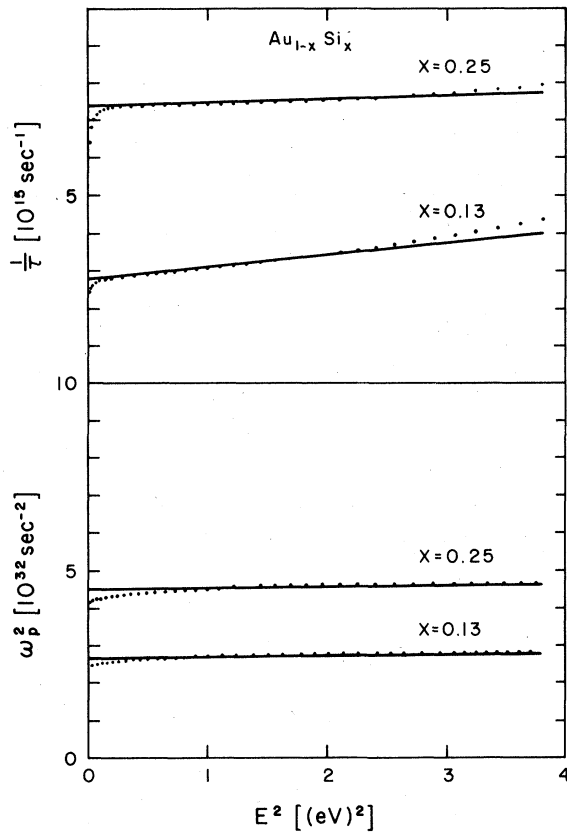


FIG. 4. Frequency dependence of the relaxation time τ and ω_p^2 in $\text{Au}_{1-x}\text{Si}_x$ films for $x=0.13$ and 0.25 .

reflectivity data although there is considerable deviation from the line for the values of $1/\tau$ and ω_p^2 themselves.

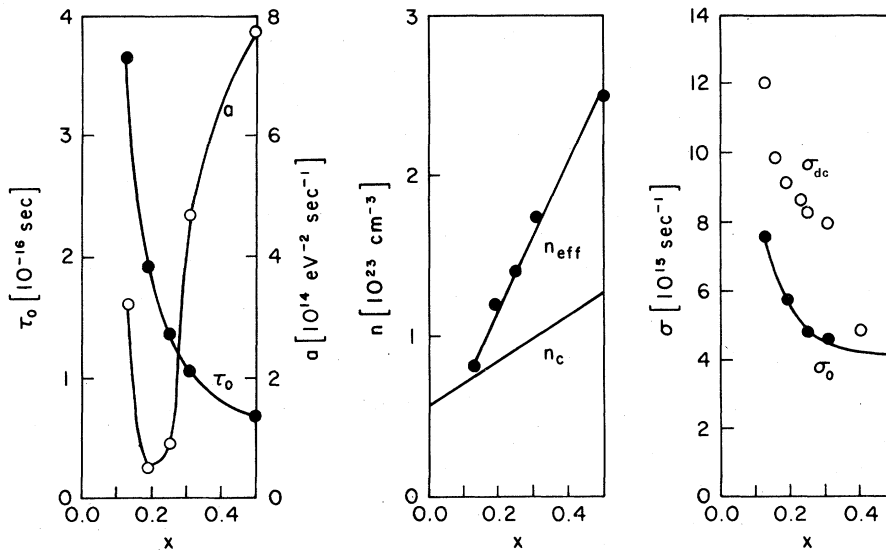


FIG. 5. Compositional dependence of the parameters in the Drude formula: (a) Zero-frequency relaxation time τ_0 and the frequency coefficient a , (b) effective electron concentration n_{eff} compared with n_c calculated from linear interpolation; and (c) zero-frequency optical conductivity σ_0 compared with the measured dc conductivity σ_{dc} .

