Experimental, Very High-Temperature, Liquid-Uranium Equation of State*

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U wire samples under very high confining gas pressures are heated Ohmically into the liquid phase. The sample diameter is measured after achievement of thermodynamic equilibrium. Enthalpy-volume isobars and resistivity-enthalpy curves are obtained. The data are fitted with a soft-sphere theory of liquids, and the critical point of U is estimated.

One of the main problems in high-temperature physics is the containment of a hot solid or liquid sample so that thermodynamic equilibrium is obtained and contamination by container material is avoided.[1] For this reason, good experimental data above 3000 K are rare. In the present Letter we describe equation-of-state and resistivity data obtained by a new method, for uranium in thermodynamic equilibrium up to 9000 K.

The apparatus consists of a pressure cell capable of holding He gas to 0.4 GPa (4 kbar) and a critically damped 45-kJ capacitor bank for resistively heating the 1-mm-diam by 25-mm-long sample. A large ballast resistor is in series with the sample so that the current pulse is independent of the sample resistivity. The energy deposited is controlled by timing the firing of a spark gap which short-circuits the sample, so that only a fraction of the capacitor charge passes through the sample. The current pulse is long enough (15-30 μsec) so that the skin effect is negligible and the sample is very near equilibrium at all times during the pulse. Further details of this part of the apparatus have been described elsewhere.[2] Refinements to the apparatus described in Ref. 2 include (1) a new sample and voltage-probe assembly which reduces the magnitude of the inductive contribution to the voltage measurement, (2) the addition of sapphire windows which allow us to replace the flash x-ray shadowgraph picture of the sample with an optical shadowgraph, and (3) the addition of a streaking camera to record the complete diameter-versus-time history of the expanding sample.

The equation-of-state data are the pressure, volume, and enthalpy of the hot liquid uranium. The pressure of the He gas surrounding the sample is constant during the expansion since the cell volume is much greater than the sample volume. This pressure is controlled and measured to within 1%. The enthalpy is controlled by varying the length of the current pulse and is comput-

ed as the time integral of the product of the current through the sample times the voltage drop across a carefully measured length of the sample. The inductive voltage is estimated and subtracted from the total voltage, although the overall correction to the enthalpy from this procedure is negligible. The sample volume is measured by streaking a slit image of the rod diameter. The sample is illuminated from behind with the 514.5-nm line from an argon-ion laser, while a narrow-band filter in front of the camera discriminates against the blackbody radiation. An actual streak record is shown in Fig. 1. Since the expansion is constrained to be only in the radial direction, the volume is proportional to the square of the diameter. Uniformity of the sample expansion along the axis has been demonstrated
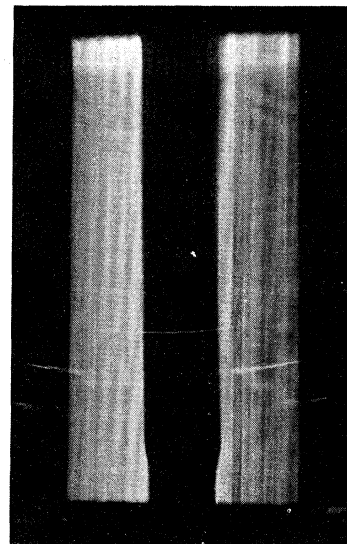

FIG. 1. A streak record of the expansion of the sample diameter. The initial diameter (bottom of record) is 1.0 mm while the final diameter (middle of record) is 1.16 mm. The pressure is 0.1 GPa (1 kbar); the final enthalpy is 0.59 MJ/kg; the streak duration is 200 μsec.

with both flash x-ray shadowgraphs[2] and optical
snapshots using a pulsed ruby laser. Based on
the accuracy of the diameter measurement in the
streak record and the diameter uniformity in the
snapshot, the estimated error in the volume mea-
surement is ±2%.

