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A Dielectric Anomaly at the Metal–Nonmetal Transition*

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The divergence in the real part of the dielectric constant which accompanies a metal–nonmetal transition is described. Particular attention is paid to metal–ammonia solutions. © 1984 Academic Press, Inc.

Introduction

In the generally accepted view, a metal–nonmetal (M–NM) transition occurs when the conductivity drops from values of, say, $10^4\ \Omega^{-1}\ \mathrm{cm}^{-1}$ to values of, say, $10\ \Omega^{-1}\ \mathrm{cm}^{-1}$. If one looks at the frequency dependence of charge transport, then the change is from a dielectric constant, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, described by a Drude model, to one for which a Lorentz model is appropriate. In particular, ε_1 goes from negative, infinite values to positive ones, at low frequencies.

There have now been a number of investigations of the dielectric constant, and there is more than the simple behavior described above. As the M–NM transition is approached from the nonmetallic side, ε_1 tends to diverge (*1, 2*). The divergence is comparable to that observed in other parameters near a critical point or consolute point, and analysis has been made applying the zero-T scaling theory. The experimental observations will be described first. Most of the detailed work has been done on doped Si, but the most extensive work is on M–NH_3 solutions. Some discussion of theory will follow.

As stated, there is a divergence in the real part of the dielectric constant, ε_1, as the metallic state is approached from the insulating side. Figure 1 shows such data for molten mixtures of K and KCl recently reported by Freyland *et al.* (*3*), and for Si : P (*1*). Thomas and co-workers, at Bell Laboratories (*1*), have used stress-tuning techniques to approach the M–NM transition in P-doped Si very closely. Following procedures standard in the treatment of critical phenomena, they plot the inverse dielectric susceptibility χ as a function of $(n_c - n)$, where n is the donor density and n_c the density at the M–NM transition on a logarithmic scale (linear in Ref. (*1*)). The susceptibility χ is related to ε_1 by $4\pi\chi = \varepsilon_1 - \varepsilon_{\mathrm{Si}}$. The divergence is expected to be algebraic, that is:

$$\frac{1}{4\pi\chi} = \frac{1}{\chi_0}\left\{\frac{n_c - n}{n}\right\}^{\zeta}.$$

Therefore, a plot of the reciprocal susceptibility yields a straight line if ζ is unity, as may be seen in Fig. 2. The conductivity in Si : P is also described by a critical exponent (*1*): $\zeta/2$. These data are nicely shown in Fig. 1 of Ref. (*1*).

The semiconductor data is the most precise available because stress-tuning of n is

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* Dedicated to Dr. M. J. Sienko.

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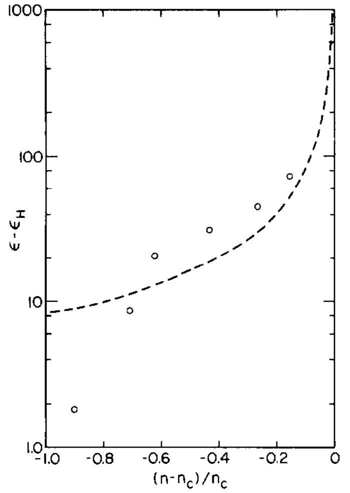

FIG. 1. The dielectric susceptibility as a function of the deviation from the critical density for the M–NM transition in Si : P (---) and KCl : K (○), from Refs. (*1*, *3*), respectively.

more controllable than changing *n* by doping. Even without this precision, studies reveal some surprising differences between Si : P or Si : As (*4*) and amorphous $Si_{1-x}Nb_x$ or compensated Ge (i.e., Ge : Sb : B) (Ref. (*5*)). The exponent describing the conductivity, $\zeta/2 = 0.5$, in the P- or As-doped Si is half of that found first in compensated Ge and later in a-Si alloy films and other alloys.

The measurements on Si were carried out at dc or at frequencies below 10^6 Hz, or at far-ir frequencies up to 500 cm^{-1}. As in many amorphous semiconductors (*6*), the low ω conductivity exhibits a sublinear dependence on frequency:

$$\sigma \propto \omega^s; \qquad s \sim 0.9.$$

A Kramers–Kronig analysis (*7*) then gives

$$\varepsilon \propto \omega^{-(1-s)} = \omega^{-0.1}$$

and a tendency to diverge at $\omega = 0$, as observed (*1*).

In metal–ammonia solutions there has been a wider variety of experiments but much less detail (*8*, *9*). The fine-grained approach to the M–NM transition is lacking. Also, the $M-NH_3$ measurements are at 200–300 K, much above the mK temperatures of the Si work. Nevertheless, there are several interesting observations and qualitative agreement with the Si data.

Data obtained on $M-NH_3$ solutions at 10 GHz are shown in Fig. 3. There is an obvious similarity to Fig. 1, despite the vast difference in temperature. At the lowest, least metallic compositions ε_1 approaches values characteristic of pure NH_3. There is then a rise to values as much as an order-or-magnitude above those characteristic of the pure fluid. The fall to the negative values seen in the metallic state is not abrupt. Data (*10*, *11*) taken in the optical range (0.65 eV or 1.5×10^{14} Hz) are also shown and have the same trend, though the effect is weaker, and the fall to negative values slower.