The quantities τ_0 and a are plotted in Fig. 5(a). The values of a plotted here were obtained with $\epsilon_0=1$. The relaxation time τ_0 monotonically decreases with x ; the constant a has a deep minimum close to the eutectic composition. There are various possible origins of the frequency dependence of τ .²⁻⁴ One may be the surface roughness of the film. Another origin of $a \neq 0$ may be that the value $\epsilon_0=1$ is not a correct choice. In gold ϵ_0 was found to be 5 but in our alloys we expect ϵ_0 to be considerably smaller since, as we show below, the interband transitions are shifted to higher energies and are considerably weaker. With $\epsilon < 5$ we could fit the data only for compositions $x=0.19$ and 0.25 . These corrections are too small to account for the values at the other compositions and this mechanism does not explain the observed minimum near the eutectic composition.

In Fig. 5(b) we compare the measured $n_{\text{eff}} = n(m/m^*)$ with the electron concentration n_c calculated from the linear interpolation of the concentrations in the pure components. We note that the difference between n_{eff} and n_c increases with increasing Si concentration. It is not likely that this is due to the dependence of m^* on x because τ is so short that in the frequency range studied we expect the optical effective mass m^* to differ only slightly from the effective mass figuring in the dc conductivity.⁵

In Fig. 5(c) we compare the optical conductivity $\sigma_0 = \omega \epsilon_0 / 4\pi$ extrapolated to $\omega=0$ ($\sigma_0 = e^2 \tau_0 n_{\text{eff}} / m$) with the dc conductivity.⁶ This comparison indicates that $\sigma_{\text{dc}} > \sigma_0$ as has been seen in many other systems.⁷ The decrease of σ_0 with alloying shows

that the decrease of τ due to stronger scattering prevails over the increase of electron concentration. τ_{dc} is somewhat larger than τ_0 but of the same order of magnitude.

The Drude formula describes the optical absorption ϵ_2/λ of $\text{Au}_{1-x}\text{Si}_x$ accurately in the low-frequency range. At higher frequencies, we observe deviations as shown in Fig. 3. We associate them with interband transitions. We determined the onset energy $E_0^{(2)}$ of the interband transitions from plotting the difference $(\epsilon_2 - \epsilon_2^D)E^2$ vs $E = \hbar\omega$. For nondirect transitions, this expression is proportional to the convoluted densities of the final and initial states, if the matrix elements can be assumed to be constant.

In Fig. 6, $E_0^{(2)}$ is shown as a function of Si concentration. The energy of the onset increases with x which corresponds to the idea that the Fermi level is shifted towards higher energies because Si contributes more electrons to the conduction band than does Au.¹ We determined the position of the Fermi level in the rigid-band approximation supposing that Au contributes one electron and Si four. In Fig. 6 the energy difference E^c between the calculated Fermi level and the d bands in Au is shown for the different alloys. We note that the shifts of $E_0^{(2)}$ are in very good agreement with the shifts calculated in this simple interpolation scheme.

If we extrapolate the value of $E_0^{(2)}$ to the case $x=0$ (i.e., to pure Au), we find the value $E_0^{(2)}(x=0) = 1.6$ eV. This is very close to the value of the onset of interband transitions in the tail for pure Au. The energy of this onset is between 1.5 eV⁸ and 1.7 eV.⁹ The rigid-band model works surprisingly well in describing the shifts occurring near the Fermi level. Presumably, however, this model should not be able to describe the electronic states which are far from E_F . This is what happens in other systems such as Pd:H.¹⁰

As seen in Fig. 2, $\epsilon_1(\omega)$ in the alloys passes through zero at frequencies ω_0 higher than in Au but much smaller than ω_p (Fig. 6); the reduction of the frequency is due not only to the polarization associated with the interband transitions as in Au (which is weakened in the alloys), but also to the smallness of τ . As shown in Fig. 7, the electron energy-loss function, $-\text{Im}\epsilon^{-1}(\omega)$, has a rather sharp maximum at ω_0 in Au. However, in the alloys, there is no structure at ω_0 because of the strong absorption.

