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Comment on electronic structure and transport in expanded liquid Hg †

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A consistent interpretation of the Knight-shift data for expanded liquid Hg is made in terms of a continuous metal-semiconductor transition intermediated by density fluctuations.

We have advanced[1,2] a coherent physical picture for the electrical and thermal transport properties of expanded liquid mercury in terms of the following four transport regimes: (a) propagation regime, $11<\bar{\rho}<13.6$ g cm^{-3}; (b) diffusion regime, $9.2<\bar{\rho}<11.0$ g cm^{-3}; (c) inhomogeneous transport regime, $8.0<\bar{\rho}<9.2$ g cm^{-3}; and (d) pseudointrinsic semiconducting regime, $\bar{\rho}<7.8$ g cm^{-3}; where $\bar{\rho}$ is the mean mass density. The nature of the electronic structure and transport properties of expanded liquid Hg in the density range 9.2–8.0 g cm^{-3} is of considerable interest as it pertains to the character of the metal-nonmetal transition in a disordered one-component material. We were able to account for the curious transport properties of Hg in that range in terms of the transport regime (c), in which density fluctuations lead to the simultaneous presence of semiconducting and metallic regions of the material. The correlation radius for the metallic regions turned out to be 15 Å, which is substantially larger than the Ornstein-Zernike decay length for density fluctuations and, more important, the phase-coherence length of the conduction electrons, <0.8 Å. Thus a picture of transport by a fluctuating local conductivity associated with relatively long-range density fluctuations and with negligible contributions from tunneling across the locally semiconducting regions is consistent with the experimental situation. The validity of this picture has been challenged by Mott[3-5] who has attempted to account for the transport properties in this intermediate region in terms of thermal excitation across a mobility gap. Mott's model encounters three serious difficulties. First, the Hall mobility μ in the density range 9.3–8.6 g cm^{-3} is constant[6] and it was argued by Mott[5] that in his model μ is then determined by the Hall mobility of electrons at the mobility edge, i.e., $\mu \propto n(E_c)$, where $n(E_c)$ is the density of states at the mobility edge and is constant in his model, in apparent agreement with experiment.[6] However, according to the Friedman theory[7] for the Hall mobility in a disordered semiconductor $\mu \propto Jn(E_c)$, where J is the transfer integral. In the semiconducting regime, J decreases with decreasing $\bar{\rho}$ and consequently μ would not be expected to remain constant if $n(E_c)$ were constant. However, it is possible on dimensional grounds that $Jn(E_c)$ is independent of the degree of disorder or the density. To test this possibility, numerical calculations of E_c and $Jn(E_c)$ were carried out by A. Antoniou for one-band tight-binding models with both diagonal and off-diagonal disorder. He found that $Jn(E_c)$ depends in general on disorder and in some cases quite strongly. The details of this work will be published elsewhere. Second we have pointed out elsewhere[8] that Mott's picture[5] leads to a substantial disagreement between the density variation of the electrical conductivity and the thermoelectric power in the intermediate density range. Mott has proposed[5] a density-dependent negative heat of transport Q to account for this discrepancy. The value of Q required varies from 0 at 9.2 g cm^{-3} to 0.25 eV at 8.0 g cm^{-3}, and it is attributed to polaron effects. Polaron theory yields a negative heat of transport $|Q| \simeq E_B$, the polaron binding energy, only at temperatures such that $4KT<|E_B|$ or, equivalently, $4KT<|Q|$. The latter condition does not apply here. Third, the density dependence of the mobility gap, as extracted from conductivity data, leads to the conclusion[2] that Mott's picture is internally inconsistent when combined with general thermodynamic considerations on density fluctuations.

Important new experimental information concerning electronic structure and transport in expanded liquid Hg was recently reported by El-Hanany and Warren[9] who measured the Knight shift throughout the density range $\bar{\rho}=13.6$–7.5 g cm^{-3}. El-Hanany and Warren have concluded that the current models for the diffusion regime (b) are inadequate and that the description of the metal-nonmetal transition in the intermediate (9.2–8.0 g cm^{-3}) density range (c) requires reexamination. The purpose of this note is twofold. First, we shall emphasize that the magnetic data[9] *are* compatible with the electrical transport properties in the range (b), within the framework provided by the diffusion theory. Second, and more important, we shall demonstrate that the Knight-shift data in the intermediate density range (9.2–7.5 g cm^{-3}) provide strong support for our physical model of the inhomogeneous transport regime (c) in this system.

