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Superconductivity and the Metal-Nonmetal Transition in Hg-Xe Films

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The electrical conductivities and transition temperatures of films consisting of random mixtures of Hg and Xe condensed onto substrates held at 4.2 K have been measured. A metal-nonmetal transition in which the temperature coefficient of resistance changes from positive to negative has been found near a volume fraction close to that expected for random percolation. This transition is accompanied by a substantial drop in the superconducting transition temperature which is measured resistively.

The electrical properties of alloys of metals and rare gases prepared by condensation onto cold substrates have been a subject of considerable experimental and theoretical interest.¹ In this Letter we report the results of an investigation into the properties of the Hg-Xe system, which has been extended beyond the work of others²⁻⁴ to low enough temperatures so as to permit the observation of the effects of dilution of the Hg atoms by Xe on the superconductivity of the resultant films. The results of the present investigation are also different from those reported for the superconductivity of the Al-SiO₂ system which also exhibits a metal-nonmetal transition but which is granular.⁵ Here we discuss the systematics of the variation of film resistance with Xe concentration and the composition dependence of the superconducting transition temperature.

Hg-Xe films would be expected to be model systems for the study of the effects of local order on conductivity and superconductivity provided that the films were indeed random and noncrystalline mixtures of their constituents. A way which should ensure this is to evaporate the films onto substrates kept at low temperatures and at the same time minimize the heating of surfaces by thermal radiation from the vapor source and by the kinetic energy of the atoms in vapor.⁶ Both of these goals can be achieved with molecular-beam deposition techniques. The present apparatus incorporates several improvements over that used to prepare Na-NH₃ films,⁷ the most significant being a change in which the molecular

beam oven, except for its orifice, is shrouded with a liquid nitrogen jacket. This, along with the fact that the metallic constituent of the beam is Hg, which is extremely volatile, results in an energy flux less than 10⁻⁴ W/cm² at the substrate surface.

Film compositions quoted here are nominal in that they are determined from parameters of the oven. The composition of the beam was adjusted by regulating the pressure of Xe gas in the oven and by controlling the temperature of the oven so as to obtain the desired vapor pressure of Hg. The Hg and Xe were thus thoroughly mixed in the oven which served as the source for the molecular beam. Because the sticking coefficients of Hg and Xe are close to unity at the beam fluxes and substrate temperatures used here, the films should be random mixtures of the constituents with the composition of the vapor.⁸ The conductances of films increased linearly with time at fixed deposition rates, indicating that the films are homogeneous in composition across their thicknesses. (A possible exception is in the first several atomic layers, for which the resistance was not measurable.) All electrical resistance measurements were made by use of a four-terminal technique in an ambient magnetic field of the order of 0.5 G. Measurements at temperatures above 10 K could not be made on as-prepared films as significant annealing was always observed above 10 K.

In Fig. 1 we plot, as functions of atomic concentration of Hg in mole percent metal (MPM), both the logarithm of the normal-state resistivity

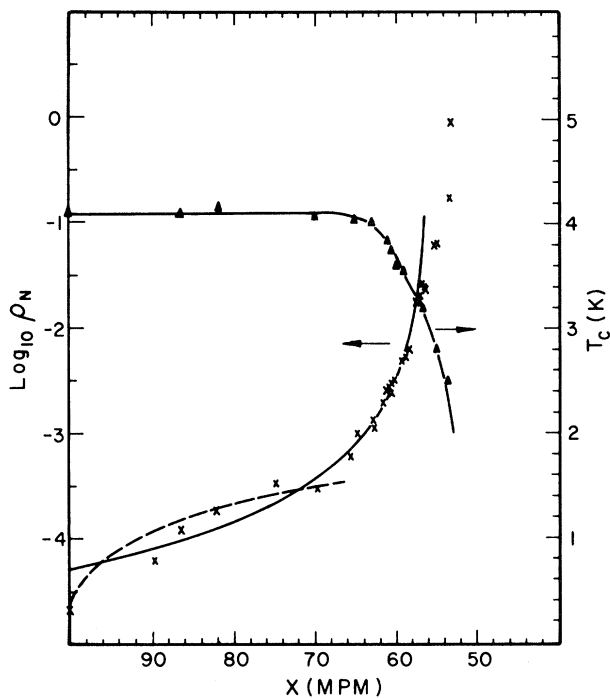


FIG. 1. Transition temperatures and logarithms of the normal-state resistivity at 4.2 K vs nominal composition X in mole percent metal (MPM) for 1500–3000-Å-thick Hg(Xe) films 0.5 mm wide and 0.4 cm long. Compositions are accurate to better than ~ 1 MPM. The solid line associated with the resistivity represents random percolation theory in 3D with an exponent of 1.7 and critical composition of 55 ± 4 MPM or 13 vol%, while the line through the transition temperatures is drawn through the data points for visual aid. The dashed line represents the qualitative variation of the resistivity with concentration assuming linear dilution. Films were prepared on substrates held at 4.2 K. The vapor effused from an oven held at 340 K. The atomic flux was 10^{18} atoms/cm² sec.