A more striking result is obtained when the frequency dependence is examined. Resonant behavior was found by Breitschwerdt and Radscheit (*9*) for compositions near the M–NM transition. That is, ε_1 shows a positive peak, zero crossing, and negative peak all near 10^{10} Hz. There is, as far as we are aware, no comparable result for any other system. The "resonance" is missing in data obtained at lower *or* higher concentrations. The conductivity is almost

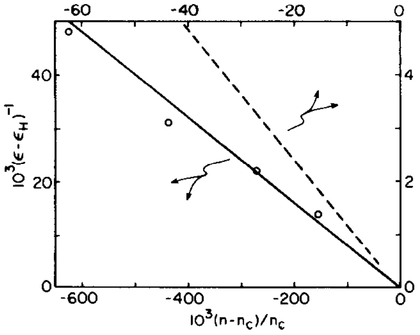

FIG. 2. The inverse susceptibility as a function of the deviation from the critical density for the M–NM transition in Si : P (---) and KCl : K (○), from Refs. (*1*, *3*), respectively. Freyland, in Ref. (*3*), fits the four points shown and two off scale (see Fig. 1) to obtain a critical exponent $\zeta = 1.4$. The solid line is the best fit to the four points which also passes through the origin. Note the different scales for the two lines.

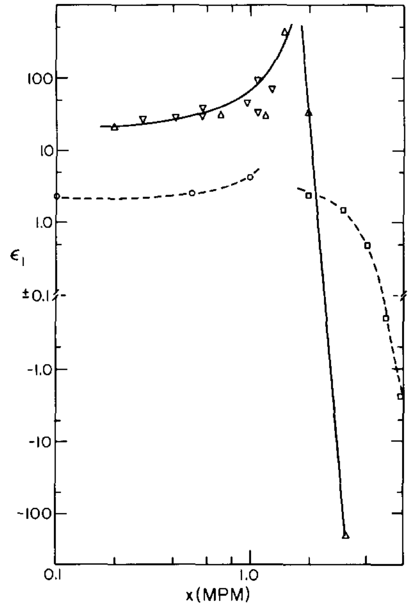

FIG. 3. The dielectric constant for M–NH$_3$ solutions. The points (▽) are from Ref. (*8*) and were taken in Na–NH$_3$ solutions at 298 K and 10 GHz; (△) from Ref. (*9*) in Na–NH$_3$ solutions at 233 K and 6 GHz; (○) from Ref. (*11*) in K–NH$_3$ solutions at 233 K and 0.65 eV (10^{14} Hz); and (□) from Ref. (*10*) in Li–NH$_3$ solutions at 233 K and 0.65 eV. Note the break in the ordinate at 0.1. The abscissa is in mole percent metal (MPM).

independent of frequency below 10^9 Hz, then rises somewhat near 10^9 Hz. There is no sign of the $\omega^{0.9}$ dependence seen in both amorphous semiconductors and in Si : P (Ref. (*1*)).

In a very recent work Freyland (*3*) has observed the beginning of the divergence at optical frequencies in molten K : KCl. The divergence seen in Fig. 1 is characterized by an exponent $\zeta = 1.4$ by Freyland. However, if only the four highest of Freyland's six points are used, a value of 1.0 is also appropriate for ζ, as in Fig. 2.

The dielectric anomaly observed in Hg vapor by Hefner and Hensel (*12*) seems to be of a different origin. There is no change in the dc conductivity (which is $<10^{-3}\ \Omega^{-1}\ \text{cm}^{-1}$) and the rise in ε_1 is almost vertical. An anomaly has also been seen in the optical dielectric constant for amorphous Hg : Xe films (*13*). There is a metal–nonmetal transition in the films at $T = 0$ K, whose effects are seen at higher temperatures, and a peak in ε_1 at the measurement temperature (ca. 10 K). There are only a few data points so that the exponent cannot be determined precisely; a value near unity is plausible.

The existence of a dielectric anomaly at the M–NM transition was predicted over 50 years ago by Herzfeld (*14*). In fact, he noted that the existence of such an anomaly is the essence of the transition. The highly efficient screening present in a metal is as important a characteristic of the metallic state as the mobility of the carriers (*15*). The divergence of ε_1 at the transition then provides a continuous transition in the *screening* as the system goes from the insulating state, with dielectric screening, to the metallic (*20*). More recently, scaling arguments have been applied to the M–NM transition and also yield a dielectric anomaly. The older theory will be examined first.

