International Journal of Thermophysics, Vol. 17, No. 5, 1996

Thermophysical Properties of Solid and Liquid Thorium[1]

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Experimental investigations of the thermophysical properties of both solid and liquid thorium have been made using our isobaric expansion facility. We have performed measurements under 0.06 GPa argon pressure up to the vicinity of the thorium boiling state (~ 5000 K). Enthalpy, volume expansion, and electrical resistivity data are reported and discussed. The electrical resistivity data display the different phase transformations in the solid and liquid states, before showing a sharp rise indicating crossing of the spinodal line. The enthalpies of transformations are measured and are in very good agreement with the available data in literature. Volume measurements show a strong expansion of liquid thorium up to the boiling state ($V/V_0 \sim 2$ at 0.68 MJ $\cdot$ kg^{-1}).

KEY WORDS: actinide; electrical resistivity; enthalpy; high temperature; liquid metals; pulse heating; thorium; volume expansion.

1. INTRODUCTION

Thorium metal, whose most stable isotope is ^{232}Th ($Z = 90$), belongs to the actinide series starting from Ac ($Z = 89$) and ending at Lw ($Z = 103$). This series is associated with the progressive filling of the shell of 5f electrons which play a fundamental role in the properties of actinides. Hence, for the light actinide elements (from Th to Pu), these 5f electrons are itinerant or delocalized and then may hybridize to the continuum states of the 6d7s conduction band [1] because of the proximity of the 5f, 6d, and 7s energy levels and the high electronic state density in the vicinity of the Fermi level (E_F). The delocalization of the 5f electrons of these actinide elements leads

[1] Paper presented at the Fourth International Workshop on Subsecond Thermophysics, June 27–29, 1995, Köln, Germany.

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0195-928X/96/0900-1001$09.50/0

to some unusual behavior due to their participation to the bonding of the conduction electrons resulting in stronger crystal cohesion. The role of the 5f electrons of actinides is well displayed by comparing them with rare earth (or 4f) elements whose 4f electrons are rather localized (except for Ce and Pr). One of these characteristics is the observation of a strong contraction of the atomic radius from Th to Pu [2, 3] similar to the one of 3d, 4d, and 5d transition elements. This variation is correlated with very dense crystal lattices of low symmetry at ambient conditions and also the increasing number of allotropic structures (2 for Th and 6 for Pu) in the P–T phase diagram. One should add that the magnetic properties of actinides are also affected by the presence of the 5f electrons: the early actinide elements are nonmagnetic, whereas the heavy ones (from Cm and onwards) present localized and magnetic states [4]. Moreover, Th has a nearly unique stability of its four valence states in compounds similar to d-transition metals (Ti, Zr, Hf) and its resistivity is typical of a transition metal.

Thorium, whose electronic configuration is $(Rn)5f^06d^27s^2$, occupies a unique position in this series, since it is the only element which presents an unoccupied 5f band. From photoemission measurements [5], Bremsstrahlung Isochromat Spectroscopy (BIS) [6], and band calculations [7], the latter lies at 0.91 eV above E_F. However, because of the strong hybridization with the 6d7s states, the conduction band is governed partially by the 5f character whose contribution at the Fermi level would be of 0.28 to the total density of states according to Skriver and Jan [7]. It is clear that this 5f contribution influences the physical properties of thorium such as the electrical resistivity, the specific heat, and the magnetic susceptibility, as shown by Fournier in his dissertation [8].

Under atmospheric pressure, Th crystallizes at room temperature in the fcc (α) structure, and then exhibits a phase transformation at 1633 K to change to the bcc (β) structure before melting at 2023 K [9].

Thorium has been the subject of studies under high pressures (up to 10 GPa) and temperatures (to 1300 K) [10], and ultrahigh pressure experiments up to 300 GPa (3 Mbar) at 300 K by using a diamond anvil cell [11]. The latter was performed in order to display the occupation of the 5f band in the vicinity of the Fermi level which was expected at higher pressures than 40 GPa [7], due to the broadening and the lowering of this electronic shell as the volume is decreased. In this work, diffraction patterns clearly displayed the emergence of a new phase at 78 GPa, indexed as a body centered tetragonal (bct) and which is found to be stable up to 300 GPa (3 Mbar). Direct evidence of conduction band to f electron transfer was provided from the measured equation of state due to the lowering of the 5f band.