measured at 4.2 K and the superconducting transition temperature T_c , of 2000–5000-Å-thick films. The dashed line drawn near $X = 100$ MPM represents the expected variation of the resistivity with concentration assuming linear dilution. The solid line associated with $\log_{10} \rho_N$ corresponds to a least-squares fit to $\rho_N \sim (X - X_c)^\alpha$ with the exponent α forced to be 1.7, a value appropriate to three-dimensional (3D) percolation.⁹ The fit, which was carried out for compositions between 58 and 75 MPM, resulted in $X_c = 55 \pm 4$ MPM. The range of the fit was chosen so as to exclude films exhibiting negative temperature coefficients of resistance (TCR's). All films with compositions to the right of the line, including many

which are not shown because their resistances are greater than the range of the graph, exhibit negative TCR's. Because of the unknown character of the crossover from percolation to the linear behavior at high metal concentrations and to hopping conduction at lower concentrations, a systematic least-squares analysis of the data for concentrations outside the range chosen was not possible. Thus the present results must be considered to be suggestive rather than proof of the applicability of microscopic random percolation. It should be noted that the value of the critical concentration X_c suggested here disagrees with the work of Refs. 3 and 4, where X_c was determined as 69 ± 5 MPM but agrees with that of Ref. 2.

It is also useful to estimate the volume fraction of metal corresponding to the critical concentration. If the films are modeled as a liquid of hard spheres of Hg and Xe of radii r_{Hg} and r_{Xe} , then the transformation between the molar or atomic fraction X and the volume fraction V_f is given by

$$V_f = 0.45 \left[1 + \left(\frac{1-X}{X} \right) \left(\frac{r_{\text{Xe}}}{r_{\text{Hg}}} \right)^3 \right]^{-1}, \quad (1)$$

where the numerical factor 0.45 is the packing fraction appropriate to an amorphous alloy. If we take r_{Hg} and r_{Xe} to be 1.49 and 2.16 Å, respectively, we find that the critical concentration of 55 MPM corresponds to a critical volume fraction of 13%, a number appropriate to random percolation in 3D. Equation (1) differs from the equation used to calculate the volume fraction in Refs. 2–4 by a factor of 0.45. This difference has its origin in the fact that we have defined the volume fraction of metal as $V_{\text{metal}}/V_{\text{system}}$ rather than $V_{\text{metal}}/V_{\text{occupied}}$, where $V_{\text{occupied}} = fV_{\text{system}}$, with f being the packing fraction. Thus with our definition an atomic or molar fraction of 100 MPM corresponds to a volume fraction of 0.45 and 55 MPM corresponds to 0.13 rather than 0.29 as would be the case in Refs. 2–4. Our definition of volume fraction should be the relevant one in a discussion of percolation.

It would thus seem that the composition variation of the resistances of films when they are dominated by metallic conduction is consistent with random percolation theory.⁹ Beyond the percolation threshold, when TCR's are negative, there is apparently a crossover to a conduction regime where activated processes dominate. The authors of Refs. 3 and 4 are led to an explanation of their data which excludes percolation as their definition of volume fraction leads to a critical

volume fraction which is too high for the continuous percolation picture.

For each of the films, the corresponding superconducting transition temperatures, which were measured with a calibrated CryoCal Ge thermometer, are also plotted in Fig. 1. T_c has been arbitrarily chosen to be the temperature at which $R = 0.9R_N$. Typically, the range from $0.1R_N$ to $0.9R_N$ spanned 0.030 K. For both pure Hg films and films containing substantial Xe, $T_c = 4.06$ K, which is close to the value reported for Hg films less than 100 Å thick in Ref. 6 where a molecular beam technique was also used. On annealing to 60 K, the transition temperatures of the films of the present work become 4.19 K which is slightly higher than T_c for crystalline Hg(α). If films are formed by use of an oven not provided with thermal shielding, a transition temperature of 3.95 K corresponding to that of Hg(β) is found. Hg(β) is the phase usually formed by quench condensation. The critical fields of the as-prepared films were the order of 16 kG, higher than those of Hg(α) or Hg(β). These observations support the notion that the connected Hg domains of as-prepared films may be a new phase which is either an amorphous, granular, or crystalline form different from Hg(α) or Hg(β) known previously.^{10,11} In the absence of electron-diffraction data a definitive statement as to structure cannot be made. Detailed studies of the conditions of formation of the conjectured new phase and various annealing experiments which establish that it is distinct in its properties from Hg(α) or Hg(β) will be published elsewhere.¹²

At the moment we have no quantitative explanation for the variation of T_c with composition although a variety of explanations which may have some relevance suggest themselves. If the picture of the film consisting of random spheres of Hg and Xe were correct, the fact that T_c does not change initially with Xe concentration might be a consequence of the existence of a connected network of domains of a characteristic size on the average greater than the superconducting coherence length. If the material were granular, size effects ought to be expected to raise T_c .¹³ The fall of T_c with Xe concentration could be a consequence of thermal fluctuations or noise, or both, disrupting the coupling between domains or grains. Alternatively, it could be an intrinsic effect not having anything to do with the fact that T_c is being determined in a transport measurement. An independent determination of T_c not involving transport would be required to resolve

this.

