Equation of state of tantalum to 174 GPa

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The volume compression of tantalum was measured to 174 GPa in a diamond-anvil cell using angle-resolved synchrotron x-ray diffraction. A third-order Birch-Murnaghan equation-of-state constrains the compression data rather well with the zero-pressure isothermal bulk modulus $B_{0T}=194.7(4.8)$ GPa and the first pressure derivative $B'=3.4(0.1)$. These values are consistent with the previous ultrasonic results, $B_{0S}=196$ GPa and $B'=3.8$, but are different from the previous x-ray compression results, $B_{0T}=231$ GPa and $B'=2.5$. The current compression data also demonstrate that the bcc phase of Ta continues to be stable to 174 GPa, which qualifies tantalum for a pressure standard in static high-pressure experiments. [S0163-1829(99)04713-X]

INTRODUCTION

Tantalum (Ta) is a body-centered-cubic (bcc) metal with high ductility and high melting temperature 3269 K at ambient pressure. The natural occurrence of Ta is strongly associated with the rare-earth elements, both of which are of fundamental importance for understanding highly correlated electronic systems. Tantalum has been an important high technology material due to high thermal, mechanical, and chemical stability for the use in jet engines and electronic devices. Accordingly, understanding the pressure and temperature dependence of thermal, mechanical, and electronic properties of Ta is of significance to engineering applications and condensed-matter physics, including melting curve, phase diagram, bulk modulus, elastic constants, and shear strength.

Tantalum has been studied under shock compression to 560 GPa,[1–4] exhibiting no clear indication of phase transition except melting at around 300 GPa.[5] Recent theoretical calculations also suggests that the bcc phase of Ta is stable to 1 TPa.[6] Thus, Ta could be a good candidate for an internal pressure standard for static high-pressure research, although it has not been widely used previously. Furthermore, its high melting temperature makes it suitable for a pressure standard at high temperatures and pressures. Most commonly used pressure standards including Au, Cu, and Al have relatively low melting temperatures. Mo, Pt, and W with high melting temperatures, on the other hand, have relatively small compressibilities, limiting the accuracy in pressure determination.

Despite the potential for an internal pressure standard, there is no consistency in the current equation of state (EOS) data for Ta among ultrasonic measurements,[7–12] static high pressure,[13–15] shock-wave results,[1–5] and theory.[6,16] The bulk moduli of Ta determined previously by ultrasonic measurements, B_{0S}, agree within 3% ranging from 190 to 195 GPa.[7–12] (Here and hereafter subscript zero denotes zero pressure, and subscripts S and T are used to represent adiabatic and isothermal conditions, respectively.) On the other hand, the isothermal bulk moduli B_{0T} measured previously by diamond-anvil cell x-ray experiments are quite different. For example, Ming and Manghnani reported $B_{0T}=194$ GPa,[15] whereas, the compression data to 77 GPa by Xu *et al.*[13] resulted in a substantially higher value $B_{0T}=231$ GPa. The former is based on a fixed value for the first pressure derivative B' obtained from ultrasonic and volume measurements to 8.7 GPa, whereas the latter result is obtained from a third-order Birch-Murnaghan fit of the measured compression data. Apparently, the latter appears to be inconsistent with the results from the previous ultrasonic and x-ray measurements. Recent theoretical calculations have estimated B_{0T} to be between 203 (Ref. 6) and 211 GPa (Ref. 16) at 0 K depending on the approximations. Therefore, it is clear that a more consistent set of data are required in an extended pressure range to qualify Ta for an internal pressure standard.

The recent development of synchrotron x-ray diffraction combined with diamond-anvil high-pressure technology enables us to accurately determine EOS, particularly in angle-resolved x-ray diffraction with high-resolution x-ray image plates. In this study, we determined the volume compression of Ta up to 174 GPa using an angle-resolved synchrotron x-ray-diffraction method.

EXPERIMENTS

Tantalum powder (less than 1.47 μm particle size with 99.9% purity) was used as a sample. Two different size anvils were used in modified Mao-Bell type cells. Flat anvils with 300-μm culet were used for low-pressure experiments up to 50 GPa; whereas, beveled ones from a 300-μm culet to a 100-μm flat with 7° bevel angle were used at higher pressures. For the high-pressure experiments, Ta powder was loaded into a 40-μm diameter hole on a rhenium gasket, together with argon pressure medium and thin gold foil (less than 10 μm) for pressure determination. Special care was taken to separate the gold foil from the gasket and the anvil faces. For the low-pressure experiments, the sample was loaded into a larger 90-μm hole with argon and a few ruby chips for pressure calibration.[17] We estimated the pressure uncertainty to be 0.7–2 % in the ruby measurements and 1.5% in the x-ray pressure standard method based on a gold EOS which will be described in the next section. The uncertainties in the ruby measurements were estimated by averaging the pressure measured from several ruby grains dispersed in the sample area.