In the paper by Vohra and Akella [11], a comparison was attempted on cerium metal, which is the 4f counterpart of thorium in the periodic table, the main difference being that, at ambient conditions, Ce has one localized 4f electron, while Th presents an unoccupied 5f band. Nevertheless, strong similarities were found under high pressure for these metals since both of them present a wide pressure range of stability in the bct phase (from 5 to 12 GPa for Ce and from 78 to 300 GPa for Th). This similar behavior under high pressure was attributed to the broadening of the 4f band and the lowering of the 5f shell for Ce and Th respectively, leading, then, to comparable electronic structures, and bonding properties.

By considering these results and those reported on cerium at high temperatures by our laboratory [12], experiments on thorium have been also performed under very high temperatures. Indeed, liquid cerium was found to display an anomalous behavior of sound velocity interpreted by the effect of the 4f electrons delocalization. Our main motivation was then to perform experiments on thorium in order to observe a possible similar effect of delocalization of its 5f band.

Moreover, the available data on thorium are scarce, especially in the liquid state; to our knowledge, even its melting curve is unknown. It should be noted that if such a curve does present a negative slope which corresponds to a volume contraction by taking into account the Clausius–Clapeyron equation [12], such an anomalous behavior of sound velocity in liquid thorium would surely be expected.

In this paper, we present an investigation of the thermophysical properties of both solid and liquid thorium using our isobaric expansion facility. We have focused our attention on electrical resistivity and volume expansion measurements. No sound velocity data are reported.

2. EXPERIMENTAL TECHNIQUE

Our experimental device operating in Bruyères-le-Châtel was described in detail in previous papers [13–15]. Wire shaped samples of thorium (diameter, 0.8 mm; length, 30 mm) are resistively pulse heated by discharging a 60-KJ capacitor bank (30 kA; 20 kV; 300 μ F; pulse duration, 100 μs). The sample is located in a pressure vessel filled with 0.06 GPa argon gas for this experiment.

At any period of time, the following electrical and optical parameters were measured: (a) current through the sample, $I(t)$; (b) voltage drop across the sample, $U(t)$; (c) diameter of the sample, $d(t)$; and (d) thermal emission from the heated sample surface, $J(t)$.

From these measured quantities, the following can be determined: enthalpy $H(t)$, electrical resistivity $\rho(t)$, and specific volume variation

$V/V_0(t)$. Since all of these parameters are functions of time, it is then easy to combine all of them in order to obtain other quantities such as $\rho(H)$, $V/V_0(H)$, $H(T)$, $\rho(T)$, $V/V_0(T)$, and C_p.

When available, sound velocity measurements give access to the determination of the equation-of-state parameters [14].

The accuracies of the current, voltage, diameter, resistivity, and enthalpy are $\pm 0.6\%$, $\pm 0.6\%$, $\pm 1\%$, $\pm 4\%$, and $\pm 1.5\%$, respectively (for further details, see Refs. 13 and 15).

3. RESULTS AND DISCUSSION

Thorium samples, whose purity is 99.5% and typical analysis is given in Table I, were provided by Goodfellow Metals Ltd. The samples were stored under vacuum before being mechanically polished in order to avoid problems of oxidation.

Since no temperature measurements have been made, most of our data are represented as a function of enthalpy. However, temperature estimations (in the solid state) may be made from enthalpy by using the data of specific heat, C_p, available in literature. For comparison with the electrical resistivity data of Sahu et al. [10] (see Section 3.1), we have used the reported C_p values of Nakamura et al. [16] of the 99.5% thorium samples in the 80–1000 K range, which are in very good agreement with those of Oetting and Peterson [17] (within the error bars) for the range 300–700 K.

Table I. Impurities in the Thorium Samples

Element	ppm (by weight)
Al	500
B	0.4
Ca	250
Cd	0.1
Cl	8
Cr	6
Cu	5
Fe	150
Li	0.1
Mg	10
Mn	13
N	250
Ni	5
Si	10
U	0.1

3.1. Electrical Resistivity Versus Enthalpy

Electrical resistivity measurements of selected actinides were reported by King [18]. The results showed that the electrical resistivity of thorium is significantly smaller than those of Np, U, and Pu as for the electronic specific heat. In order to explain such a difference, King [18] suggested that the density of states of the 6d and 5f bands at the Fermi surface would be lower for thorium than for its counterparts.

