PREWETTING PHENOMENA IN MERCURY VAPOR

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ABSTRACT. The acoustic characteristics of mercury in molybdenum and niobium cells have been measured in detail at high temperatures (to 1900 K) and high pressures (to 1800 bar). The sound velocity, and the transmitted and reflected signals were observed simultaneously. Apparent first-order phase transitions appear in the vapor region of the mercury phase diagram. The transition curve (for Mo) meets the bulk liquid-gas coexistence curve tangentially at $(T_0, P_0) \cong$ (1250 K, 300 bar) and terminates above 1860 K and 1830 bar. The data provide strong evidence that these observations represent prewetting transitions, bounded below by a wetting transition at $(T_W, P_W) \equiv (T_0, P_0)$ and above by prewetting critical points which lie well above the bulk critical point ($T_c \cong$ 1764K, $P_c \cong$ 1670 bar).

KEY WORDS: acoustical properties, data, critical state, wetting and prewetting transitions, mercury.

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1. INTRODUCTION

The properties of mercury in the broad vicinity of the critical point have attracted considerable attention in the last three decades. This has arisen thanks to a general interest in the problem of the metal-nonmetal transition [1], and, in particular, owing to work of Landau and Zeldovich [2] where such a transition in expanded liquid metals was discussed theoretically. The choice of mercury is natural because it has the lowest critical temperature among the metals. (According to the latest results, the critical parameters of mercury are $(T_c, P_c) \cong$ (1764 K, 1670 bar) [3]; these data agree well with the most accurate previous results and, in particular, closely coincide with the data of Neal and Cusak [4].)

On the basis of experimental observations of the electronic properties (see, for example [5]) supported by a theoretical model of the structure variations [6], it is now generally accepted that the metal-nonmetal transition in mercury occurs in the liquid phase near the isochore of density 9 g/cm$^3 \cong 1.5\rho_c$. (The critical density, ρ_c, is close to 6 g/cm^3 [7, 8].)

However, already in the 70's it was known that some features of mercury behave abnormally even far away from the metal-nonmetal transition region, in particular, near the critical isochore (the thermopower: see for instance [4, 9]) and in the vapor phase (the thermopower [4] and the optical reflectivity [10, 11]). In order to clarify this situation a series of acoustical experiments have been performed [3, 12, 13].

The results found in 1993 [12] testified to the presence of a previously unknown first-order phase transition situated in the vapor part of the phase diagram, in the same region

where the anomalies of thermopower and optical reflectivity were observed earlier. It was tentatively suggested that the new transition had a “cluster” origin.

After the second, more searching experiment [3] it became clear that another, namely, a prewetting interpretation of the acoustical anomalies should be investigated: this was the purpose of the most recent experiments. The principal results of this study have been published in [13]. Here we present additional details along with results of further experiments.

2. EXPERIMENTS

The measurements have been performed by using a pulsed phase-sensitive technique [14]. This technique provides precise sound velocity data (with errors within 0.4 %) and allows one to measure with moderate accuracy the amplitudes of the acoustical signals transmitted through the cell and reflected against the buffer-rod/sample boundary. The frequency of the sound oscillations was 10 MHz.

In order to prevent strong convective flows near the liquid-gas transition, a vertically oriented cell of a special construction was used [3]. The orientation and construction of the cell played an important role in the observations [13].

Another important characteristic of the experiments was the uniformity of the temperature field over the sample. It was measured by two thermocouples arranged in the cell body near the edges of the upper and lower faces of the sample volume [3]. (In the latest experiments, a third thermocouple was installed above the center of the upper sample/buffer-rod boundary and used to monitor the radial temperature gradient). All the

thermocouples (including the thermocouples used in [12] and [3]) were manufactured from one pair of (W-Re5%) and (W-Re20%) wire coils calibrated according to international standards [7b]. The thickness of the wall between the thermocouples and the sample space was 0.5 mm. The temperature gradient in the first experiments [12] was, as a rule, within 10-15 K (so the relative gradient was of order 10^{-3}**);** in the later experiments it varied from 2 to 8 K. The temperature gradient is the main factor controlling the BC section of the observed sound-velocity anomalies that are illustrated in Fig.1 [13]; the extent of this

