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Observation of the Approach to a Polarization Catastrophe

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Optical measurements of phosphorus-doped silicon yield a donor susceptibility which can be fitted with a critical form that extrapolates to a polarization catastrophe at the insulator-metal transition. The exponent is about twice classical predictions and demonstrates the quantum nature of the transition.

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As an ensemble of atoms approach one another, a transition from an insulating to a metallic state can occur.[1] A classic example in which such a transition occurs is the random array of impurity atoms in a crystalline semiconductor. Analysis of a variety of measurements on such materials[1] has indicated that at low impurity concentrations the electrons are localized. The behavior of the dc electrical conductivity is nonanalytic at zero temperature, being zero over a finite range (in density) in the insulator and finite in the metal, but the conductivity varies smoothly at finite temperatures. The behavior of the donor electric susceptibility χ is less clear. (χ is related to the total dielectric constant, ϵ, and that of the host Si, ϵ_{Si}, through $\epsilon = \epsilon_{Si} + 4\pi\chi$.) In the insulator, χ should be finite and positive,[2] and in the metal it may be either large and negative, as indicated by the Drude theory, or infinite, as suggested by Altshuler and Aronov[3] for a disordered system.

Classical analyses[4,5] based on percolation theory for metallic inclusions in a dielectric predict a critical divergence of χ, with various values of the exponent. In contrast to this prediction of a polarization catastrophe, Ghazali and Leroux-Hugon[6] find that χ is enhanced by only a factor of 3 (relative to the result for noninteracting donors) for their model of a doped semiconductor in which the donors are arranged on a lattice.

The experimental behavior of χ is also the subject of some disagreement. In 1956, D'Altroy and Fan[7] found a large enhancement in χ at microwave frequencies and low temperature for doped Ge. Measurements of metal ammonia solutions[8] near room temperature suggested only a small enhancement and a value of $\chi = 0$ at the critical density, n_{MI}. Reflectivity of doped Ge at two far-infrared frequencies and low temperatures was interpreted[9] as indicating no enhancement whatever of χ in the insulating phase. In contrast, Castner *et al.*[2] found enhancements up to a factor of 3 based on low-frequency capacitance measurements extrapolated to zero temperature for several dopants in Si and Ge. Townsend[10] found similar results based on oscillations due to interference in the transmitted intensity as a function of far-infrared frequency.

We use an optical method of determining χ which appears to be particularly suitable for investigating a phase transition at $T = 0$ K. We measure the absorption coefficient $\alpha(\omega)$ at energies $\hbar\omega$ in the range 2.5 to 58 meV and a temperature $T \approx 2$ K at which $\hbar\omega \gg kT$ and $\alpha(\omega)$ is in the zero-T limit. To obtain $\alpha(\omega)$ we pass far-infrared radiation through a Michelson interferometer, a cold filter that cuts off photons above $\omega \approx 500$ cm^{-1}, and the Si:P sample. We detect the transmitted intensity using a Ge:In bolometer at T near that of the sample, Fourier transform the resulting interferograms, and then ratio the Si:P data to a Si reference. Finally, we transform $\alpha(\omega)$ to obtain the $\omega = 0$ refractive index $n(0)$ using the Kramers-Kronig relation,

$$n(0) = n_{Si} + (c/\pi)\int_0^{\omega_\infty} [\alpha(\omega)/\omega^2]d\omega, \quad (1)$$

where c is the speed of light. We correct the values of α for $n_D > 10^{18}$ cm^{-3} for the donor reflectivity using the Kramers-Kronig relations at finite frequency in a self-consistent manner. The

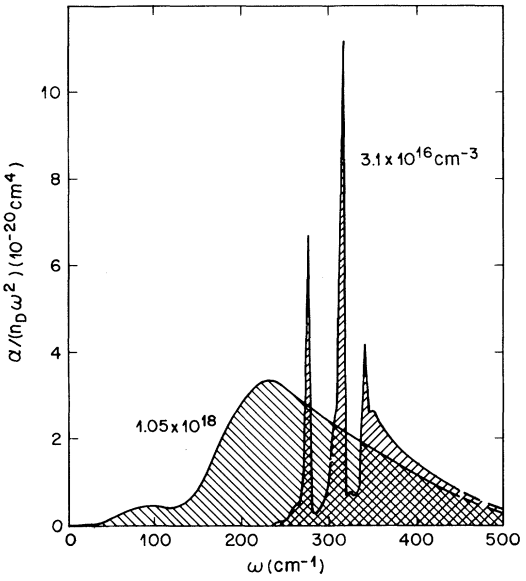

FIG. 1. Graph of the integrand in the Kramers-Kronig relation for the $\omega = 0$ dielectric susceptibility χ for samples of Si:P as a function of photon energy ω. The area under each curve gives χ for the P donors. With increasing n_D the curves show the strong growth of the absorption cross section α/n_D at lower ω which, with $1/\omega^2$ factor, enhances χ. The dashed line is an ω^{-2} tail added analytically to satisfy the sum rule on $\alpha(\omega)$.