Electrical resistivity measurements have also been reported previously by Sahu et al. [10] up to 10 GPa and in the 300–1300 K range (which corresponds to a 0–0.13 $MJ \cdot kg^{-1}$ enthalpy range according to the C_p values of Nakamura et al.) [16]. These results show a decrease in the electrical resistivity as a function of pressure at room temperature (from 15.85 $\mu\Omega \cdot cm$ at atmospheric pressure to 13.5 $\mu\Omega \cdot cm$ at 10 GPa), indicating that thorium becomes less metallic at higher pressures. The temperature dependence presents a linear behavior (positive coefficient) from 300 K up to 750 K, while a nonlinear dependence is observed (slight curvature toward the T-axis) at higher temperatures, from 750 up to 1300 K. This nonlinear behavior was interpreted by considering a two-band model developed by Fradin [19], who explained the high-temperature resistivity of Pd due to the rapid variation in the density of states at the Fermi level in the narrow d band. This model was then extrapolated to thorium by Sahu et al. [10] by integrating the temperature variation of the electron density of states at the Fermi level $N_d(E_F)$ in the narrow fd band.

Figure 1 presents the electrical resistivity of thorium (not corrected for thermal expansion) as a function of enthalpy (this term refers to the

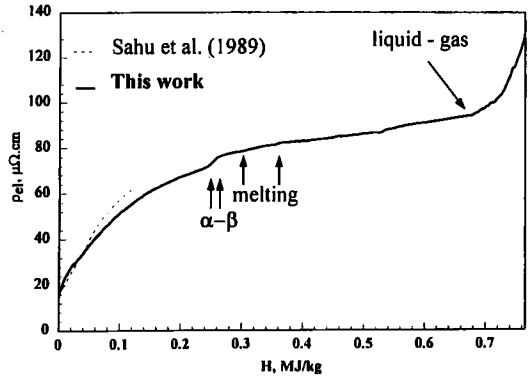

Fig. 1. Variation of electrical resistivity (without correction for thermal expansion) versus enthalpy. Experimental conditions: bank voltage = 6000 V; $P = 0.06$ GPa.

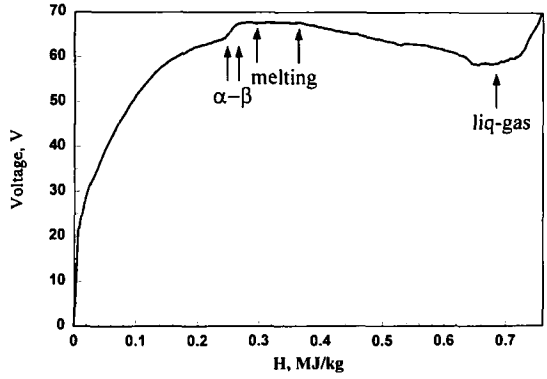

Fig. 2. Voltage across the sample as a function of enthalpy.

$H_T - H_{298}$ value) obtained for the present work. Our data are compared with the values of Sahu et al. [10] in the 0–0.13 MJ · kg^{-1} enthalpy range. From Fig. 1, we can remark that the results of both experiments are in very good agreement in the low enthalpy (temperature) range up to 0.05 MJ · kg^{-1}. The nonlinear behavior in the 750–1300 K range (or 0.06–0.13 MJ · kg^{-1}) reported by Sahu et al. [10] is also observed here, even if our data are somewhat lower. The electrical resistivity still continues to increase before showing a jump at about 0.25 MJ · kg^{-1} attributed to the α–β phase transformation (which should then correspond to 1633 K [9], if one considers that the melting point does not change from atmospheric pressure up to 0.06 GPa). This curve then shows a nearly linear behavior up to about 0.36 MJ · kg^{-1} before presenting a slight change of slope indicating melting. Although this is not well displayed from electrical resistivity data, such a change is more clearly observed on the voltage measurements, as shown in Fig. 2. Moreover, the pyrometry response presented in Fig. 3 exhibits a melting plateau (the threshold of this pyrometer being too high to evidence the α–β transformation), which temporally corresponds to the change of slope associated to the melting.

The enthalpy of the α–β transition and the latent heat of fusion were determined from the jump of electrical resistivity and the width of the melting plateau, respectively. The calculations give values of 15 and 60 kJ · kg^{-1} for the α–β transition and the melting, in excellent agreement with data reported in literature [9, 20].

It should be noted that for the results reported in this paper corresponding to one experiment (in all, three shots have been performed), the second ignitron (which is supposed to stop the current pulse) did not work.