The long duration of constant expanded volume
in Fig. 1 indicates that thermodynamic equilibri-
um has been achieved within a few microseconds
of the end of the current pulse, and that the hy-
drodynamic instabilities characteristic of a long
liquid column do not set in for at least several
hundred microseconds. The final volume mea-
surement is made during this time interval. The
highest enthalpy shots for both 0.1- and 0.2-GPa
isobars showed short stagnations (10–20 μsec)
followed by rapid expansion. This could be due
to the entry of all or part of the sample into the
liquid-vapor two-phase region. Work is under-
way to investigate the cause of this late-time ex-
pansion.

The enthalpy-versus-volume isobars along with
static ($P = 1$ bar) experimental data[3] and theoreti-
cal curves are shown in Fig. 2. The hard-sphere
Van der Waals theory[4] (which has no adjustable
parameters) shows poor agreement with the ex-
perimental data. This is probably due to the un-
realistic coefficient of thermal expansion predict-
ed by the hard-sphere model. We use instead a
"soft-sphere" theory based on Monte Carlo cal-
culations with smooth inverse-power interparti-
cle potentials.[5] This theory is used as an empir-
ical fit to the data, since we do not have a relia-
ble theory of liquid uranium at expanded volumes.
The soft-sphere pressure and energy are given
by

$$\frac{pV}{NkT} = 1 + \frac{1}{3} n C_n \rho^{n/3}\left(\frac{\epsilon}{kT}\right) + \frac{1}{18} n(n+4)\rho^{n/9}\left(\frac{\epsilon}{kT}\right)^{1/3}$$

$$- m\rho^m\left(\frac{\epsilon}{kT}\right), \qquad (1)$$

$$\frac{E}{NkT} = \frac{3}{2} + C_n \rho^{n/3}\left(\frac{\epsilon}{kT}\right) + \frac{1}{6}(n+4)\rho^{n/9}\left(\frac{\epsilon}{kT}\right)^{1/3}$$

$$- \rho^m\left(\frac{\epsilon}{kT}\right) + \frac{E_0}{NkT}, \qquad (2)$$

$$\rho = N\sigma^3/\sqrt{2}\,V. \qquad (3)$$

Here N is the number of atoms, k is Boltzmann's
constant, C_n is the lattice constant[6] correspond-
ing to n, and E_0 is the cohesive energy. There
are four adjustable parameters: n, m, ϵ, and σ.
The parameters ϵ and σ are determined from the
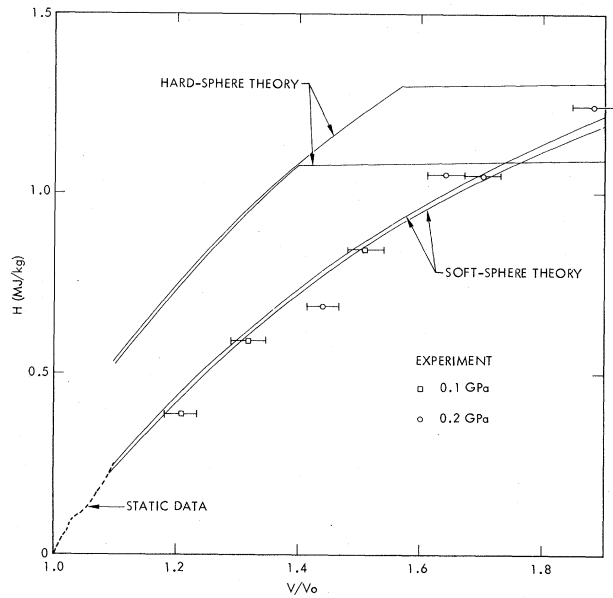properties of uranium at the melting point. The

FIG. 2. Experimental enthalpy—relative-volume iso-
bars compared with static data and theory. The breaks
in the hard-sphere curves represent entry into the li-
quid-vapor region. The soft-sphere theory has been
fitted to the experimental data. In both pairs of theore-
tical curves the upper and lower curves correspond to
0.2 and 0.1 GPa, respectively. The static data are
available up to the melting point of uranium and the
curve shows a change of curvature due to solid-solid
phase transformations. In this plot the enthalpy at
room temperature and normal volume (V_0) is taken to
be zero. The corrections to the experimental enthalpy
points due to the initial compression are negligible.

