Dielectric Anomaly and the Vapor-Liquid Phase Transition in Mercury

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Measurements are reported of the pressure dependence of the real part of the dielectric constant of subcritical and supercritical Hg vapor. Abrupt upward deviations from normal Clausius-Mosotti behavior, which are exhibited in an extremely narrow pressure range in the subcritical vapor phase, indicate that the vapor-liquid phase transition near the critical region is preceded by a heretofore undetected "plasma transition." It is concluded that the dielectric anomaly is caused by the formation of dense, charged thermodynamically stable droplets.

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Despite considerable experimental and theoretical efforts over the past ten years, there still remains a fundamental controversy about the nature of the gas-liquid critical point of metals. While the pioneering studies[1-3] explored the interrelation between the gas-liquid phase separation and the metal-nonmetal (M-NM) transition which occurs at reduced densities of the fluid metal,[4] more recent theoretical concepts emphasize the role of plasma phase transitions which are connected with ionization phenomena and many-particle interactions in the dense metal vapor.[5,6]

In this Letter we report the first experimental result which we regard as compelling evidence that in Hg vapor close to its gas-liquid critical point ($T_c = 1750$ K, $p_c = 1670$ bars) the interaction of charges with neutral atoms leads to a phenomenon similar to a "phase transition." To our knowledge this transition has never before been reported in the literature.

We used optical reflectivity and absorption measurements to determine the real part of the low-frequency dielectric constant ϵ_1, which appears to be particularly suitable for investigating a transition in a metal vapor.[7] Our experiments were performed with use of an internally heated autoclave pressurized with argon gas. The Hg sample was contained in a cylindrical cell closed with long synthetic sapphire windows which led out of the hot part of the cell into a cold high-pressure closure. The cell was connected to an external reservoir maintained at the same pressure as the autoclave. The sample temperature was measured with use of two thermocouples in close contact with the hot part of the cell where the Hg sample was located. Since it is impossible to avoid systematic errors in temperature measurement arising from convection in the compressed argon gas, we calibrated the sample temperature by employing the most accurate vapor pressure data.[8,9] At a given pressure the vaporization temperature could easily be found as an abrupt change in the transparency when the Hg sample is vaporized. The low-frequency limit of the optical measurements is given by the cutoff of the sapphire windows.

Selected experimental results for the real part of the dielectric constant ϵ_1 at the constant infrared energy $\hbar\omega = 0.6$ eV as a function of pressure are presented in Fig. 1 for the subcritical and supercritical temperatures $T = 1710$ and $T = 1800$ K, respectively. $p_v(1710\ \mathrm{K})$ is the vapor pressure of Hg at 1710 K. The most surprising feature of the data is the sharp enhancement of ϵ_1 by a factor of roughly 4 at a pressure of about 1400 bar, i.e., relatively far away from the critical value. This is in contrast to the behavior of nonmetallic fluids for which a comparatively

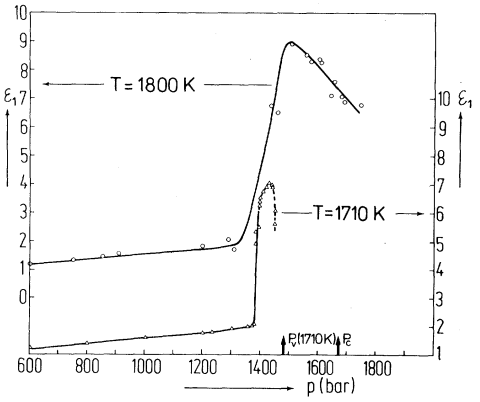

FIG. 1. Real part of the dielectric constant ϵ_1 of Hg vapor at the constant infrared energy $\hbar\omega = 0.6$ eV as a function of pressure p for the subcritical and supercritical temperatures $T = 1710$ and 1800 K, respectively. The arrows indicate the vapor pressure p_v at 1710 K and the critical pressure p_c.

moderate dielectric anomaly occurs very close to the critical point.[10-12]

More physical insight is obtained when ϵ_1 is plotted as a function of density N, as shown in Fig. 2. Values of N for each set of p-T coordinates were obtained from recent work of Schmutzler.[8] For comparison we show in Fig. 2 a graph (dashed line) of the behavior of ϵ_1 calculated with the Clausius-Mosotti relation for $\hbar\omega = 0$ using the polarizability of the isolated Hg atom. A striking upward deviation from Clausius-Mosotti behavior is observed in an extremely narrow density range near $N = 9\times10^{21}$ cm^{-3}, followed by a smooth decrease of ϵ_1 at larger N. The onset of the dielectric anomaly is accompanied by an abrupt change of the character of the absorption spectrum.[13] For $N < 9\times10^{21}$ cm^{-3} a steep, nearly exponential edge with negligible absorption in the infrared spectral range is observed, whereas for $N \gtrsim 9\times10^{21}$ cm^{-3} strongly temperature- and density-dependent absorption tails appear at energies below the edge ($\lesssim 1$ eV). At the same time the dc conductivity $\sigma(0)$ remains very small ($\lesssim 10^{-3}$ Ω^{-1} cm^{-1}). The shape of the spectral dependence of the optical conductivity $\sigma(\omega)$ derived from a careful analysis of reflectivity, absorption, and $\sigma(0)$ is shown schematically in the inset of Fig. 2. It is easily seen from an analysis of $\sigma(\omega)$, applying the Kramers-Kronig dispersion relation for ϵ_1 [Eq. (1)], that the density-induced increase of ϵ_1, which is smeared out over a certain density range at the finite frequency $\hbar\omega = 0.6$ eV, becomes extremely sharp and more enhanced in the very-low-frequency limit $\hbar\omega \to 0$ as indicated by the dotted lines in Fig. 2:

$$\epsilon_1(\omega) = 1 + 8\,\mathrm{P}\int_0^\infty \frac{\sigma(\omega')d\omega'}{\omega'^2 - \omega^2} \qquad (1)$$

(where P denotes the principal part).