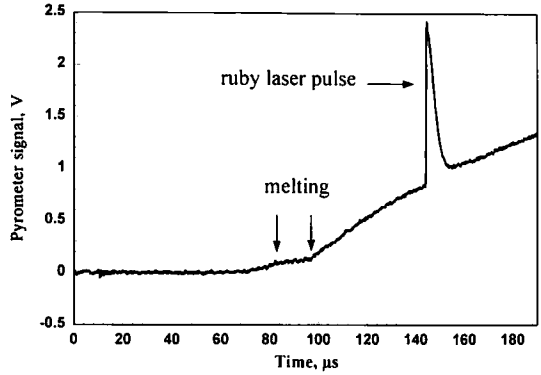

Fig. 3. Voltage response of the 750-nm pyrometer channel versus time. The ruby laser pulse (devoted to sound velocity measurements) is well displayed here. No temperature data are presented (not calibrated system).

Then, instead of having a temperature being kept constant at the end of the current pulse, its value still continues to increase (see Fig. 3) since the energy supply is not stopped. This phenomenon is correlated to an amount of energy which is sufficient for the specimen to first cross to the liquid state and then to reach the binodal (liquid–vapor equilibrium line), and the spinodal (corresponds to the boundary of thermodynamic stability of the superheated metastable liquid) [21, 22]. Indeed, the crossing of the spinodal line should cause an increase in the electrical resistivity because of the breakdown of electrical conductivity, and the volume rise (see Section 4). Figure 1 displays such an event, which occurs at about 0.68 $MJ \cdot kg^{-1}$.

4. VOLUME MEASUREMENTS

As described by Berthault et al. [13], volume measurements were obtained by coupling a shadowgraph technique and the use of a streak camera. For this purpose, a continous argon laser backlights the sample, whose shadow is imaged on the slit of the streak camera, which then records continuously the diameter of the wire during the experiment. Since the two ends of the sample are blocked, only radial expansion occurs leading then to a quadratic dependence of specific volume V/V_0 versus diameter.

The expansion streak image is then analyzed and treated by image processing in order to calculate the V/V_0 ratio evolution as a function of time or even of other parameters by integrating these data to a specific data processing software developed in our laboratory.

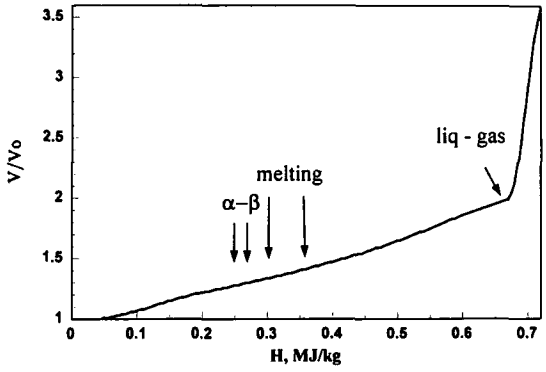

Fig. 4. Variation of the specific volume as a function of enthalpy.

The V/V_0 versus enthalpy curve, obtained for the same experiment as for electrical resistivity measurements, is shown in Fig. 4. One may remark that the specific volume monotonously increases before presenting a sharp rise at about 0.68 $MJ \cdot kg^{-1}$. It should be noted that thorium notably expands since its volume variation is about twofold in the vicinity of the boiling state. This large variation is surprising compared to other actinides and is not explained at the present time. However, this result seems to be reproducible since we also observed a similar expansion in other experiments.

The sharp rise in volume occurring at 0.68 $MJ \cdot kg^{-1}$ is surely correlated to the increase of electrical resistivity observed in Fig. 1 and would then correspond to the crossing of the spinodal line. Indeed, as the latter statisfies the following condition:

$$-\left(\frac{\partial P}{\partial V}\right) = \frac{kT}{\Delta V^2} = 0 \tag{1}$$

This derivative function is inversely proportional to the fluctuation of the volume ΔV^2, leading then to a strong variation in volume near the spinodal resulting in the formation of homogeneous small vapor nuclei in the superheated liquid. According to Seydel et al. [21] and Pottlacher and Jäger [22], the crossing of the spinodal line is correlated with the generation of a shock wave (the so-called phase explosion) in the surrounding medium, which should vanish at pressures higher than the critical pressure. Such a method is very powerful in order to determine the critical pressure P_c, since for $P \geqslant P_c$ one should observe no change of electrical resistivity and volume variation.