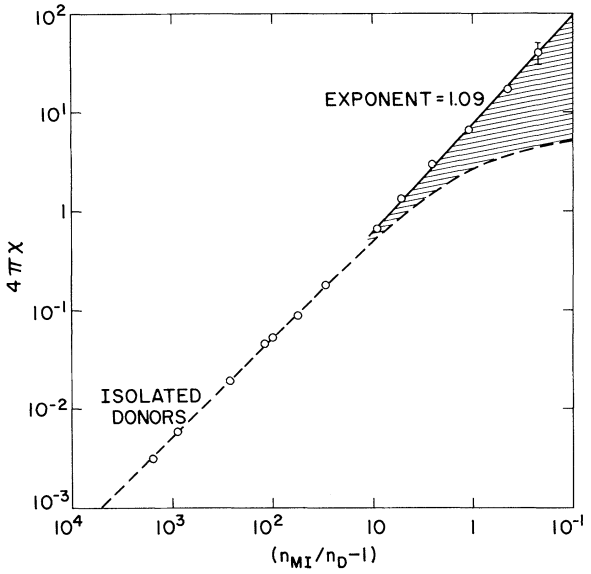

FIG. 2. Log-log plot of $4\pi\chi$ vs $n_{MI}/n_D - 1$. The open circles are obtained for samples of Si:P as illustrated in Fig. 1. The dashed line, $\chi = D_P n_D$, fitted for $n_D < 10^{17}$, determines the isolated-donor polarizability D_P. The solid line, Eq. (4), determines the exponents $\zeta = 1.09 \pm 0.1$ as $n_D \to n_{MI} = (3.8 \pm 0.2)\times10^{18}$ cm^{-3}.

energy $\hbar\omega_\infty$ is large enough to include transitions from the donors to the conduction-band states, but is below the Si band gap (1.17 eV). Since $n(0)^2 = \epsilon$ and $n_{Si} \equiv \epsilon_{Si}{}^{1/2} = (11.4)^{1/2}$, χ follows from

$$4\pi\chi = [n(0)]^2 - \epsilon_{Si}. \tag{2}$$

This optical method has the additional advantage of directly measuring the donor contribution to χ, rather than the total ϵ.

We have plotted in Fig. 1 the integrand in Eq. (1) (normalized to the impurity concentration,[11] n_D), for two values of n_D for Si:P. The $1/\omega^2$ factor enhances the contribution to χ from low energies. At low concentrations, such as $n_D = 3.1 \times 10^{16}$ cm^{-3}, we have found[12] that the lowest-energy tail of the sharp isolated donor peaks arises from charge-transfer D^+D^- states of donor pairs which are excitons in the Mott-Hubbard gap between the D^+ and D^- bands. For $n_D \gtrsim 0.1 n_{MI}$, e.g., 1.05×10^{18} cm^{-3}, the corresponding states of larger clusters are dominant and, in addition, the forbidden transition between the upper and lower levels of the valley-orbit–split ground state is seen near $\omega = 100$ cm^{-1}. In this range of n_D, a simple phenomenological model of absorption by randomly occurring clusters[12,13] can describe the shape and density dependence of the absorption edge.

The frequency range of the measurements (20–470 cm^{-1}) does not fully satisfy the f-sum rule, which can be written[13]

$$\int_0^{\omega_\infty} \alpha(\omega)\,d\omega = 2\pi^2 n_D e^2/(m^* c n_{Si}), \tag{3}$$

where m^* is the optical electron mass $1/m^* = 1/3m_\parallel + 2/3m_\perp$. To satisfy Eq. (3), we have added a Drude tail to $\alpha(\omega)$, for $\omega > \omega_c = 470$ cm^{-1}, of the form $\alpha(\omega_c)(\omega_c{}^2 + \Omega)/(\omega^2 + \Omega)$, adjusting the constant Ω (dashed line, Fig. 1). The contribution to χ from $\omega > \omega_c$ is small because of the $1/\omega^2$ weighting and we find χ to be insensitive to the shape of the tail. (We have also tested a triangular shape.)