Herzfeld (*14*), using the Clausius–Mossotti (CM) relation, predicted that a "polarization catastrophe" would occur. There has been extensive discussion of the way this effect occurs at the M–NM transition; this idea has even been explored for the periodic table by Edwards and Sienko (*16*). In the present context, the argument may be stated as follows. The Clausius–Mossotti relation gives a correction for the local field in a medium with atoms or molecules of polarizability α: $(\varepsilon_1 - 1)/(\varepsilon_1 + 2) = 4\pi n\alpha/3$, where n is the number density of polarizable species. The relation predicts a divergence in ε_1, given by

$$\varepsilon_1 = (1 + 2r)/(1 - r),$$

where $r = n/n_c$. The composition, n_c, at the transition is given by $n_c = (4\pi\alpha/3)^{-1}$ and this clearly depends on the polarizability α.

So then if α is sufficiently large, ε_1 must diverge at n_c. The critical exponent, ζ, is 1.0. Note that this exponent is found in Fig.

2 and elsewhere. Nevertheless, this semiclassical model cannot be expected to adequately describe all that occurs. Interactions among the molecules are ignored in the CM view so that α remains unrealistically independent of concentration. Castner (*2*) has shown how partially to correct for this in doped Si, using a phenomenological approach. Nevertheless, the CM model does possibly provide an intuitive basis for a description of the effect of frequency.

If a frequency dependence is introduced into the polarizability in the usual way (*17*), then the point of the divergence in ε_1 shifts:

$$\varepsilon_1 = (1 + 2r - u)/(1 - r - u),$$

where $u = (\omega/\omega_0)^2$. This elementary result suggests that as the frequency increases toward ω_0, the composition at which the peak in ε_1 is observed moves downward. This is qualitatively consistent with the M–NH_3 data of Fig. 3, where the composition of the peak in ε_1 is well below the 4 MPM transition in the dc conductivity. The optical peak is at 2 MPM, but less sharp. The Clausius–Mossotti relations cannot provide a basis for understanding the "resonance" observed at 10^{10} Hz.

McMillan (*18*) has provided a discussion of the M–NM transition in terms of scaling theory and there have been further contributions by Imry (*19*) and by Lee (*20*), among others. There are two problems. One is the treatment of the Anderson localization process within the one-electron approximation. The other is the addition of electron–electron interactions within the disordered system. At present there is no *complete* theory including both facets of the transition. The conductivity is expected to go continuously to zero, in contrast to Mott's idea of a minimum metallic conductivity. Grest and Lee (*20*) include only certain processes and predict that on the metallic side, $\sigma \propto (n - n_c)^{0.6}$, nearly as observed in Si : P. On the nonmetallic side of the transition they find ε_1 diverging: $\varepsilon_1 \propto (n - n_c)^{-1.4}$. The ratio of the two exponents for ε_1 and σ is 2.3. Imry and Gefen (*19*), on the other hand, reiterate the relations

$$\varepsilon_1 \propto \xi^2,$$
$$\sigma \propto \xi^{-1},$$

where ξ is the correlation length and diverges itself as $(n - n_c)^{-\gamma}$. Thus the ratio of the exponents for ε_1 and σ, is 2.0, but γ remains unknown. McMillan (*18*) and others find $\gamma = 1.0$, but a value close to 1/2 is found by the incorrect estimate of Grest and Lee (*20*).

There has been growing consideration given to the ramification of the existence of the dielectric anomaly at the M–NM transition. From a macroscopic viewpoint, the increase in the dielectric constant significantly reduces the interaction energy of any charge or dipole. The screening length increases smoothly through n_c, even as ξ diverges. However, when considering any microscopic interaction, the origin of the enhanced polarizability must be considered. For example, in metal–ammonia solutions ε_1 is a parameter in determining both the energy and extent of the isolated solvated electron (*21*). Yet it is precisely this polarizability of the solvated electron which enhances the dielectric constant. Self-consistency must be maintained in any computation. Similar problems exist for an F-center in molten salts or a donor in Si.

There are nevertheless secondary effects of the enhanced dielectric constant to be expected in a variety of properties. The cohesive energy should drop and the presence of a phase separation in M–NH_3 solutions might well follow from this effect alone (*22*). The observation that a salt added to a M–NH_3 solution preferentially goes to the dilute, nonmetallic phase may also be attributed to the large ε_1 there (*23*). The concentration-independent surface tension observed (*24*) just below the M–NM transition may also derive from the enhanced ε_1. A somewhat more substantial effect should be observed in any nuclear relaxation process involving electric quadrupolar coupling (*25*). For example, the peak and subsequent fall in the nuclear (^{133}Cs) relaxation rate as Cs is added to CsI (*26*) near the M–NM transition may well be related to this mechanism, as relaxation in the pure salt is quadrupolar. It would be interesting to look for the effects on the relaxation of As nuclei or even muons (*27*) added to Si : P as the M–NM transition is tuned by stress (assuming more direct stress effects are absent). The high dielectric constant should presumably screen any quadrupolar effects. The electric field gradient responsible for Mössbauer effect splittings should be modified. One can also imagine using the Si : P as a window (for ir light) and backing it with, say, an Ag film. As ε_1 goes up in the Si, the surface plasmon in the Ag would be shifted to lower energies (*28*).

Acknowledgments

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