

and by using a different gun which produced 1-keV electrons incident at 75° from the sample normal. In all cases the shape of the edge was unchanged from that observed with 2-keV electrons.

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Anomalous Conductivity of Quench-Condensed Sodium-Ammonia Films*

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Films of sodium and ammonia have been formed on substrates held at 5 K. The electrical resistivity of the films has been measured and a metal-nonmetal transition has been observed, but the transition was found to be anomalous in that the resistivity was not a monotonic function of the sodium concentration. No evidence was found for the anomalously high electrical conductivity reported for bulk sodium-ammonia solids which were quick-frozen from liquid solutions.

Recently, attention has been focused on the properties of quick-frozen sodium-ammonia solutions in which a transient high electrical conductivity was reported.^{1,2} The results seemed to provide support for the thirty-year-old claim by Ogg³ that sodium-ammonia solid solutions were superconducting and have resulted in a flurry of speculations relating to the existence of time-dependent superconductivity in such solutions.⁴⁻⁷ Recent measurements,⁸ however, indicate that this apparent transient conductivity is a result of the freezing process.

In an attempt to determine the intrinsic resistivity of sodium-ammonia solid mixtures, we

measured the electrical resistivity of solid sodium-ammonia films formed directly from vapor onto substrates held at or below 5 K. The investigations, which were carried out as a function of sodium concentration, do not confirm the existence of high-conductivity states. The films do exhibit a metal-nonmetal (MNM) transition as a function of composition at concentrations in the 45-50 mole-percent-metal (MPM) range. The MNM transition is anomalous in that there appears to be what may be enhanced conductivity on the nonmetal side of the transition. The anomalous behavior may also be interpreted as a resistivity enhancement on the metallic side. Extreme-

ly high contact resistances were observed at low voltage which, in the presence of finite leakage resistances in the measuring system, could result in I - V characteristics suggestive of the zero-voltage currents of superconducting films. Such high resistances are well known for systems of metals and semiconductors in contact.

Formation of the films by quench-condensing onto cold substrates allows samples with sodium composition ranging from 100 MPM sodium to 3 MPM were formed from vapor produced in a small molecular-beam oven suspended in a vacuum chamber whose walls were cooled to 4 K by liquid helium. The walls, which were gold plated to reduce heat losses by radiation from the oven, also served to cryopump the vacuum chamber containing the oven and the substrate. The composition of the beam was adjusted by varying the pressure of ammonia gas supplied from a tank external to the cryostat and by controlling the temperature of the oven so as to obtain the desired vapor pressure of sodium. The sodium and ammonia were thus mixed in the oven which then served as the source for a molecular beam of the mixed vapor. The oven and the walls of the vacuum chamber were baked out and pumped by a 100-1/s ion pump before the Dewar was filled with liquid helium. During film deposition the ion-pump pressure never exceeded 10^{-8} Torr. This value is probably an upper limit on the pressure near the substrate and oven orifice, a quantity which was not measured directly and is hard to estimate. However, the pumping speed of the cooled surfaces in this part of the apparatus is estimated to exceed 3000 l/s, suggesting that the residual gas pressure in the vicinity of the molecular beam was much lower than the 10^{-8} Torr registered at the ion pump. Furthermore, in a separate series of investigations which will be reported elsewhere, a MNM transition occurring at 53 MPM in the sodium-argon system was studied using the same apparatus. No evidence of nonmonotonic behavior of the resistivity was found in this system, suggesting that the feature displayed in Fig. 1 is not a result of a contaminant peculiar to the apparatus.

Films were deposited through a mask onto glazed ceramic substrates which were provided with electrical leads for four-terminal resistance measurements. A shutter was used to intercept the beam, preventing it from impinging on the substrate until the composition was adjusted properly. The oven temperature was monitored by a platinum resistance thermometer and the ammo-