parameters n and m are then adjusted to fit the
experimental data. There are a number of (n, m)
sets that fit the data, so an additional condition
is required to narrow the choices further. We
choose this condition to be reasonable agreement
with the critical temperature and pressure as
predicted by the hard-sphere Van der Waals theo-
ry. We have some confidence in these numbers,
based on correlation of theory and experiment for
the alkali metals and mercury.[4]

The best soft-sphere theory fit is obtained for
$n = 6$ and $m = 0.75$. This fit predicts the tempera-
tures for the highest experimental enthalpy points
to be 6730 K (0.1 GPa) and 9260 K (0.2 GPa). The
entry into the liquid-vapor region is predicted to
take place at $V/V_0 = 1.95$ (0.1 GPa) and $V/V_0 = 2.30$
(0.2 GPa). The predicted critical constants are
$T_c = 12\,434$ K, $V_c = 0.2662$ m³/Mg, and $p_c = 0.4950$
GPa. The critical temperature is in close agree-
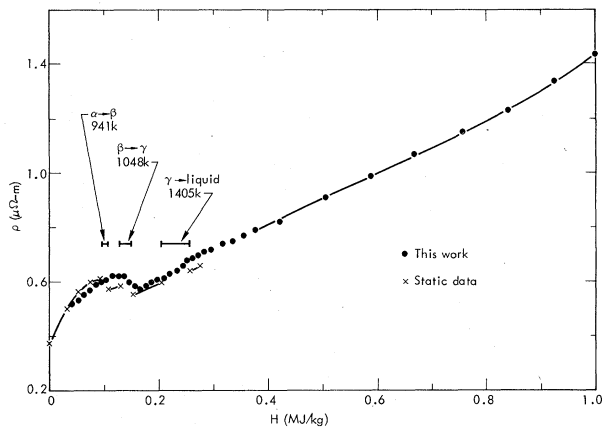ment with Grosse's estimate[7] of 12 500 K.

FIG. 3. Resistivity of uranium compared with static data. The solid-solid and solid-liquid transitions are indicated by the horizontal bars, along with the transition temperatures.

Since the sample diameter, the current, and the voltage are all measured as a function of time, the resistivity of the sample can be measured during the expansion. These data are presented in Fig. 3, with a comparison with the moderate-temperature static data of Busch, Guntherodt, and Künzi.[8] The quantitative agreement between the dynamic and static data is another indication that the sample is close to thermodynamic equilibrium at all times during the heating pulse. We have not attempted to make a theoretical calculation of the resistivity. The resistivity-versus-volume curve is, however, similar to that reported for expanded copper by Ben-Yosef and Rubin.[9]

By overcoming the containment problem and achieving thermodynamic equilibrium we have been able to extend equation-of-state and resistivity measurements to much higher tempera-

tures than were before possible. Also, by using an inert gas as the confining medium, we can subject the sample to accurately measured pressures comparable to the sample critical pressure, thus covering a large portion of the liquid range. Experiments are now being continued with carbon, and will later be extended to other materials. The experiment will be improved by extension of the pressure range and by direct measurement of the temperature.

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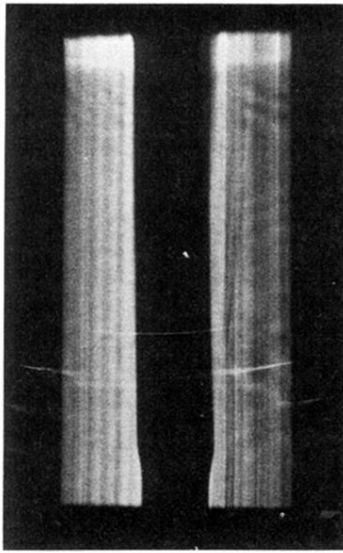[9]N. Ben-Yosef and A. G. Rubin, Phys. Rev. Lett. 23, 289 (1969).

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