The observed variations of the Knight shift[9] are (i) in the propagation regime (a) the Knight shift K drops by 25%, which is typical of simple metals and needs no further discussion.[9] (ii) In the diffusion regime (b), K is constant within experimental error. (iii) In the density range 9.0–7.5 g cm^{-3}, K exhibits a sharp drop from 2.01% to 0.13%.

We start our discussion of (ii) from the familiar expression for the Knight shift

$$K=\tfrac{8}{3}\pi\langle|u_F(0)|^2\rangle\chi_p/N, \tag{1}$$

where $\langle|u_F(0)|^2\rangle$ is the mean probability density at the nucleus of an electron at the Fermi energy. The conduction-electron wave functions are normalized to unity within an atomic volume, on average. χ_p is the volume spin susceptibility

$$\chi_p=\chi_p^0 h, \tag{2}$$

where

$$\chi_p^0\propto n(E_F) \tag{3}$$

is the Pauli susceptibility, and the enhancement factor h arises from exchange and correlation. N is the atomic density. The density dependence of K can be expressed through its logarithmic derivative,

$$\frac{d\ln K}{d\ln\bar{\rho}}=\frac{d\ln\langle|u_F(0)|^2\rangle}{d\ln\bar{\rho}}+\frac{d\ln n(E_F)}{d\ln\bar{\rho}}+\frac{d\ln h}{d\ln\bar{\rho}}-1. \tag{4}$$

For a free-electron metal, the first term is unity and the second term is $\frac{1}{3}$. Writing

$$\langle|u_F(0)|^2\rangle=NA,$$
$$n(E_F)=n_{\text{fe}}(E_F)g, \tag{5}$$

where $n_{\text{fe}}(E_F)$ is the free-electron density of states, leads to

$$\frac{d\ln K}{d\ln\bar{\rho}}=\frac{d\ln A}{d\ln\bar{\rho}}+\frac{d\ln g}{d\ln\bar{\rho}}+\frac{d\ln h}{d\ln\bar{\rho}}+\frac{1}{3}. \tag{6}$$

In the diffusion regime, Friedman's model[7] results in

$$\sigma=\tfrac{2}{3}\pi z(e^2/\hbar a)X^2,$$
$$R=z^{-1}R_{\text{fe}}X^{-1}, \tag{7}$$
$$\mu=\tfrac{2}{3}\pi(ea^2/\hbar)X,$$

where a is the internuclear separation, R_{fe} is the free-electron Hall coefficient $(Ne)^{-1}$, z is the number of nearest neighbors, and where we have taken the number of triangular closed paths around each lattice site to be equal to z. The parameter

$$X=Ja^3n(E_F) \tag{8}$$

contains the nearest-neighbor transfer integral J and the density of states $n(E_F)$, at E_F. We conclude that the variations of σ, R, and μ in the diffusion regime are not merely induced by changes of $n(E_F)$ but can be considerably affected[8,10] by changes in J, which decreases with decreasing ρ. The Mott relation[11,12] $\sigma\propto[n(E_F)]^2$, i.e., $\sigma\propto\chi_p^2$ or $\sigma\propto K^2$, is inapplicable for the diffusion regime in Hg and is expected to be of limited applicability for other materials. A proper diagnostic tool for the identification of the diffusion regime is provided by the explicit relations between the Hall coefficient and other electrical transport properties[2,6], i.e., $\sigma\propto(R_{\text{fe}}/R)^2$ and $\mu\propto R_{\text{fe}}/R$. These relations among σ, R, and μ are of more general validity[13] than the simple tight-binding s-band model used by Friedman.[7] The density dependence of σ may be written from (7) and (8) as

$$\frac{d\ln\sigma}{d\ln\bar{\rho}}=-1+2\left(\frac{d\ln J}{d\ln\bar{\rho}}+\frac{d\ln g}{d\ln\bar{\rho}}\right). \tag{9}$$