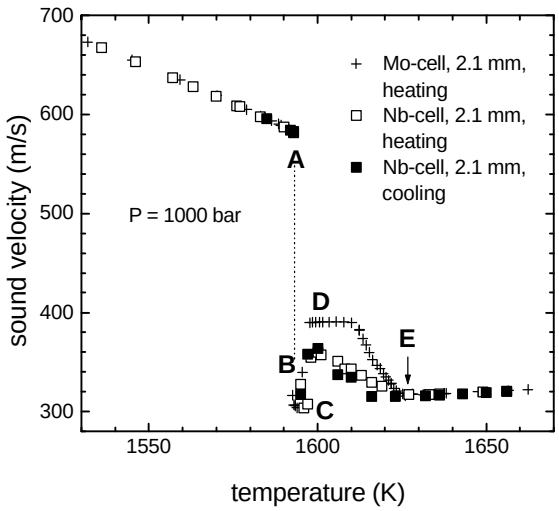

Fig.1. Sound velocity in mercury at 1000 bar measured in the various cells.

section is reduced when the temperature gradient is lower [3]. One can thus expect that the BC segment will disappear in a uniform temperature field. Essentially, however, the gradient was much smaller than the overall temperature interval occupied by the acoustical anomalies.

The cells used in the experiments [3] and [12] were made of molybdenum; the sample length was close to 2.1 and 2.6 mm, respectively. But if wetting phenomena are involved, some dependence on the cell (that is on the substrate) material should be seen. So the next experiment was performed with a cell of the same construction and sample length (2.1 mm), but made of niobium.

The sound velocity data at pressure 1000 bar obtained with the molybdenum and niobium cells are compared in Fig.1. (See also [13].) They support the wetting scenario. Further, stronger support was found from the results of the amplitude measurements of the acoustical signals. In Fig.2 typical results obtained with a new molybdenum cell of sample length 0.7 mm are shown. In fact, they do not differ significantly from the analogous results for the niobium cell [13]. Features such as the different jump positions of the signals reflected in the upper and the lower buffer rods (correspondingly at the A- and E-point) exclude the possibility of a bulk interpretation and testify to the prewetting scenario.

3. DISCUSSION

As noted in [13] and visible in Fig.2, the transmitted signal jumps (or oscillates sharply) near the high-temperature end of the anomalous region, that is near the E-point. (Note that the scales for the liquid and vapor branches of the transmitted signal in Fig.2 are

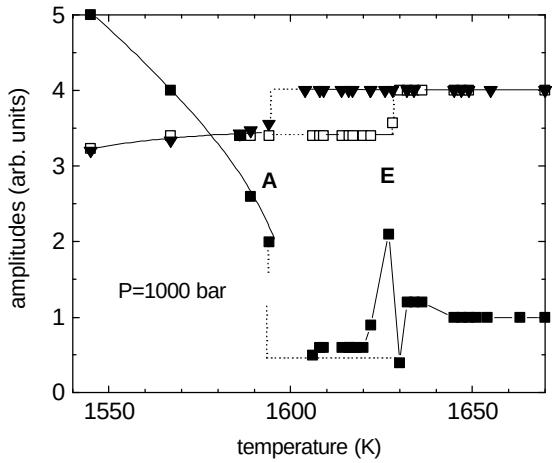

Fig.2. Amplitides of the acoustial signals for the Mo cell with *L* = 0.7 mm: solid squares, transmitted through the cell; open squares, reflected in the lower buffer rod; solid triangles, reflected in the upper buffer rod. Note that the lower data branch of the transmitted signal (above 1600 K) is plotted on a different, larger scale.

different: the signal in the vapor was much smaller than in the liquid.) In Figs.3 and 4 the sound velocity and the transmitted-signal amplitude obtained using a molybdenum cell [3] are shown. The locations of the E-points, that is the points of a first-order prewetting phase transition, are shown in the phase diagram in Fig. 5, that was published originally in [13]. The fact that one is dealing with a first-order transition is supported by the hysteresis seen at the E-points on heating and cooling the sample: see, especially, Fig.1 and Fig. 6 (below).

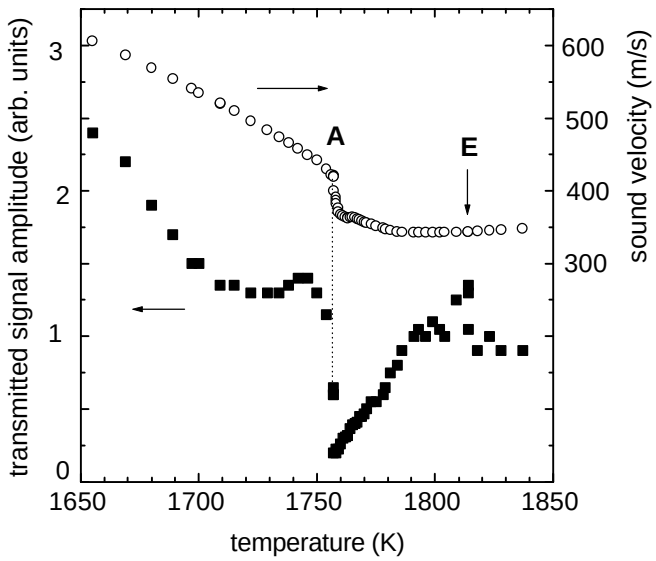

Fig.3. Transmitted signal amplitude and sound velocity at 1640 barin a molybdenum cell. (The dotted line corresponds to the boiling temperature.)

