NATURE OF THE THERMOELECTRIC POWER OF MERCURY IN THE TRANSCRITICAL STATE

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Much attention has been paid recently to the study of the transition from gaseous conductivity to metallic conductivity of metals near the critical parameter values. There are data on the equation of state and the conductivity of Cs [1] and Hg [2, 3]. The thermoelectric properties of Cs were investigated in [4] experimentally and theoretically in the region of critical temperatures and pressures. The calculated thermoelectric power on the isobar had a minimum as a function of the temperature. Unfortunately, what was measured was the integral of the thermoelectric power over a large temperature interval ($\Delta T/T \sim 1$) at a constant pressure, and the accuracy was not sufficient to observe an inflection in the observed values of the stresses. The thermoelectric power of mercury was measured recently [5, 6] near the critical values. A sharp decrease of the absolute magnitude of the thermoelectric power with increasing temperature was observed in [6], from large negative values $\sim 10^2$ μV/deg to about zero. No similar effect was observed in [5], where the experimental data terminated near the line where sharp changes of the thermoelectric power were observed in [6]. We present here the results of a measurement of the thermoelectric power of mercury in a wider range of pressures and temperatures, and call attention to the possible existence of one more minimum of the thermoelectric power at p = const with increasing temperature.

The thermoelectric power of mercury was measured in an internally-heated high-pressure chamber. A pressure up to 3.5 kbar was produced by freezing out argon with liquid nitrogen in a thermocompressor, followed by heating and compressing the gas in a booster with a press at a force of 200 tons.

High temperatures were produced with a graphite oven whose construction was described earlier [4].

The measuring element is a tungsten tube, sealed on the bottom with a tungsten cap into which a VR5-VR20 tungsten-rhenium thermocouple is welded. The cap is made as thin as possible (0.2 - 0.35 mm) at the location of the thermocouple. The upper end of the tube ends in an expander. An insulator (usually a BeO tube) is placed coaxially inside such a tungsten ampule, and an upper electroce is inserted in the insulator. The upper electrode is a thin-wall tungsten tube, on the lower end of which is welded a thin tungsten cap, in which a tungsten-rhenium VR5-VR20 thermocouple is welded. The leads of the thermocouple, insulated with a BeO sleeve, pass through the upper end of the tube.

The measuring element was filled with mercury, so that the mercury working volume was a cylinder 0.5 - 2 mm high and 2 - 5 mm in diameter, bounded by the insulator, the lower end face of the upper electrode, and the bottom cap of the lower tungsten ampule, which served as the second electrode.

The thermoelectric power was thus measured relative to tungsten, the absolute thermoelectric power of which was taken into account in the data reduction in accord with [7].

The small gap between the electrodes made it possible to perform the measurements at low temperature gradients, so that the thermoelectric power could be measured by a differential method at sufficiently low temperature.

With increasing temperature, the temperature difference between the ends of the working volume increased, and the measured values of the thermoelectric power corresponded to $\int_{T_1}^{T_2}(T)dT$.

The use of tungsten-rhenium thermocuoples and tungsten electrodes made it possible to measure the thermoelectric power of mercury at T > 2000°C.

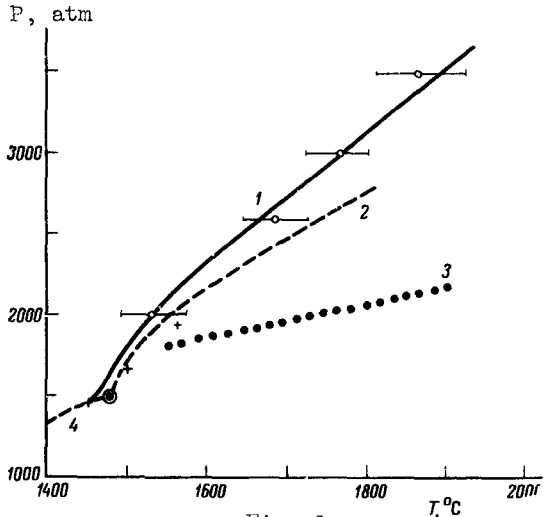

Fig. 1

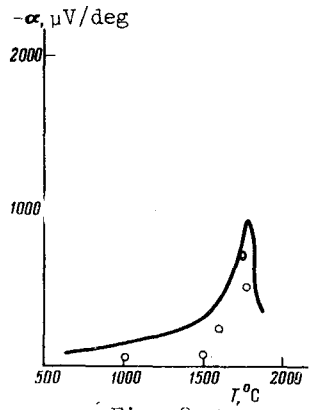

Fig. 2

Fig. 1. Pressure-temperature plane. Line 1 - Theoretical positions of the minima of the thermoelectric power of mercury. + - Experimental points obtained in [6]. o - Present data. Line 2 - Critical isochore of Hg from the data of [2]. Line 3 - Theoretical positions of the second minima of the thermoelectric power, calculated from the equation of state of the ideal gas. Line 4 - Liquid-gas transition line. ⊙ - Critical point of mercury.

Fig. 2. Thermoelectric power of mercury at constant pressure. Line - Theoretical calculation at p = 3000 atm. o - Experimental points of present work.

We performed the measurements at pressures from 500 to 3500 atm and temperatures up to 2100°C. In the temperature range up to 1700°C there is a reasonable agreement with the published data [5, 6]. The measurements at higher temperatures revealed the presence of lines of minima of the thermoelectric power and yielded an estimate of the thermoelectric power on this line. The measurement results are shown in Figs. 1 and 2.

