DIRECT MEASUREMENTS OF THERMODYNAMIC FUNCTIONS AND ELECTRICAL RESISTIVITY OF FLUID TUNGSTEN OVER A WIDE RANGE OF DENSITIES

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Outline of the presentation

- We have found earlier [V. N. Korobenko, A. D. Rakhel, PRB 85, (2012)] that fluid iron has a first order phase transition with the critical pressure $P \approx 5$ GPa, that is about one order of magnitude higher than the predictions of $P_c$ for the LV transition.

- In this work we have developed a supplementary technique and made sure that our measurements are accurate enough so that the question indeed arose: what is the reason of the unexpectedly high value of $P_c$? To get the answer we need to examine the other refractory metals.

- This is why we carried out the measurements of thermophysical properties of fluid $W$ over wide range of densities [V. N. Korobenko, A. D. Rakhel, PRB 88, (2013)]. We found that its critical pressure is also substantially (one order of magnitude) higher than the values of the estimates based on the similarity between the thermodynamic functions of $W$ and the low-melting point metals ($\text{Hg, Cs, Rb}$).
Photo of a tungsten foil strip (1) sandwiched together with a ruby plate (2) between two sapphire plates (3)
Schematic of the pulse heating experiments with the pressure measurements using the ruby scale

- Switch
- 180 nH, 0.18 Ω, 15 nH, 0.01 Ω
- Voltage divider
- To oscilloscope
- W sample
- Sapphire plate
- The lower electrode
- Ruby plate
- Beam splitter
- Nd-YAG laser
- Spectrometer
- Streak camera

\[ C_0 = 72 \, \mu F \]
\[ U_0 = 10-20 \, kV \]
Simultaneous measurements of the electric resistivity and the caloric EOS. Technique #1

The primarily measured quantities: \( I(t), U(t), P(t) \)

Resistance: \( R = \frac{U_R}{I} \)

Specific Joule heat: \( Q = \frac{1}{M} \int_0^t I U_R dt \)

Density: using \( P(t) \) dependence and EOS of sapphire the displacement of the sample-sapphire interface is determined

Internal energy: \( E = Q - A \)

Conductivity: \( \sigma = \frac{l}{R(t)h d(t)} \)

\( A = \int_{V_0}^V P(t) dV \)
Pressure as a function of time
Displacement of the metal-sapphire interface (symmetrical case)

\[ P = \frac{B}{n} \left[ \left( \frac{\rho}{\rho_0} \right)^n - 1 \right] \]

Sapphire EOS (isentropic flow)
\[ P < 100 \text{ kbar} \]

\[ J_{\text{\_}} = u - \int \frac{dP}{\rho c} = \text{const} \]

\[ u = \frac{2c_0}{n-1} \left[ \left( \frac{\rho}{\rho_0} \right)^{\frac{n-1}{2}} - 1 \right] \]

\[ \Delta X_1(t) = \frac{2c_0}{n-1} \int_0^t \left[ \left( \frac{nP(\tau)}{B} + 1 \right)^{\frac{n-1}{2n}} - 1 \right] d\tau \]

Displacement of the interface
Outcome of an experiment

$$\sigma = \sigma(P, V)$$

$$E = E(P, V)$$ - caloric EOS

along a line in the $PV$-plane
Simultaneous measurements of the electric resistivity and the caloric EOS. Technique #2

The primarily measured quantities: \( I(t), U(t), V(t) \)

Resistance:  \( R = \frac{U_R}{I} \)

Specific Joule heat:  \( Q = \frac{1}{M} \int_0^t IU_R dt \)

Density: using \( V(t) \) dependence and EOS of sapphire the pressure near the sample surface is determined

Internal energy: \( E = Q - A \)

Conductivity:  \( \sigma = \frac{l}{R(t)hd(t)} \)

\[ A = \int_{V_0}^V P(t)dV \]
By recording the light intensity of the interfering beams 2 and 3 we determine the displacement of the sample surface

\[ \phi_3 - \phi_2 = \Delta \phi_3 - \Delta \phi_2 - \omega_0 \tau \]

\[ \tau_1 = \frac{1}{c} \int_{X_1(t)}^{X_2} n_r \, dx \]

\[ n_r = a + b \rho \]

\[ X_1(t_{m+1}) - X_1(t_m) = \frac{\lambda_0}{2a} \]

\[ a = 1.7285 \text{ [B.J. Jensen et al, J. Appl. Phys. (2007)]} \]
Determination of pressure from the measured time dependence of the displacement of the sample surface