The abrupt change of the optical properties of Hg at $T = 1710$ K for $N \gtrsim 9\times10^{21}$ cm^{-3} and, in particular, the sharp rise of ϵ_1 provide strong evidence for a plasma transition in Hg vapor. We are aware of only one mechanism which can cause such a transition in a weakly ionized gas under conditions when the Coulomb interaction between charged particles is still negligible. Because of the attractive electron-atom interaction the electrons can polarize a cloud of neutral atoms around themselves to form negatively charged clusters. Since a charge present in a medium of neutral atoms causes a local density increase, which can lead to a gas-liquid phase transition in the compressed region,[14] we conclude that the dielectric anomaly in Hg vapor is caused by the formation of dense, charged stable droplets for $N \gtrsim 9\times10^{21}$ cm^{-3} at temperatures close to the gas-liquid critical temperature. It is obvious that this effect sharply shifts the ionization equilibrium. The first specific reference to the possible existence of such a "plasma transition" that we have seen is given by Lifshitz

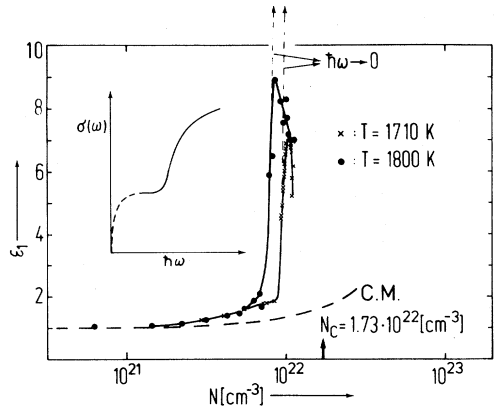

FIG. 2. Real part of the dielectric constant ϵ_1 of Hg vapor at $\hbar\omega = 0.6$ eV as a function of the number density N for the subcritical temperature $T = 1710$ K and the supercritical temperature $T = 1800$ K. The dashed line (C.M.) is the Clausius-Mosotti relation using the polarizability of the isolated Hg atom. N_c is the critical density. The inset gives a schematic illustration of the shape of the optical conductivity $\sigma(\omega)$ of Hg vapor at densities $N \gtrsim 9\times10^{21}$ cm^{-3}.

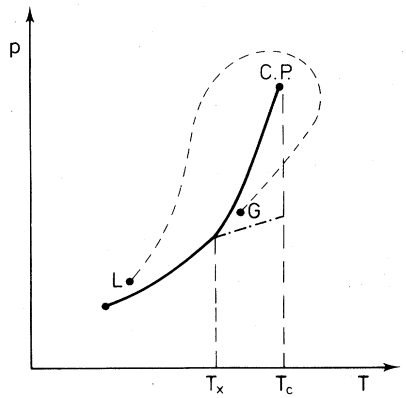

FIG. 3. Schematic illustration of the phase diagram of liquid mercury in the p-T plane. The solid line is the vapor pressure curve up to the critical point (C.P.). The dash-dotted line indicates the location of the dielectric anomalies at subcritical temperatures. The dashed line and T_x are described in the text.

and Gredescul,[14] who showed by an analysis of the free energy of a system consisting of an electron and a medium of classical particles that the appearance of an indirect particle interaction via the electron can cause a transition from a normal gas distribution to a dense cluster in a narrow interval of T or N, respectively.

We remark finally (p-T plane in Fig. 3) on the possible relation between the gas-liquid phase boundary (solid line) of Hg and the dielectric anomalies (dash-dotted line), which occur in an extremely narrow pressure range for $T < T_c$ and which are smeared out for $T > T_c$ (see, e.g., Fig. 1). On the basis of the foregoing discussion we assume that across the dash-dotted line a "transition" occurs from a normal slightly ionized gas phase to an equilibrium disperse system containing charged dense droplets. Of special interest is the point marked T_x which subdivides the liquid-vapor coexistence line into two parts. For $T < T_x$ a transition from a normal rarefied vapor to a microscopically homogeneous metallic liquid is observed. With increasing T a gradual diminution of metallic properties is observed in liquid Hg along the coexistence line. At $T = T_x$ the electrical transport[4] and magnetic properties[15] of the liquid change over smoothly to distinctly nonmetallic behavior. Conflicting models for the mechanism of this M-NM transition have been advanced by Mott[16] and by Cohen and Jortner[17] emphasizing, respectively, the roles of disorder-induced electronic localization and inhomogeneities due to density fluctuations. The existence of stable heterophase fluctuations in the vapor for $T \geq T_x$ certainly favors an inhomogeneous model for the M-NM transition at least along the dashed path from point G to point L (in Fig. 3) around the critical point. The gas-liquid phase transition for $T \geq T_x$ thus appears to us as a condensation of the vapor containing disjoint dense, charged stable clusters to a liquid which retains a very complex structure of its own. We suggest that an improvement of the theory of Lifshitz and Gredescul,[14] to the point where it can deal with dense systems in which extensive interaction between the heterophase fluctuations occurs, can answer the long-standing question of whether liquid Hg in the range $T_x \leq T \leq T_c$ is microscopically inhomogeneous. The present experimental evidence is insufficient to provide a clear-cut answer.

However, the following noteworthy phenomena specifically support the above hypothesis of two different liquid-phase transitions in Hg: An analysis of the existing liquid[18] and vapor[8] densities along the coexistence curve by Schmutzler shows a clear change of the shape of the coexistence curve for $T > T_x$. The corresponding change in the slope of the vapor pressure curve has also been observed.[9]

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