

A precursor of liquid–liquid coexistence in the metal–nonmetal transition range of fluid mercury

Keisuke Kobayashi¹, Hiroaki Kajikawa², Yusuke Hiejima³, Taiki Hoshino, Makoto Yao^{*}

Department of Physics, Graduate School of Science, Kyoto University, 606-8502 Kyoto, Japan

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Abstract

We have carried out precise measurements of sound velocity c for fluid mercury at high temperatures and high pressures. The temperature coefficient of the sound velocity at constant pressure is negative in the metallic region, but it becomes small and positive in the non-metallic region. Similarly, the pressure coefficient at constant temperature is positive in the metallic region, while it is negative in the non-metallic region. Moreover, there appears a hump in the temperature or pressure dependence of c in the metal–nonmetal (M–NM) transition range. These anomalous behaviors could be understood if we would assume a hypothetical two-phase region in the M–NM transition range.

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1. Introduction

Landau and Zeldovich [1] proposed in 1943 that the electronic transition could introduce additional lines of first-order transitions in the phase diagram of the fluid state. However, their proposal has not been proved experimentally thus far, though liquid–liquid transitions attract much interest recently, especially after Katayama's experiment on liquid phosphorous [2]. In this paper we present experimental evidence that could be understood if we would assume hypothetical liquid–liquid coexistence in the M–NM transition range of expanded liquid Hg.

Since Hg has the lowest critical temperature (=1478 °C) among the metallic elements and relatively low critical pressure (=167 MPa), its physical properties have been extensively studied, which reveals that Hg exhibits an M–NM transition in the density range 8–9 g/cm³ [3]. From measurements of the optical gap [4], the Knight shift [5] etc. as well as *ab initio* molecular dynamics simulations [6], it is concluded that the M–NM transition in liquid Hg is mainly due to the lack of overlapping between the 6s and 6p bands (i.e. a Wilson transition).

Recently, we have found that the M–NM transition also influences liquid dynamics [7]. Besides the critical attenuation, a secondary maximum of the sound absorption is observed at the M–NM transition density. From the frequency dependence of the sound absorption, the structural relaxation time is estimated to be about 2 ns, which is remarkably long compared with the characteristic time (<ps) of the single-particle motion in simple liquids. Furthermore, an appreciable increase in small angle X-ray scattering has been found in this density range [8].

^{*} Corresponding author. Tel.: +81 75 753 3774; fax: +81 75 753 3780.
E-mail address: yao@scphys.kyoto-u.ac.jp (M. Yao).

¹ Present address: Taiyo-Yuden Co. Ltd., Gunma, Japan.

² Present address: NMIJ, AIST, Tsukuba, Japan.

³ Present address: Department of Chemistry and Chemical Engineering, Kanazawa University, Kanazawa, Japan.

Since these results are reminiscences of critical phenomena, we were prompted to perform precise sound velocity measurements to search for a phase transition. It has been known, since the pioneering work by Suzuki et al. [9], that the density dependence of the sound velocity exhibits an inflection in the M–NM transition range, but detailed data are still lacking for discussing the phase behavior.

2. Experimental

The sound velocity measurements were carried out at temperatures up to 1560 °C and pressures up to 200 MPa. The liquid Hg sample was contained in a sample cell, in which two single-crystalline sapphire rods, 8 mm in diameter and 89 mm in axial length, were inserted into a single-crystalline sapphire tube. At the center of the cell, the sapphire rods faced each other beyond a narrow gap, 0.2 mm to 0.4 mm in width, into which the liquid sample intruded. At the other end of each rod, which was kept near room temperature, a Pb(Zr–Ti)O₃ transducer with the fundamental resonance frequency ranging from 7.8 MHz to 16 MHz was bonded, and the sound was propagated through the rod to the liquid sample. The cell was put in an internally-heated high pressure vessel, which was pressurized with Ar gas. A detailed description of the sample cell and pressure vessel was given elsewhere [10].