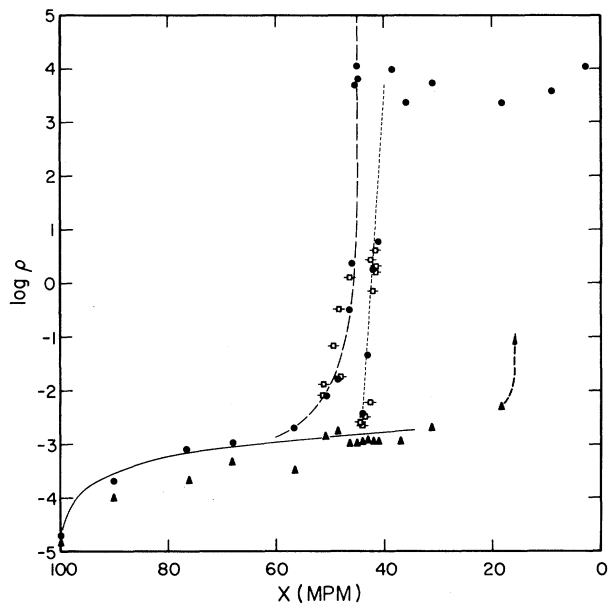


FIG. 1. Plot of the logarithm of the resistivity in ohm centimeters vs nominal sodium concentration in mole-percent metal (MPM). The circles represent data obtained with the films at 4 K after being formed at 5 K where composition was controlled to $\pm 0.5\%$. The squares represent data obtained with films prepared in the same manner but with composition control of $\pm 1\%$. The triangles represent measurements made at 77 K after the films represented by the circles were warmed to 100 K. The solid line represents the expected variation of the resistivity with concentration assuming linear dilution. The dashes are a fit to percolation theory. The dashed line with an arrow indicates the concentration below which the films warmed to 100 K became electrically discontinuous.

nia pressure by a capacitance manometer. A germanium resistance thermometer was used to monitor the substrate temperature.

Under the best conditions the ammonia pressure was controlled to $\pm 3 \times 10^{-4}$ Torr and the oven temperature to ± 0.1 K. This resulted in a relative composition uncertainty for the vapor of $\pm 0.5\%$. It was further assumed that the compositions of the vapor and the resultant film were identical. This is equivalent to assuming that the accommodation coefficients for both constituents of the vapor are unity at 5 K. Compositions which are reported are nominal in that they are calculated from the parameters of the oven which was always operated in a molecular beam mode, at temperatures which never exceeded 300°C . The thicknesses of the films were calculated to be 5000 \AA . This is based on the assumption that the density of the resultant film was the average of the densities of the component solids. A direct

check on the thickness of a pure sodium film was made which indicated that the calculated deposition rate for sodium was accurate to within 5%. This was done by depositing a thick layer of sodium over an extended period of time, removing the film from the apparatus and measuring its thickness mechanically. If any of the above assumptions are violated, the nominal compositions of the films would be in error.

Figure 1 shows a plot of the logarithm of the resistivity versus nominal sodium composition. The form is, in general, typical of matrix isolation of metal^{9,10} although the transition occurs at a different concentration than that measured for sodium-argon in our own and in previous investigations.¹¹ Conducting films exhibited temperature-dependent resistivities which are considered to be typical of amorphous metal films. The resistivities of pure sodium films were near $10^{-5} \Omega \text{ cm}$, indicating that they were good conductors. Reversible variation of resistance with temperature was observed in the range from 2 to 12 K. Irreversible behavior with a negative temperature coefficient of resistance was found in the range from 14 to approximately 100 K. When a film was warmed above 100 K, it transformed into a material with positive temperature coefficient of resistance and thereafter its behavior with temperature was completely reversible. The only exceptions to this behavior were films of sodium concentration below about 15%. These films became insulators (i.e., they were electrical open circuits) when warmed to 100 K.

An important consideration is the question of whether the samples were random alloys or segregated samples. The evidence in favor of ran-

dom alloys, in the absence of optical data, is the linear dependence of resistivity on sodium concentration in the range of 70 to 100 MPM. Each added ammonia molecule contributes to the resistance as expected in a random, but not in a segregated, specimen. No direct evidence exists for other compositions.