A smooth coalescence of the A and E points was found at a pressure near 300 bar. That accords with the theoretical requirement (see [15], for example) that a prewetting line must meet the bulk gas-liquid boundary tangentially at the wetting point (T_W, P_W). We believe that the wetting transition in mercury on a molybdenum substrate is located near (1250 K, 300 bar); however, this should be considered as an upper bound on the wetting point parameters in view of the obvious difficulty of determining experimentally the point of tangency of two curves.

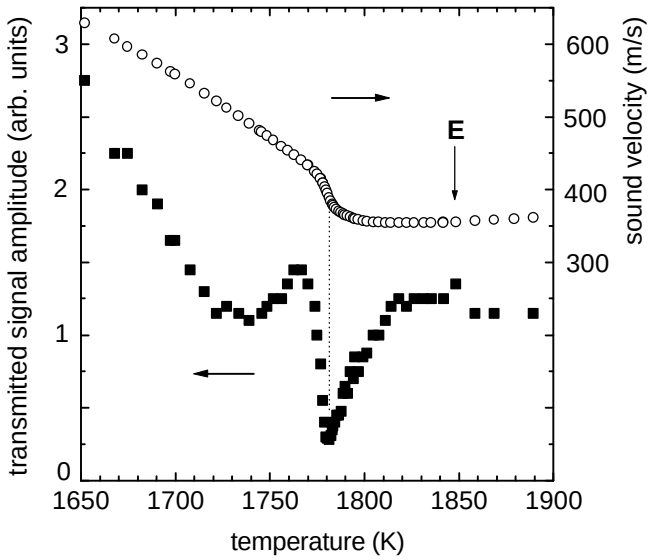

Fig.4. Transmitted signal amplitude and sound velocity at 1750 bar. (The dotted line corresponds to the critical isochore.)

The present results allow us to make a rather rough estimate of the prewetting critical point parameters for mercury on molybdenum: ($T_{c,\,pre}$, $P_{c,\,pre}$) ≥ (1860 K, 1830 bar); it is certain, however, that the prewetting critical point lies *well above* the bulk liquid-gas critical point. This is consistent with theoretical predictions when the substrate enhances the local effective interaction [16].

A striking resemblance of the phase diagram shown in Fig. 5 to the results of Tostmann *et al*. [17] may be noted. These authors studied wetting and prewetting in the

metallic fluid K-KCl in a *sapphire* cell probed by second-harmonic light generation. They also found, in contrast to dielectric systems, that the wetting transition occurs *well below* the bulk critical (or consolute) point, the prewetting line is *well separated* from the coexistence curve, and the prewetting critical point lies *well above* the bulk point. On the other hand, according to [18] the prewetting critical point of mercury on *sapphire* lies *below* the bulk critical point and the wetting transition takes place at a reduced temperature $(T_c - T_.)/T_c < 0.1$.

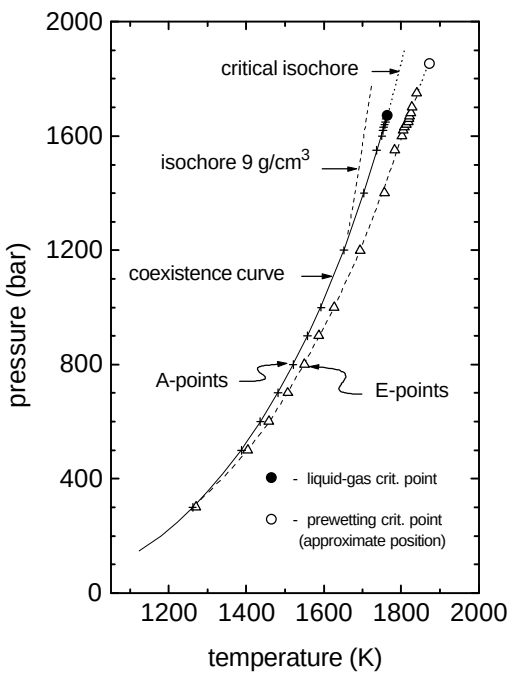

Fig.5. Phase diagram of mercury showing the prewetting line on a molybdenum substrate. (After Ref.[13].)

