On the metal–nonmetal transition in metal–ammonia solutions*

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(Received 2 February 1973)

Concentrated (>10 MPM)[1] metal–ammonia solutions[2–4] (MAS) are liquid metals which correspond to the propagation, weak scattering, electronic transport regime.[4–11] In the intermediate concentration region[4,5,12–18] (9–1 MPM) MAS exhibit rapid variations with concentration of their static and transport properties, which signify the occurrence of a metal–nonmetal transition (MNMT).[4,5,19–23] From the analysis of the available experimental data[2–5] we conclude that electron transport in the intermediate concentration region cannot be described in terms of the diffusion, strong scattering, microscopically homogeneous transport regime[24–26] as the Friedman relations[26] between the electrical conductivity and the deviations of the Hall coefficient, R, from the free electron value, R_{fe}, are not satisfied. Furthermore, as localization resulting in MNMT in a disordered system is always associated with fluctuations,[27–30] the two carrier model[31] for electronic transport in a homogeneous medium is not applicable.

We propose that MAS in the intermediate concentration range are microscopically inhomogeneous with regard to electron transport, with a volume fraction, C, of the material occupied by metallic clusters of a mean concentration of $\sim$9 MPM or higher, the remainder volume, $(1-C)$, consisting of small solvated electron–cation diamagnetic complexes. Applying semiclassical theory, the electronic structure and transport problem reduces to that of percolation of classical particles in a random potential.[27,32] The density of states, $n(E_F)$, is reduced by the allowed volume fraction,[29] $n(E_F)=n_0(E_F)C$, where $n_0(E_F)$ is the density of states at $C=1$. The inhomogeneous regime can be subdivided into: (a) Pseudometallic regime, $1>C>C^*$, where the major contribution to electronic transport originates from continuous metallic paths; (b) the pseudoelectrolytic regime, $C^*>C>0$, where the solution contains finite metallic clusters and electron transport occurs by conventional ionic conduction or by Mott hopping[33] between the isolated clusters. The condition for the MNMT in this inhomogeneous system is $n(E_F)/n_0(E_F)=C^*$, where on the basis of numerical data[34] we choose the percolation limit, $C^*\simeq 0.2$–0.25.

For Li, we set $C=1$ at 9 MPM, where R starts exhibiting deviation[4,14–18] from R_{fe}. This choice of upper limit to the inhomogeneous regime is somewhat arbitrary and is expected to vary with solute. The dependence of C on the metal concentration, M, was obtained from the analysis of the Knight shift data[35–36] for Na at 240°K, where from the linear dependence of $K(M)$ on M in the range 1–9 MPM we take $C\simeq(M-1)/8$.

The transport properties were analyzed in terms of a modified effective medium theory. The semiclassical effective medium theory (EMT) for the conductivity, σ, results in[37–40]

$$\begin{aligned}\sigma&=\bar{\sigma}_0 f(C,x),\\ f(C,x)&=a+[a^2+\tfrac{1}{2}x]^{1/2},\\ a&=\tfrac{1}{2}[(\tfrac{3}{2}C-\tfrac{1}{2})(1-x)+\tfrac{1}{2}x],\\ x&=\sigma_1/\bar{\sigma}_0,\end{aligned}\tag{1}$$

where $\bar{\sigma}_0$ and σ_1 are the conductivities in the metallic and in the electrolyte regions, respectively. For MAS, transport within the extended metallic clusters corresponds to the propagation case, and Eggarter's theory[41] was utilized to account for scattering from the boundaries of the metallic regions. The modified EMT (EMTZ) yields

$$\begin{aligned}\sigma&=\sigma_0 D(C)\bar{f},\\ \bar{f}&=f(C,x(C)),\\ D(C)&=zC/(1-C+zC),\\ x(C)&=\sigma_1/\sigma_0 D(C),\\ z&=L/l,\end{aligned}\tag{2}$$

where σ_0 is the conductivity at $C=1$ and z corresponds to the ratio between the sampling length, L, for concentration fluctuation and the mean free path $l=12$ Å at the lower limit[5] of the propagation regime.

In Fig. 1 we display the analysis of the conductivity data.[11–17] For low values of $x\sim 10^{-3}$–10^{-4}, σ/σ_0 in Eqs. (1) and (2) is independent[42] of x in the range $0.4<C<1.0$ being given by the $x=0$ value, $\sigma/\sigma_0=D(C)\times(\frac{3}{2}C-\frac{1}{2})$. The EMT results in a systematic positive deviation from experiment in this range, where the experimental data were utilized to determine z via the EMTZ. Subsequently, the data in the range $0<C<0.4$

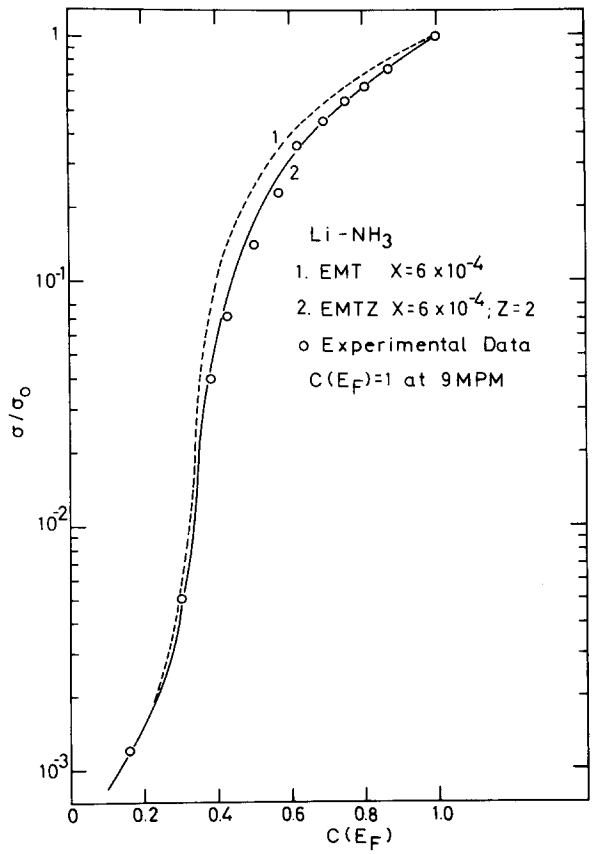

FIG. 1. Electronic transport data for Li–NH_3 solutions at 223°K in the intermediate concentration range taken from Refs. 13–17.

were used to fit x. The EMTZ with $x=6\times10^{-4}$ and $z=2$ results in a good fit to experimental data. The parameter $z=2$ yields $L=25$ Å which implies that in the pseudoelectrolytic regime an isolated metallic cluster contains $\sim$100 interacting solvated cations snd solvated electrons.

The EMTZ for the Hall coefficient[42] accounts for the moderate increase of R with decreasing M and for the maximum exhibited by R/R_{fe} in the intermediate region.[4,13–15]

The MNMT occurs at $C^*=0.2$–0.25, i.e., $M=2.6$–3.0 MPM. Our physical picture for the MNMT in MAS implies that between the propagation and the electrolyte regimes there is an inhomogeneous transport regime where concentration fluctuations and consequently percolation effects result in a continuous decrease in σ. This is a general feature[29,30,42–44] of the MNMT in disordered systems.

* This research was supported in part by ARO(D) and benefited from general support of Materials Science by NSF at The University of Chicago, and by the Israeli Council for Research and Development at the Tel-Aviv University.

[1] MPM refers to mole percent metal.

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