\[ P = \frac{B}{n} \left[ \left( \frac{\rho}{\rho_0} \right)^n - 1 \right] \]

\[ J_\perp = u - \int \frac{dP}{\rho c} = \text{const} \]

\[ P(t) = \frac{B}{n} \left[ \left( \frac{n-1}{2c_0} U_1(t) + 1 \right)^{2n/(n-1)} - 1 \right] \]

\[ u = \frac{2c_0}{n-1} \left[ \left( \frac{\rho}{\rho_0} \right)^{\frac{n-1}{2}} - 1 \right] \]

\[ U_1(t) = \frac{dX_1}{dt} \]
Photodetector signal for an experiment with a tungsten sample of 22 µm thickness ($\lambda_0 = 1550$ nm)
The density measurements of W in the solid and liquid phase. The difference between the values measured by the two methods < 4%, and the values are consistent (within 3%) with the dilatometric measurements whose error is <2%.
Determination of density on isobares

[V. N. Korobenko and A. D. Rakhel, J. Phys.: Condens. Matter (accepted, 2013)]

\[ \rho(W, P) \approx \rho(W, P_0) + \left( \frac{\partial \rho}{\partial P} \right)_W (P - P_0) \]

\[ \left( \frac{\partial \rho}{\partial P} \right)_W = \beta \left( 1 + \frac{1}{\Gamma} \right) \]

\[ \beta = -\left( \frac{\partial \ln \rho}{\partial W} \right)_P \]
\[ \Gamma = \left( \frac{\partial PV}{\partial E} \right)_V \]
\[ V = \rho^{-1} \]
Thermodynamic paths of the experiments in the $PV$-plane

Estimates of the critical point of W
Caloric EOS. The linear dependence of $E$ on $PV$ for $E > 7$ kJ / g where $P$ was nearly const

\[ c_V = \frac{1}{\gamma - 1} = \text{const?} \]

\[ E = \frac{PV}{\gamma - 1} + E_{\text{sub}} \]

$E_{\text{sub}} = 4.62 \text{ kJ/g}$

$I_1 = 4.2 \text{ kJ/g}$

$I_2 = 9.3 \text{ kДж/г}$
Near $V/V_0 \approx 1.8$ there is a transition in the two-phase state?

$$c_s = V \sqrt{-\left(\frac{\partial P}{\partial V}\right)_E + P\left(\frac{\partial P}{\partial E}\right)_V}$$

- Blue triangles: Hixson&Winkler
- Blue line: Fit to the values
- Red circles: This work values
Why $c_V$ does not depend on temperature on the isobars, but depends on pressure?

$$c_V = 1 / (\gamma - 1)$$

$$E = E_1(P)(1 - x_2) + E_2(P)x_2$$

$$V = V_1(P)(1 - x_2) + V_2(P)x_2$$

$$\left( \frac{\partial E}{\partial PV} \right)_P = \frac{d \ln P}{d \ln T} - 1$$

$$P = A \exp \left( - \frac{Q}{RT} \right)$$

$$\left( \frac{\partial E}{\partial PV} \right)_P = \frac{Q}{RT} - 1$$
Let us assume that the saturated vapor curve is closely logarithmic

\[ \ln P = C - \frac{D}{T} \]

From this work data we determined the constants \( C \) and \( D \) and compared them with those calculated from the saturated vapor pressure data for \( T < T_b \). Our values are about 10% smaller.

\[ \left( \frac{\partial E}{\partial PV} \right)_p = \frac{D}{T} - 1 \]

\[ \ln \left( \frac{P_A}{P_B} \right) = \left( \frac{\partial E}{\partial PV} \right)_{P_A} - \left( \frac{\partial E}{\partial PV} \right)_{P_B} \]

Using the values of \( C \) and \( D \) we verified that the values of pressure and the derivatives satisfy Eq. (1).
What about consistency of the vapor pressure curve determined here with the values of the velocity of sound in the two-phase state?

\[ c_m = \frac{D}{T} \frac{PV_1}{\sqrt{TC_{P1}}} \approx 1.6 \text{ km/s} \]
Conclusions

- Direct measurements of electrical resistivity and the caloric equation of state have been performed for fluid $W$ in a wide range of densities with an accuracy better than ± 10%.

- It has been shown that the critical pressure of the fluid exceeds 7 GPa.
Thank you for attention!