Knight shift and dielectric anomaly in fluid mercury

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The temperature and density coordinates for the ^{199}Hg Knight shift in expanded liquid mercury have been redetermined using new vapor pressure and equation-of-state data. The drop of the Knight shift at the metal-nonmetal transition is now seen to be even sharper and to occur at slightly higher density than reported in the original work of El-Hanany and Warren. The point of vanishing Knight shift in the liquid (8.9 ± 0.2 g cm^{-3}) coincides accurately with the occurrence of a "plasma transition" reported by Hefner and Hensel in the vapor when the two phases are in equilibrium.

Mercury is one of the few metals whose liquid-gas critical points occur at temperatures and pressures accessible in the laboratory ($T_c = 1750$ K, $P_c = 1670$ bar). For this reason it has proven to be an important substance for investigation of the metal-nonmetal transition of a divalent metal at low density and for study of the relationship between microscopic electronic structure and the liquid-gas phase transition.[1] The metal-nonmetal transition occurs in the subcritical liquid when the density is reduced sufficiently by thermal expansion. The transition to the nonmetal is signaled by the onset of characteristic semiconducting dc electrical transport properties[2] and a sharp drop in the ^{199}Hg Knight shift (Ref. 3, hereafter denoted as I). In the vapor, a striking and unexpected "plasma transition" has recently been discovered by observation of a sharp anomaly in the real part of the near-infrared dielectric constant (Ref. 4, hereafter denoted as II).

The purposes of the present Communication are twofold. First we present a revised version of the plot, first presented in I, showing the Knight shift versus density for liquid mercury near the coexistence curve. The revision is necessitated by the availability of new and more accurate data for the vapor pressure[5,6] and equation of state.[2] These new results affect the temperatures and densities assigned to the measurements reported in I. Second, we point out a striking correspondence between the revised location in the P-T plane of the metal-nonmetal transition determined from the Knight shift in the liquid, and the location of the dielectric anomaly in the vapor.

In the Knight-shift measurements (I), a thermocouple near the NMR sample was calibrated against the vapor pressure curve of mercury. The method employed was to heat the sample at a constant pressure until the liquid boiled out of the cell at the vaporization point. After liquid was recondensed into the cell, measurements were taken just below the vaporization temperature. Calibration of the thermocouple reading at each pressure was necessary because of large temperature gradients within the internally heated high-pressure vessel. These gradients resulted from convection currents in the gaseous argon pressure medium. The corrections resulting from use of the new vapor pressure data[6] range downward from about 50 K in the interval 1600–1700 K and are negligible below about 1300 K. Given a corrected set of P-T coordinates, the density was redetermined from the latest equation-of-state data obtained by Schönherr *et al.*[2,7]

A revised plot of Knight shift (KS) versus density in liquid mercury is presented in Fig. 1. For comparison, the variation of KS according to the original calibration is also shown. The essential differences are the shift to somewhat higher density and the sharper character of the drop in KS between 9.0 and 9.5 g cm^{-3}.[8] The density at which the shift vanishes, 8.9 ± 0.2 g cm^{-3}, is in excellent agreement with the estimate of Schönherr *et al.*[2] for the appearance of a finite activation energy for the dc conductivity. Since the Knight shift is proportional to the density of states at the Fermi level, both measurements indicate that a gap in the density of states opens at this density. Opening of a gap between states of essentially $6s$ and $6p$ character can be understood as a consequence of the combined effects of reduced atomic coordination number and increased interatomic spacing in the low-density liquid.[9]

In Fig. 2 we present a P-T phase diagram showing the liquid-gas coexistence curve in the high-pressure, high-temperature region. On the liquid side, near the coexistence curve, the point of vanishing Knight shift may be seen. Assuming that the metal-nonmetal transition occurs at a constant density in the liquid

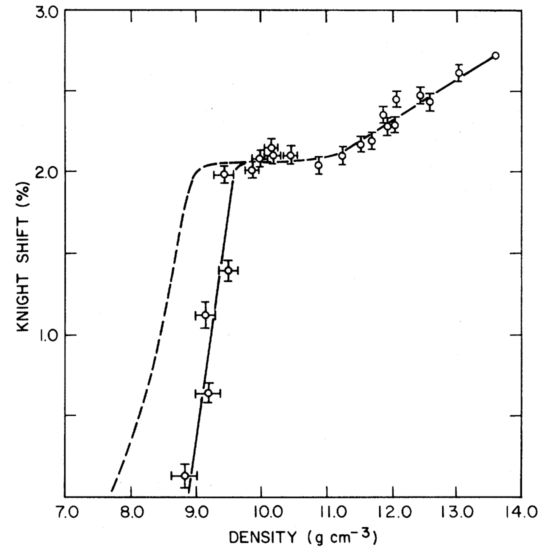

FIG. 1. ^{199}Hg Knight shift vs density close to the liquid-gas coexistence curve in expanded liquid mercury. Densities were determined from new equation-of-state parameters given in Ref. 2 as described in text. Broken line shows approximate variation of Knight shift as presented in Ref. 3 (I).