Combining (6) and (9) and recalling that $d\ln K/d\ln\bar{\rho}$ is near zero in the diffusion regime,[7] we obtain

$$\frac{d\ln\sigma}{d\ln\bar{\rho}}=-\frac{5}{3}+2\left(\frac{d\ln J}{d\ln\bar{\rho}}-\frac{d\ln A}{d\ln\bar{\rho}}-\frac{d\ln h}{d\ln\bar{\rho}}\right). \tag{10}$$

Let us take for J the form

$$J\propto e^{-4ar_s}, \tag{11}$$

appropriate to exponentially decaying "atomic orbitals" or "Wannier functions," where the Wigner-Seitz radius r_s, $\propto\bar{\rho}^{-1/3}$, is 2.0 Å and a value of 1.33 Å^{-1} can be inferred from the asymptotic behavior of the atomic Hg 6s function[14] for the decay constant a. The corresponding value of $2d\ln J/d\ln\bar{\rho}$ is 7.1. The experimental value of $d\ln\sigma/d\ln\bar{\rho}$ is 13.1. Putting these figures into (10) gives

$$\frac{d\ln A}{d\ln\bar{\rho}}+\frac{d\ln h}{d\ln\bar{\rho}}=-3.8. \tag{12}$$

Equation (12) is consistent with a change in the value of A of a factor 2 (associated with an increase in s character at low densities) with no change in h over the density range (b). Since h can also be expected to increase, we can conclude that the Knight-shift data are consistent with transport via diffusion and that changes in the transfer integral and in the density of states contribute comparably to the changes of σ. Inserting (12) into (6), we obtain 3.5 for $d\ln g/d\ln\bar{\rho}$ corresponding to a factor of 1.7 change in g over the diffusion regime (b). Devillers and Ross[11] have calculated the band structures of several modifications of crystalline Hg. They conclude that "In the region $11 > \rho > 9$ g cm^{-3}, the main feature is that the dominantly p-like character of the states at the Fermi level is changing to more s-like. . . ." This feature should occur also for the liquid; their results are consistent with our proposed variation of A.

Turning now to the cardinal problem of the intermediate (9.2–8.0 g cm^{-3}) density range, our interpretation of the metal-semiconductor transition is that an energy gap opens *locally* via Mott's[12] s-p band overlap mechanism at a local density ρ_g. The allowed metallic volume fraction is[2]

$$C = \int_{\rho_g}^{\infty} P(\rho)\,d\rho, \tag{13}$$

where $P(\rho)$ is the probability distribution of the local density ρ. The Knight shift is

$$\bar{\rho}K = \int_{0}^{\infty} \rho K(\rho) P(\rho)\,d\rho, \tag{14}$$

where $K(\rho)$ is the value of the Knight shift at the local density ρ. This expression can be simplified by the application of the mean-value theorem after setting $\rho = \bar{\rho}$ inside the integral

$$\begin{aligned} K &= CK_0 + (1-C)K_1\,, \\ K_0 &= \int_{\rho_g}^{\infty} K(\rho)P(\rho)\,d\rho \Big/ \int_{\rho_g}^{\infty} P(\rho)\,d\rho, \\ K_1 &= \int_{0}^{\rho_g} K(\rho)P(\rho)\,d\rho \Big/ \int_{0}^{\rho_g} P(\rho)\,d\rho, \end{aligned} \tag{15}$$

which define mean values of metallic and nonmetallic Knight shifts, K_0 and K_1, respectively. The experimental data[9] in the density range 9.5 ± 0.3–7.5 ± 0.5 g cm^{-3} result in $K(\bar{\rho}=7.5)/K(\bar{\rho}=9.5) \simeq 0.6$, so we neglect the small chemical shift in the semiconducting regions and set $K_1 \simeq 0$ whereupon $C(\bar{\rho}) = K(\bar{\rho})/K_0$. Taking $K_0 = K(9.5 \pm 0.3) = 2.01\%$ together with the experimental K values[9] we have obtained the relation between C and $\bar{\rho}$ (the C scale) presented in Fig. 1. We have previously determined[2] the C scale in Hg from an analysis of the electrical conductivity data[2] based on the effective-medium-theory conductivity relation reduced via the mean-value theorem to its two-component form. That C scale, also presented in Fig. 1, should be regarded as a theoretical prediction for the (macroscopic) density of states and the Knight shift throughout the inhomogeneous regime. The agreement of the C scale extracted from conductivity data and the new Knight-shift data is as good as can be expected in view of the rather large experimental uncertainty in the magnetic data. Keeping ρ inside the integral in Eq. (14) would improve agreement with experiment, but the errors in the data are too large to justify this nicety. Our model[1,2] of the continuous metal-nonmetal transition intermediated by density fluctuations in Hg is thus supported by the new Knight-shift data.[9]