If the drop in T_c is intrinsic, it might be due to one of several mechanisms. With decreasing Hg concentration, the electron concentration is reduced in a way which could lead to a drop in T_c . Alternatively, when the temperature coefficient of resistance becomes negative, there may be hopping between localized states. Cooper pairs associated with such states might exhibit a reduced T_c .¹⁴ A third possibility is a reduction of T_c from a coupling of order-parameter fluctuations to electromagnetic field fluctuations which may be important in high-sheet-resistance films.¹⁵ In this instance the superconducting transition would be postponed until the condensation energy could in effect expel the black-body radiation of the environment.¹⁶ Such a model predicts that all type-I superconductors have transitions which are weakly first order.¹⁷ A fourth possibility is a lowering of T_c by a modification of the phonon spectrum of Hg by intimate contact with Xe atoms. Near the percolation threshold there is a large Hg surface-to-volume ratio and such an effect could be much larger than that reported in an adsorbed layer geometry.¹⁷

In Fig. 2 we show representative normalized $R(T)$ curves for as-prepared films. Exhibited are results characteristic of (a) films with a high metal concentration, (b) films exhibiting tails in $R(T)$, (c) films with higher Xe concentrations, tails in $R(T)$, and negative TCR's near T_c , and (d) films which exhibit a metal-insulator transition with decreasing temperature rather than a superconducting transition. For as-prepared films such as film *d* no simple behavior of $\ln R$ vs $T^{-\lambda}$ with $\lambda = \frac{1}{2}$, $\frac{1}{3}$, or $\frac{1}{4}$ was found. However,

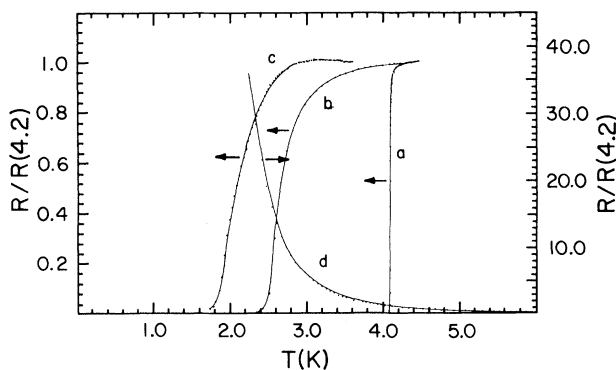


FIG. 2. Representative curves of $R(T)$ for films *a*, *b*, *c*, and *d* with $X = 100$, 55, 54, and 52 MPM, respectively. Lines have been drawn through discrete data points for clarity.

after annealing to 20 K, $\ln R \sim T^{-1/4}$ was found. These films did not exhibit superconductivity as measured resistively down to the lowest temperatures attainable ($T \sim 1.5$ K).

The above-described behavior suggests that the Hg-Xe system exhibits a metal-nonmetal transition which occurs with a dependence on concentration and with a critical concentration close to that of continuous percolation in 3D. Beyond the percolation threshold, the systems acquire a negative TCR but are still superconductors. With further increase in Xe concentration, a regime in which the conductivity is dominated by hopping is entered. The approach to an insulating configuration beyond the percolation threshold is probably the Mott-Anderson transition of Refs. 2-4 and is accompanied by the eventual disappearance of superconductivity as determined resistively.

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Superconductivity in the Presence of Strong Pauli Paramagnetism: CeCu_2Si_2

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A comparison was made between four low-temperature properties of LaCu_2Si_2 and CeCu_2Si_2 . Whereas LaCu_2Si_2 behaves like a normal metal, CeCu_2Si_2 shows (i) low-temperature anomalies typical of "unstable 4f shell" behavior and (ii) a transition into a superconducting state at $T_c \approx 0.5$ K. Our experiments demonstrate for the first time that superconductivity can exist in a metal in which many-body interactions, probably magnetic in origin, have strongly renormalized the properties of the conduction-electron gas.

The relationship between different collective phenomena in metals has continued to interest both experimentalists and theorists. Recent

interest has shifted to materials in which ferromagnetism and superconductivity occur at different temperatures, either because of the addition