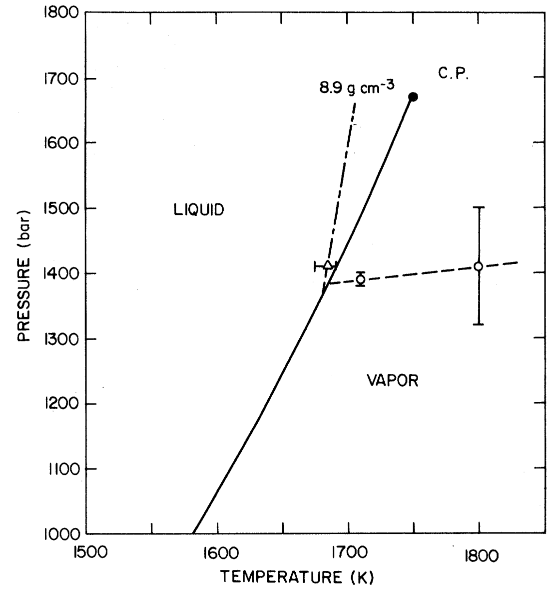

FIG. 2. Pressure-temperature phase diagrams of mercury at high pressures and temperatures. Solid line denotes vapor pressure variation (Ref. 6) up to critical point (C.P.); triangle, point of vanishing Knight shift determined from revised temperature calibration; open circles, location of plasma transitions reported in Ref. 4 (II). Dot-dash line in liquid field indicates 8.9 $g\,cm^{-3}$ isochore (Ref. 2).

near the coexistence curve, we indicate the approximate variation of the transition point by the isochore for 8.9 $g\,cm^{-3}$. On the vapor side we have shown the locations of the plasma transitions reported in II. It may be seen that the liquid and vapor transitions extrapolate, within experimental error, to a common point on the coexistence curve.

The result shown in Fig. 2 reveals an unexpected symmetry between the liquid phase metal-nonmetal transition and the vapor phase plasma transition or ionization catastrophe in mercury. Expressed another way, the result implies that as the temperature of a two-phase sample is raised through a special temperature $T_x \cong 1685$ K, *simultaneous* transitions occur in the liquid and in the vapor with which it is in equilibrium. It was concluded in II that the transition in the vapor corresponds to formation of dense, thermodynamically stable, charged droplets. This interpretation is supported by recent theoretical calculations by Hernandez[10] and by Hefner *et al.*[11] The detailed thermodynamic nature of these transitions and the nature of the liquid in the nonmetallic state are poorly understood at the present time. However, these effects, which have no counterpart in insulating fluids, clearly illustrate the important interplay between electronic and thermodynamic properties near the critical region of a metallic fluid.

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[1]For a review with numerous references, see N. F. Mott, *Metal-Insulator Transitions* (Taylor and Francis, London, 1974).

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[5]S. R. Hubbard and R. G. Ross, Nature 295, 682 (1982).

[6]R. W. Schmutzler, private communication.

[7]These corrections result from the use of the unpublished vapor pressure data of Schmutzler (Ref. 6). Use of the data of Ref. 5 leads to an additional downward correction of 15–20 K in the highest-temperature range. Since the temperature measurement and calibration procedures of Refs. 2 and 6 were closely similar, we considered the use of Ref. 6 to be preferable for establishing the density scale

of the Knight-shift data. However, the principal conclusions of this paper are not dependent on this choice.

[8]The sharply decreasing value of the Knight shift should not be confused with a change in *intensity* of the NMR which is to be expected at the vaporization transition. Thus the effect shown in Fig. 1 occurs entirely within the liquid range and cannot reflect accidental crossing of the phase boundary.

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[11]W. Hefner, B. Sonneborn-Schmick, and F. Hensel, Ber. Bunsenges. Phys. Chem. (in press).