As shown in Fig. 1, at concentrations below 70 MPM sodium, the resistivity rises above a linear extrapolation from high sodium concentrations, reaches a peak at 45 MPM, and drops sharply, not rising again until 40 MPM. This anomalous feature is not understood. It may be the result of bond ordering near 50 MPM sodium leading to a resistivity maximum. Alternatively, the anomaly could result from enhancement of the conductivity on the insulating side of the transition resulting from superconducting fluctuations of some unknown type or from a drastic increase in the dielectric constant on the insulating side of the transition. Dielectric-constant enhancements have been studied experimentally and theoretically for both percolation transitions and Mott transitions.¹²⁻¹⁴ A large increase in the dielectric constant could make carrier traps significantly more shallow, leading to a flood of carriers and an enhancement of the conductivity. A further possibility is the occurrence of a structural phase change at 45 MPM.

The conductivity in the vicinity of the anomaly, when it is greater than $10^{-1} \Omega \text{ cm}$, exhibits a temperature dependence suggestive of a system in which carriers conduct by variable-range hopping. In Fig. 2 plots of the logarithm of the resistivity, $\ln \rho$, vs $T^{-1/4}$ seem to fall on straight lines whereas plots of $\ln \rho$ vs T^{-1} appear not to

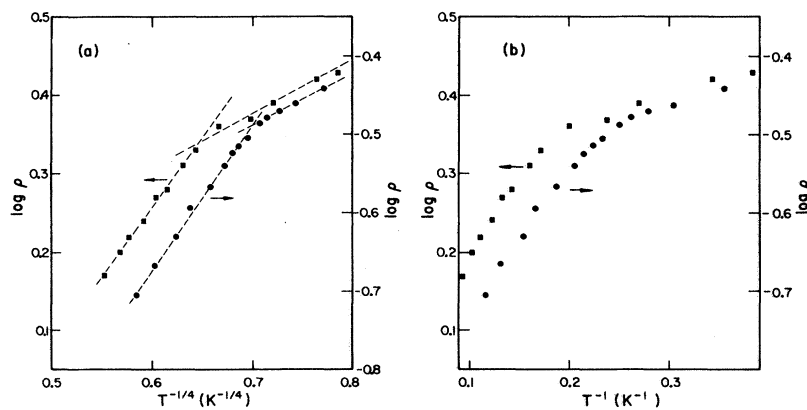


FIG. 2. Temperature dependence of the resistivities in ohm centimeters of films of selected compositions: The circles and squares represent data of films with 47 and 42 MPM, respectively. (a) $\ln \rho$ plotted as a function of $T^{-1/4}$; (b) as a function of T^{-1} . When films are either metallic or insulating, no temperature dependence is found over the same temperature range.

show linear behavior. A linear variation of $\ln\rho$ with $T^{-1/4}$ is a signature of variable-range hopping.¹⁵ The limited domain of temperature over which data are plotted is a consequence of the onset of irreversible behavior in films warmed above 12 K. Neither insulating nor metallic films exhibited appreciable temperature dependence over the range of temperatures over which the behavior was reversible.

Attempts were made to detect whether the conductivity was at all magnetic-field dependent. The maximum available field was 4 kOe. No significant magnetoresistive effects were observed.

The general character of the MNM transition resembles that of a percolation transition. The dotted line in Fig. 1 is a plot assuming $\rho(X_c) \sim (X - X_c)^{-S}$ with X_c taken to be 45 MPM and $S = 2.1$ as measured by Phelps, Avci, and Flynn.¹⁰ The percolation transition should occur at a metal volume fraction of about 15%.¹⁶ However, an amorphous film with a small packing fraction may have a critical mole fraction of metal much greater than 15%. The anomaly in the range from 50 to 40 MPM spoils the agreement with these considerations.

In conclusion, we have formed solid films of sodium and ammonia directly from vapor and observed a metal-nonmetal transition which is anomalous. The conductivity in the vicinity of the transition exhibits a temperature dependence consistent with "variable range hopping." There is no evidence at all of the anomalous high-conductivity states reported by Dmitrenko and Shchetkin,¹ but there are high contact resistances which can complicate four-terminal resistance measurements. The fact that high conductivity is not observed here does not mean that it was not observed in the work reported in Ref. 1. The only safe conclusion is that the results probably depend critically on the manner in which samples are prepared. Quick-frozen bulk liquid is probably not the same as a film prepared directly from the vapor. It may be necessary to vary other parameters of the films in a regular way in order to sweep systematically through all the possible mechanical and physical configurations of

the quick-frozen solutions.

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