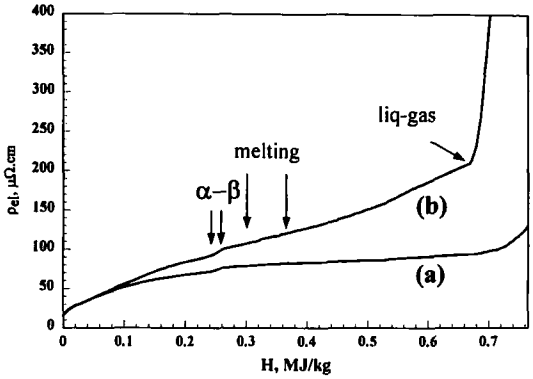

Fig. 5. Electrical resistivity versus enthalpy: (a) without volume correction; (b) with volume correction.

By integrating the volume data, it is then possible to correct the electrical resistivity for thermal expansion. The results are presented in Fig. 5 and show the strong effect of expansion especially in the liquid state.

5. CONCLUSION

To our knowledge, we first reported selected thermophysical properties of liquid thorium up to the vicinity of the boiling state ($\sim$5000 K). Electrical resistivity data (volume uncorrected and corrected) have been presented. These results clearly show the solid–solid transformation, the melting, and a sharp rise in resistivity, indicating the crossing of the spinodal line. Such a phenomenon is confirmed from volume measurements.

Further experiments should be performed and then focused on sound velocity measurements in order to display a possible effect of the 5f electrons delocalization. In such a case, one should expect an anomalous behavior of sound velocity associated with the observation of a positive temperature coefficient.

ACKNOWLEDGMENTS

We would like to thank Hervé Bacchetta and Jérémie Liébart for having, respectively, developed the new data processing software and integrated the new InGaAs detector for the pyrometry measurements.

REFERENCES

1. J. M. Fournier, *J. Phys. Chem. Solids* **37**:235 (1976).
2. B. T. Matthias, W. H. Zachariasen, G. W. Webb, and J. J. Engelhardt, *Phys. Rev. Lett.* **18**:782 (1967).
3. W. H. Zachariasen, *J Inorg. Nucl. Chem.* **35**:3487 (1973).
4. U. Benedict, *Handbook on the Physics and Chemistry of the Actinides*, A. J. Freeman and G. H. Lander, eds. (Amsterdam, 1987), p. 227.
5. T. Baer and J. K. Lang, *Phys. Rev. B* **22**:2160 (1980).
6. J. R. Naegele, J. Ghijsen, and L. Manes, *Actinides: Chemistry and Physical Properties, Structure and Bonding* (Springer, Berlin, 1985), p. 197.
7. H. L. Skriver and J. P. Jan, *Phys. Rev.* **B22**:1489 (1980).
8. J. M. Fournier, Ph.D. thesis (University of Grenoble, CNRS Report No. AO 10568, 1975).
9. F. L. Oetting, M. H. Rand, and R. J. Ackermann, *The Chemical Thermodynamics of Actinide Elements and Compounds. Part 1: The Actinide Elements* (IAEA, Vienna, 1976), pp. 6–65.
10. P. C. Sahu, M. Yousuf, and K. Govinda Rajan, *Physica B* **160**:177 (1989).
11. Y. K. Vohra and J. Akella, *High Press. Res.* **10**:681 (1992).
12. M. Boivineau, J. B. Charbonnier, J. M. Vermeulen, and Th. Thévenin, *High Temp. High Press.* **25**:311 (1993).
13. A. Berthault, L. Arlès, and J. Matricon, *Int. J. Thermophys.* **7**:167 (1986).
14. M. Boivineau, L. Arlès, J. M. Vermeulen, and Th. Thévenin. *Int. J. Thermophys.* **14**:427 (1993).
15. M. Boivineau, L. Arlès, J. M. Vermeulen, and Th. Thévenin, *Physica B* **190**:31 (1993).
16. J. I. Nakamura, Y. Takahashi, S. I. Izumi, and M. Kanno, *J. Nucl. Mat.* **88**:64 (1980).
17. F. L. Oetting and D. T. Peterson, *J. Less-Common Met.* **128**:231 (1986).
18. E. King, *The effect of very high pressures on the electrical resistance of the actinides elements from thorium to plutonium*, Report No. AERE-R 5913 (1968)
19. F. Y. Fradin, *Phys. Rev. Lett.* **33**:158 (1974).
20. L. I. Katzin and D. C. Sonnenberger, *The Chemistry of the Actinide Elements, Vol. 1* (Chapman and Hall, London, 1986), pp. 50–53.
21. U. Seydel, H. Bauhof, W. Fucke, and H. Wadle, *High Temp. High Press.* **11**:635 (1979).
22. G. Pottlacher and H. Jäger, *Int. J. Thermophys.* **11**:719 (1990).