We analyzed the data in terms of a Drude term and interband transitions. This separation may not be justified because τ is extremely short and consequently the conditions under which the Drude formula is deduced (i.e., $\hbar/\tau \ll E_F$) are poorly satisfied at small x and not at all at large x , as

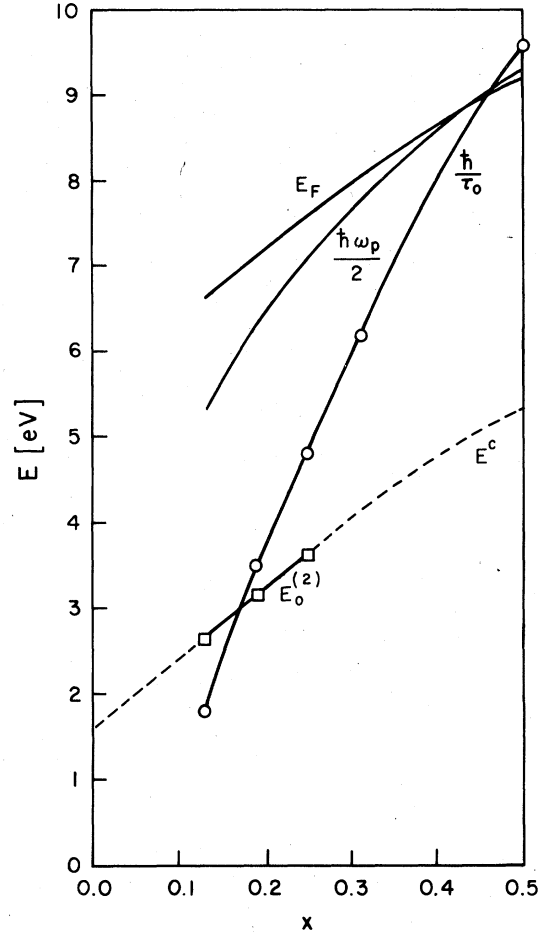


FIG. 6. Dependence on composition of various energies appearing in the data. \hbar/τ : collision frequency multiplied by \hbar . $E_0^{(2)}$: energy obtained from the plot of the difference $(\hbar\omega)^2(\epsilon_2 - \epsilon_2^D)$ vs $\hbar\omega$; the dashed line E^c was calculated with the rigid-band approximation as described in the text. E_F : Fermi energy. $\hbar\omega_p/2$: plasma energy defined in Eq. (5) (it is divided by 2 so as to be able to plot it on the same scale as other energies).

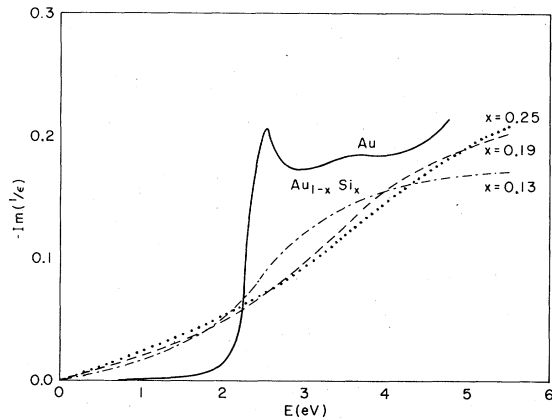


FIG. 7. Energy-loss function $-\text{Im}\epsilon^{-1}(\omega)$.

seen in Fig. 6. Let us note, however, that although the form of the Drude formula provides a good description of the IR data, the effective electron concentration found from the fit differs substantially from the calculated concentration of conduction electrons n_c . This concentration n_c was determined by assuming that Au contributes one electron and Si four; this simple assumption agrees with the shift of the Fermi level with x as observed in the shifts of the onsets of interband transitions.