Figures 2 and 3 show our results for χ vs n_D. The dashed line in both figures is the linear behavior of isolated donors, fitted for $n_D < 10^{17}$ cm^{-3} in Fig. 2, which determines the isolated-donor polarizability

$$D_P \equiv \lim_{n_D \to 0} (\chi/n_D) = (11 \pm 1)\times10^4\ \text{Å}^3,$$

in agreement with Lipari and Dexter's[14] calculated $D_P = 12\times10^4$ Å^3, whereas earlier measurements[2] gave 24 and 16×10^4 Å^3. The solid line is

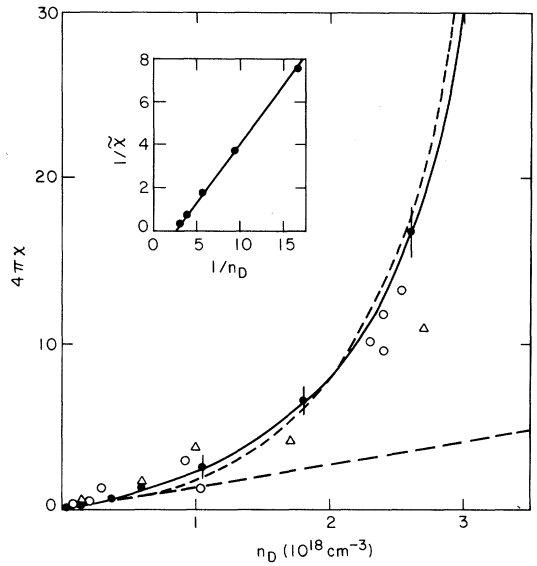

FIG. 3. Linear plots of χ vs n_D showing comparison of our results (solid circles) with those of Ref. 2 (open circles) and Ref. 10 (triangles) as well as with the same theoretical curves as in Fig. 2 and that of Eq. (5) (dotted line). In the inset, the linear behavior of $1/\tilde{\chi} \equiv 1/\chi^{1/1.09}$ vs $1/n_D$ (in units 10^{-17} cm^{-3}) shows the intercept at $1/n_{MI}$ where the data extrapolate to a polarization catastrophe.

a fit to our data of the form

$$\chi = \chi_0 (n_{MI}/n_D - 1)^{-\zeta}, \quad (4)$$

where χ_0 is a constant. The slope in Fig. 2 as $n_D \to n_{MI}$ determines $\zeta = 1.09 \pm 0.1$, and the same solid line is shown in Fig. 3, with $\chi_0 = 0.56$. The error quoted for ζ is statistical and neglects the systematic uncertainty due to a lack of data closer to n_{MI}. However, the classical percolation theories give $\zeta = 0.6$ (Ref. 4) or less.[5] Recently, McMillan,[15] using scaling arguments for quantum diffusion, has suggested that χ scales with the square of the localization length for $n_D < n_{MI}$ and diverges with ζ between 1.2 and 2.

The dotted line in Fig. 3 is a theoretical estimate of χ based on scaling the calculated fractional reduction in the energy gap E_G/E_{G0} between the D^+ and D^- band edges. We use

$$\chi/D_P n_D = (E_{G0}/E_G)^2, \quad (5)$$

where D_P is from our experiment and the form $1/E_G{}^2$ reflects the $1/\omega^2$ weighting in Eq. (1). The variation of E_G/E_{G0} is obtained from a polarized orbital calculation[16] for a simple-cubic lattice. This scaling form does not fit the data completely, but illustrates the qualitative behavior. Recent results by Castner *et al.*[2] are shown as open circles and those by Townsend[10] as triangles. The data appear to be reliable with good accuracy[2] at higher n_D. We have checked for consistency of our choice of n_{MI} by inverting Eq. (4) and plotting $1/\tilde{\chi} \equiv 1/\chi^{1/1.09}$ vs $1/n_D$ as shown in the inset in Fig. 3. This form extrapolates to a polarization catastrophe at $n_{MI} = (3.8 \pm 0.2) \times 10^{18}$ cm^{-3}. This value agrees with that indicated by our measurements of the resistivity.[13]

In conclusion, we have shown, through an analysis of the absorption spectrum of donors in Si:P, the tendency of the donor susceptibility to diverge, as $n_D \to n_{MI}$ at $T = 0$ K, with an exponent much larger than classical percolation theories. While we cannot prove that χ diverges at n_{MI}, its enhancement by over an order of magnitude and its shape suggest quantum behavior leading to an infinite donor susceptibility at the insulator-metal transition.

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