The sharp minimum of the thermoelectric power observed in [6] is confirmed by our measurements in the entire range of investigated pressures. A theoretical calculation of the thermoelectric power at densities above critical encounters at present great difficulties. We can estimate tentatively the behavior of the thermoelectric power on the isobar as a function of the temperature, by using a variant of the free electron model similar to that used in the calculation of the thermoelectric power of Cs [4]. To calculate the concentration n_e of the "free" electrons, we used the data of [2] on the temperature dependence of the conductivity on the isochore. If we estimate $n_e \sim \exp(-\Delta E/T)$, then it follows from the indicated data that ΔE reaches a maximum of ~ 3 eV at $\rho \sim 7$ g/cm^3, and decreases sharply at both higher and lower densities[1]. The

[1]We note that an analogous maximum of the activation energy is observed in experiments on solutions of lithium [8] (at a lithium concentration x ∿ 3 molar per cent) and of sodium (at x ∿ 1 mpm) [9] in liquid NH_3. Unfortunately, there are no data on the thermoelectric power of Li in NH_3, and the data of [10] for Na do not contradict the possibility of a minimum of the thermoelectric power at x ∿ 1 mpm. More precise measurements are needed.

presence of this maximum, which is apparently a reflection of the competition between the growth of the depth of the wells capturing electrons through density fluctuations, on the one hand, and the simultaneous growth of the Fermi level, on the other, and is the cause of the minimum of the thermoelectric power, which was observed in [6] and by us. Figure 2 shows a tentative calculation of the thermoelectric power and the values obtained by reducing the experimental data. It should be noted that the conductivity itself is a monotonic function of the density, the main dependence on which is of the form $\sigma \sim e^{-A/\rho}$ [11]. At densities lower than critical, an activation energy again appears and is an approximately linear function of the density, $\Delta E \sim (T_0/2)(1 - \rho/\rho_c)$ [12] (I_0 = 10.4 eV). Such a dependence is obtained theoretically if account is taken of the interaction of the charged particles with the neutrals (cf. [12], where the calculations are given for Cs). Calculation for Hg yields for $I_0/2\rho_c \approx (h^2\sqrt{\pi\sigma}/m) + (4\pi\alpha e^2/r_0)$ (σ is the cross section for elastic scattering of an electron by a mercury atom, α is the polarizability, r_0 is the "radius" of the atom) a value 8×10^{-34} erg/cm^3, whereas experiment yields $I_0/2\rho_c \sim 10^{-33}$ erg/cm^3. Such a behavior of the "gap" should also lead to one more minimum of the thermoelectric power, analogous to the minimum obtained in the calculations for Cs [4], since $\alpha \sim (k/e)(\Delta E/T)$. The line of the second minima was estimated from the equation of state of an ideal gas, since there were no data on the equation of state of real mercury in the vicinity of this line. In conclusion we note that if our explanation of the observed minimum of the thermoelectric power of mercury is correct, then analogous phenomena should be observed also in measurements of the Hall effect in the indicated range of densities ($|R|$ should have a maximum at $\rho \sim 7$ g/cm^3)[2]. To draw more definite conclusions concerning the behavior of the thermoelectric power of Cs at densities above critical we need additional measurements of the conductivity and of the thermoelectric power, similar to those made for mercury.

[1] V.A. Alekseev, Teplofiz. Vys. Temp. 6, 961 (1968); H. Renkert, F. Hensel, and E. Frank, Phys. Lett. 30A, 494 (1969).
[2] I.K. Kikoin and A.P. Senchenkov, Fiz. Met. Metallov, 24, 843 (1967).
[3] E.U. Frank and F. Hensel, Phys. Rev. 141, 109 (1966); Ber. Bunsen, 70, 1154 (1966).
[4] V.A. Alekseev, A.A. Vedenov, L.S. Krasitskaya, and A.N. Starostin, ZhETF Pis. Red. 12, 501 (1970) [JETP Lett. 12, 351 (1970)].
[5] R. Schmutzler and F. Hensel, Phys. Lett. 35A, 55 (1971).
[6] L.I. Duckers and R.G. Ross, Phys. Lett. 38A, 291 (1972).
[7] N. Cusack and P. Kendall, Proc. Phys. Soc. 72, 898 (1958).
[8] R.D. Nasby, and I.C. Thompson, J. Chem. Phys. 53, 109 (1970).
[9] C.A. Kraus, J. Am. Chem. Soc. 43, 749 (1921).
[10] M.H. Cohen and I.C. Thompson, Adv. in Phys. 17, 856 (1968).
[11] V.A. Alekseev, ZhETF Pis. Red. 14, 295 (1971) [JETP Lett. 14, 195 (1971)].
[12] F. Hensel and E.U. Frank, Rev. Mod. Phys. 40, 697 (1968).
[13] V.A. Alekseev and A.A. Vedenov, Usp. Fiz. Nauk 102, 665 (1970) [Sov. Phys.-Usp. 13, 830 (1971)].
[14] R.D. Nasby and I.C. Thompson, J. Chem. Phys. 49, 969 (1968).

[2] For solutions of Li in liquid NH_3, a similar effect was observed in [14] at Li concentrations $\sim$3 molar per cent. We note, however, that the same authors consider this result in [8] to be a false signal, owing to the non-ohmic contact between the electrodes and the solution.