If the sound velocity within the wetting layer in our experiments is similar to that observed in the bulk liquid, the data obtained suggest a thickness of order 0.1 mm on the face of the lower buffer rod. Such a large layer thickness was, previously, the main obstacle to accepting a prewetting interpretation. But, as noted in [13], such a “swollen” layer probably results from a dynamic equilibrium established between the shedding of liquid down from the prewetting layers on the upper and vertical walls (with thickness of order 100 Å [13]), and a more-or-less bulk layer boiling off the lower buffer-rod face. In order to check this interpretation a new experiment has been performed.

As can be seen from Fig.5 of Ref.3, the value of the sound velocity at the D-point (that corresponds to the maximal thickness of the layer) changed just a small amount on a 20 %-reduction of the sample length in two experiments [3, 12] with molybdenum cells. This might be considered as a demonstration of a lack of dependence of the results on the cell geometry and, therefore, as evidence for a bulk character of the anomaly. But, as also noted [3], the temperature inhomogeneities were different in the two experiments under comparison. Consequently, the observed coincidence could well be merely a result of the different temperature conditions. Thus a new experiment was performed, again using a molybdenum cell with a heater of the same construction as in [3] and [13], but with a much smaller sample length, namely, 0.7 mm.

The corresponding amplitude results at 1000 bar are shown in Fig. 2; as has already been noted, they are not, in fact (on taking account of the difference in the acoustical impedance of molybdenum and niobium), very different from the corresponding data for the niobium cell [13]. But the sound velocity behavior in the anomalous region did change

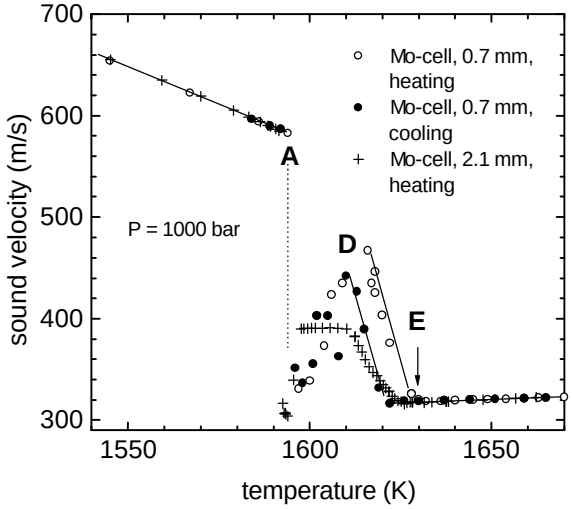

Fig.6. Sound velocity in mercury at 1000 bar measured in molybdenum cells with different sample lengths.

drastically: see Fig.6. The data thus support the “dynamic equilibrium” scenario suggested in [13]. The much smaller sample volume, comparable in length with the layer thickness of the previous experiment [3], creates difficulties in establishing the same dynamic equilibrium as appeared in the longer cells. It should also be noted again that strong hysteresis is observed near the point of the prewetting transition at E.

We conclude that the new results provide additional support for the prewetting interpretation of the acoustical anomalies, and, in particular, for the phase diagram shown in

Fig. 5 [13]. Therefore, they also support the view that the prewetting phenomena, although rather weak in themselves, can be intensified many-times under suitable conditions. Indeed, they might prove useful for certain technical applications.

Finally, we may return to the specific features of the thermopower observed in mercury in cells with *ceramic* (AlO_2 and BeO) isolators near the critical isochore, as well as to the strange absence of the "critical minimum" of the sound velocity in various experiments [3, 12, 19, 20] performed with molybdenum and *sapphire* cells. We believe that the phase diagram of Fig.5, and, in particular, the location of the prewetting critical point above the bulk point, might cast new light on these peculiarities, permitting one to hypothesize that they find an origin in the prewetting phenomena. However, this issue certainly requires further study.

ACKNOWLEDGMENTS

We are grateful to Dr. J.M.H. Levelt Sengers for her active interest and encouragement. We have benefited from comments by and discussions with W. Freyland, F. Hensel, Yu. Kagan, M. Moldover, K. Tamura and V. Vaks. Colleagues A.A. Borzhievskii, E.V. Grodzinskii, and N.A. Naumenko kindly assisted in the preparation of the experiments, which were supported by the Russian Basic Research Foundation via Grant No. 94-02-03656; M.E.F. acknowledges support from the National Science Foundation (under Grants No. CHE 93-11729 and CHE 96-14495).

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