The electron relaxation time τ obtained from the Drude fit is extremely short, on the order of 10^{-16} sec, and is a decreasing function of x . \hbar/τ plotted in Fig. 6 varies from about 2 to 10 eV (this quantity is about 0.3 eV in liquid Au and on the order of 10^{-3} eV in crystalline Au). The mean free path $l = \tau v_F$ ($v_F = \sqrt{2E_F/m}$) becomes smaller than the interatomic distances at $x = 0.31$; the samples are apparently in the boundary region of the metallic conductivity, just below the critical value for the electrical resistivity. This is in good agreement with the resistivity and x -ray data, previously reported,⁶ namely, that when x is large the x -ray pattern changes and there is also a marked increase in the resistivity. A consequence of the extremely small value of τ is the dominance of the free-carrier absorption over an unusually broad frequency range (up to our maximum frequency). We suggested¹ that $n_{\text{eff}} > n_c$ is related to the smallness of τ .

For estimating the oscillator strength of the interband transitions, we assumed that Eqs. (5), (8), and (9) hold in the whole frequency range and can be extrapolated into the region of the interband transitions. This is not an easily justifiable assumption, and it must be understood that the validity of the comments in the following paragraph rests on the acceptance of this assumption.

We may calculate the effective concentration of electrons participating in the interband transitions up to frequency ω :

$$n_{\text{eff}}^i(\omega) = \frac{2\pi^2 e^2}{m} \int_0^\omega \omega' (\epsilon_2 - \epsilon_2^D) d\omega'. \quad (10)$$

If we compare $n_{\text{eff}}^i(\omega)$ in the alloys with that found in pure gold (Fig. 8) we see that it is strongly reduced in the frequency range considered. The reduction increases with x and is larger than one

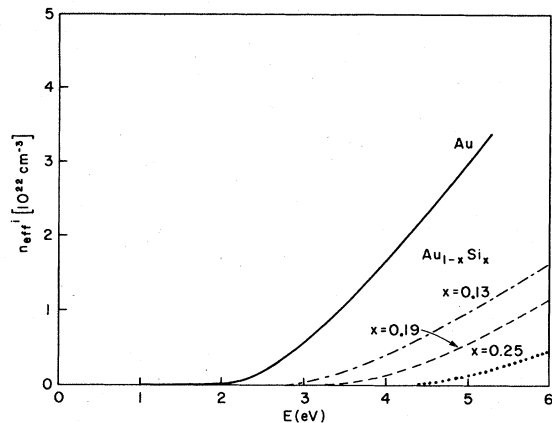


FIG. 8. Effective concentration of electrons participating in interband transitions, as defined in Eq. (10).

would expect on the basis of the fact that the gold content is reduced.

In conclusion, in our interpretation of the data the short lifetime of an electron of definite momentum at the Fermi surface enhances the oscillator strength of the intraband transitions in the spectral range considered. Close to the glass forming composition ($x \approx 0.20$) the interband transitions are still easily observable. Recently Schlegel *et al.*¹¹ determined $\epsilon(\omega)$ of the bulk $\text{Pd}_{81}\text{Si}_{19}$ glass and interpreted it also by a superposition of intraband and interband transitions. However, the latter start already at 0.65 eV and their contribution to $\epsilon(\omega)$ appears to be substantial. Apparently, the relative contributions of the intra- and interband transitions depend on the particular alloy. In $\text{Au}_{1-x}\text{Si}_x$ we found that for $x \geq 0.31$, ϵ_2/λ is practically Drude-like in the whole spectral range considered.

ACKNOWLEDGMENTS

Technical assistance of T. R. Kirst and J. E. Bernardini is gratefully acknowledged. We thank K. P. Ackerman and H. J. Güntherodt for sending us a preprint of Ref. 11. This work was supported in part by Army Research Office Grant No. DAAG-29-76-G-0221 and NSF Grant No. DMR-77-09931, and by the Materials Research Laboratory-NSF programs at Brown University and at the University of Chicago.

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