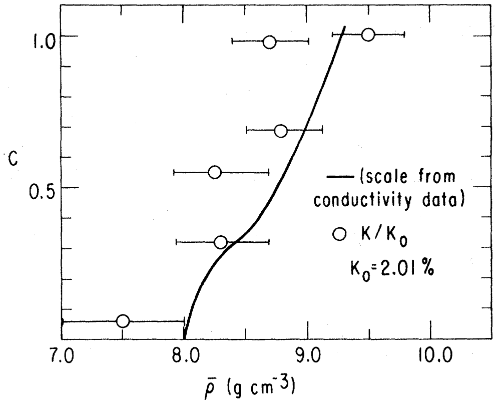

FIG. 1. The C scale for expanded liquid Hg in the inhomogeneous transport regime. Solid curve, C scale from conductivity data (Ref. 2); open circles, C scale from Knight-shift data (Ref. 9).

The next question is whether these data distinguish between Mott's model[12] and ours. In its simplest form, the general expression for the Knight shift becomes

$$\begin{aligned} K = K_1 &+ \tfrac{8}{3}\pi \frac{\langle |u_F(0)|^2\rangle}{N} \chi_p(E_F) \\ &+ \tfrac{8}{3}\pi \frac{\langle |u_c(0)|^2\rangle}{N} \chi_p(E_c). \end{aligned} \tag{16}$$

In (16), the first term corresponds to the chemical shift from occupied states below the Fermi energy. As it increases with decreasing density and is small at $\rho = 7.5$ g cm^{-3}, it can be neglected. The second term is the contribution of electrons near the Fermi energy; we designate it K_2. The third term is the contribution of electrons near the mobility edge and is proportional to the conductivity. Thus (16) implies the following correlation between Knight shift and conductivity

$$\sigma/\sigma_0 = K/K_0 - K_2/K_0, \tag{17}$$

if and only if the density dependence of the transfer integral can be neglected. In Eq. (17), σ_0 and K_0 are the conductivity and Knight shift at 9.2 g cm^{-3}. This is to be compared with the predictions of our model using effective-medium theory,[2]

$$\sigma/\sigma_0 = a + (a^2 + \tfrac{1}{2}x)^{1/2},$$
$$a = \tfrac{1}{2}[(\tfrac{3}{2}K/K_0 - \tfrac{1}{2})(1 - x) + \tfrac{1}{2}x], \qquad (18)$$
$$x = \sigma_1/\sigma_0,$$

where σ_1 is the conductivity in the nonmetallic regions, which we have shown to fit the data within combined experimental error. K_2 decreases rapidly with decreasing density in Mott's model because of the decrease in $n(E_F)$ and therefore of $\chi_p(E_F)$. Mott's model thus states that σ/σ_0 vs K/K_0 has an initial slope > 1 which decreases to 1. However, as pointed out above, the density dependence of the transfer integral cannot be neglected, so that Eq. (17) must be modified to

$$\frac{\sigma}{\sigma_0} = \left(\frac{J}{J_0}\right)^2\left(\frac{K}{K_0} - \frac{K_2}{K_0}\right), \qquad (19)$$

where J_0 is the transfer integral at 9.2 g cm^{-3}. Assuming the form given by Eq. (11) for the density dependence of J in Eq. (19) gives a more rapid fall of σ/σ_0 with K/K_0 than is predicted by Eq. (18). Our model has an initial slope near $\frac{3}{2}$ which remains constant down to $\bar{\rho} = 8.7$ g cm^{-3}, below which it makes a transition to a slope of about 0.5. The present magnetic data are too inaccurate to distinguish between the two models. On the other hand, the predictions of the two models for the longitudinal relaxation rates[15] are quite dissimilar. Until such data are available, our preference for the inhomogeneous transport model rests on the three objections to Mott's model cited above.

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