In the present work, a phase-sensitive-detection technique was employed in the ultrasonic pulse transmission–reflection experiments. The absolute value of the sound velocity was roughly estimated by a conventional method in which the amplitude of transmission or reflected signals was utilized, and then the accurate value was determined by the phase of the signals. In order to keep the phase information correctly, the temperature step in the isobaric measurements was sometimes less than 1° and the pressure step in the isothermal measurements was usually 0.5 MPa. In this way the relative experimental error in the sound velocity was reduced to less than 0.2%. Further details of the phase-sensitive-detection technique are described elsewhere [11].

3. Results

Representative results of the sound velocity are displayed in Fig. 1 as a function of temperature. The measurements were done at constant pressures with a very small temperature step. The sample thickness was 0.21 mm and the ultrasonic frequency was 16 MHz. At supercritical pressures, the sound velocity c decreases smoothly with increasing temperature and approaches the ideal-gas values. At subcritical pressures, however, there is a small anomaly before the big drop due to the liquid–gas (L–G) transition. In the inset of Fig. 1, c near the anomalous change is depicted in an enlarged scale for 127 MPa. On the low temperature side (presumably, metallic side), the temperature coefficient $(\partial c/\partial T)_P$ of c at constant pressure is large and negative, while on the high temperature side

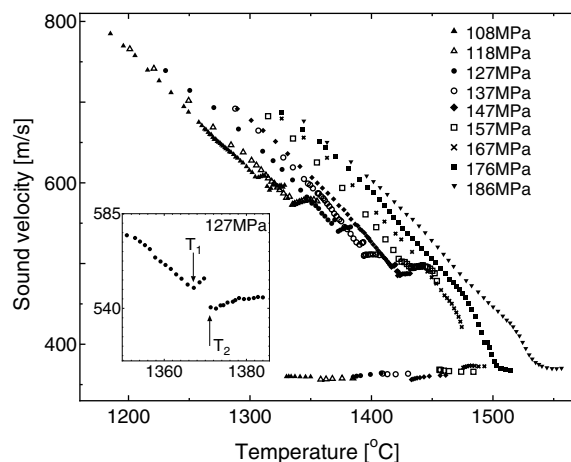


Fig. 1. Representative results of sound velocity c measured at various pressures are displayed as a function of temperature. The inset shows the temperature dependence of c for 127 MPa in an enlarged scale. Explanation of T_1 and T_2 is given in the text.

(non-metallic side), it is small and positive. The change of $(\partial c/\partial T)_P$ may correspond to the inflection in the density dependence of c , which was observed by Suzuki et al. [9] and subsequent workers [10,12,13]. In the present experiment, however, it is more clearly demonstrated because of improved accuracy. Moreover, there exist two characteristic temperatures: at a temperature T_1 , c begins to rise, and at a temperature T_2 , it drops abruptly. Such anomalous changes in the temperature dependence of c are still clearly seen at 147 MPa, but they are substantially damped at 157 MPa and washed out at higher pressures. No appreciable dependence of c on the frequency and intensity of the sound wave used were observed.

Another interesting feature expected from Fig. 1 is that the pressure coefficient of c , $(\partial c/\partial P)_T$, at constant temperatures should change its sign. In fact, we have confirmed this by measuring c along an isotherm as a function of pres-

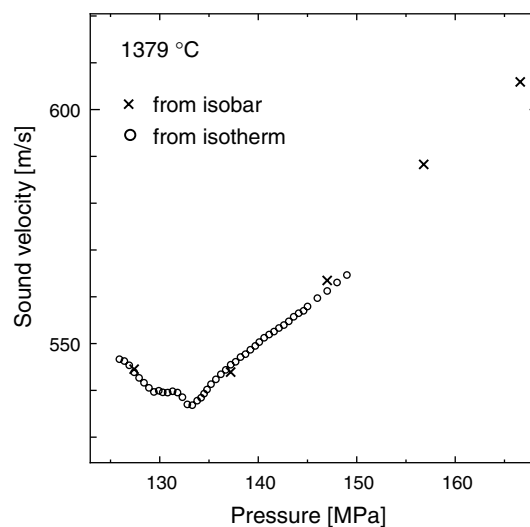


Fig. 2. The sound velocity c measured along an isotherm of 1379 °C is plotted by the circles as a function of pressure. The crosses denote c deduced from the isobaric results shown in Fig. 1.

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