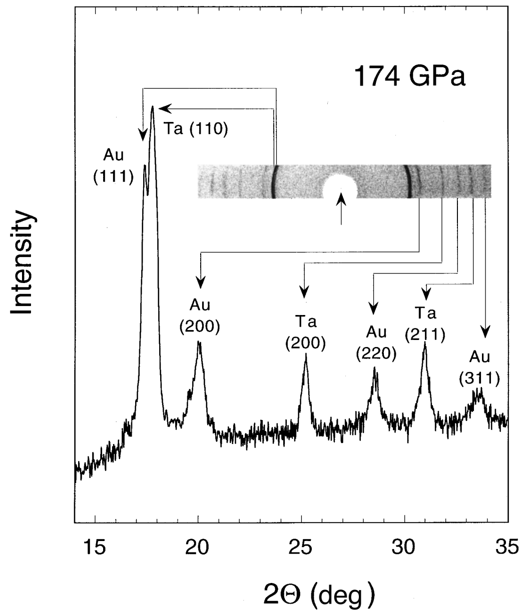

FIG. 1. An integrated x-ray-diffraction pattern of Ta and Au at 174 GPa, together with the raw image-plate record in an inset. The arrow at the center of the image indicates the direct x-ray beam. The diffraction was obtained at $E = 20.000$ kV.

Angle-resolved x-ray powder diffraction of tantalum and gold in a diamond-anvil cell was obtained by using a monochromatic x-ray radiation at 20.000 keV from the beam line 10-2 of the Stanford Synchrotron Radiation Laboratory (SSRL). Details of the x-ray setup have been described elsewhere.[18,19]

Two diffraction patterns were recorded for each pressure run at two different positions, whose separation is accurately measured to one μm by using a micrometer device (Sony Magnescale Inc. LH20-C). The sample to image-plate distance was then calculated by using a few pairs of corresponding diffractions knowing the separation. A small collimator, either 10 μm in diameter for the high-pressure experiments or 30 μm for the low-pressure experiments, was placed less than 2 cm away from the sample. In this way, one can obtain a diffraction pattern completely free of the diffractions from Re gasket as shown in Fig. 1. X-ray exposures were made for about 50–60 min for the high-pressure experiments and 20 min for the low-pressure experiments. The image-plate record was then digitized by using a scanner (BAS 2500, Fuji) with a 100 μm resolution and integrated by using a modified NIH program.[20] The integrated diffraction pattern was further analyzed to refine cell parameters by using a Jade program (MDI, CA). The readout error of the image-plate record is estimated to be around 0.14% of the d spacing measured in this setup with the data processing scheme described above.

RESULTS AND DISCUSSION

Figure 1 shows an integrated diffraction pattern measured at the maximum pressure of this work, together with its raw image-plate record in an inset. Seven reflections in the region of $2\Theta = 16°$ to $35°$ are identified, all of which have been observed at lower pressures. These reflections are well indexed to bcc Ta and face-centered-cubic (fcc) Au, as denoted in Fig. 1. The cell parameters at 174 GPa are $a = 2.8665$ Å for Ta and $a = 3.6019$ Å for Au (see Table I). Note in Table I that the uncertainty of the lattice constant is substantially larger in Au than in Ta. This is probably due to larger crystal anisotropy of gold. The anisotropy of Au and Ta has been reported to be about 6.2 and 1.8 at the ambient condition, respectively.[11,21]

A third-order Birch-Murnaghan EOS data of gold[22] is used to determine the sample pressure with $V_0 = 10.215$ cm^3/mol, $B_{0T} = 166.6$ GPa, and $B' = 5.5$. This EOS is consistent with the previously reduced shock data[23] $B_{0T} = 160$ GPa and $B' = 5.7$. The pressures obtained from this EOS also agree with those calculated from a first-principles linearized muffin-tin orbitals (LMTO) method[24] and a classical thermodynamic analysis,[21] within 2 GPa in the pressure

TABLE I. Refined cell parameters of tantalum and gold at 174 GPa.

hkl	d_0 (Å)	d_c (Å)	Δd (Å)
	Ta: $a = 2.8665 \pm 0.0003$ Å		
110	2.0272	2.0270	−0.0002
200	1.4329	1.4333	0.0004
211	1.1704	1.1703	−0.0001
	Au: $a = 3.6019 \pm 0.0023$ Å		
111	2.0766	2.0795	0.0029
200	1.8033	1.8009	−0.0024
220	1.2759	1.2735	−0.0024
311	1.0867	1.0860	−0.0007

TABLE II. Compression data of tantalum to 174 GPa at ambient temperature.

Pressure (GPa)[a]	a (Å)	V (cm^3/mol)	V/V_0[b]
8.23 (*R*)	3.2790	10.6187	0.9773
13.11 (*R*)	3.2290	10.1407	0.9333
21.82 (*R*)	3.2043	9.9096	0.9121
31.50 (*R*)	3.1677	9.5740	0.8812
41.67 (*R*)	3.1176	9.1269	0.8400
47.46 (*G*)	3.1156	9.1093	0.8384
55.96 (*G*)	3.0900	8.8868	0.8179
57.07 (*G*)	3.0854	8.8470	0.8143
93.70 (*G*)	2.9989	8.1236	0.7477
99.74 (*G*)	2.9847	8.0087	0.7371
110.66 (*G*)	2.9639	7.8425	0.7218
113.88 (*G*)	2.9573	7.7901	0.7170
123.95 (*G*)	2.9361	7.6239	0.7017
137.00 (*G*)	2.9126	7.4423	0.6850
137.88 (*G*)	2.9125	7.4415	0.6849
144.08 (*G*)	2.9046	7.3811	0.6793
144.08 (*G*)	2.9002	7.3476	0.6763
153.45 (*G*)	2.8825	7.2139	0.6640
157.95 (*G*)	2.8824	7.2133	0.6639
174.23 (*G*)	2.8665	7.0894	0.6525

[a]Pressures were measured using rub scale (*R*) and internal gold standard (*G*).
[b]$V_0 = 10.865$ cm^3/mol.

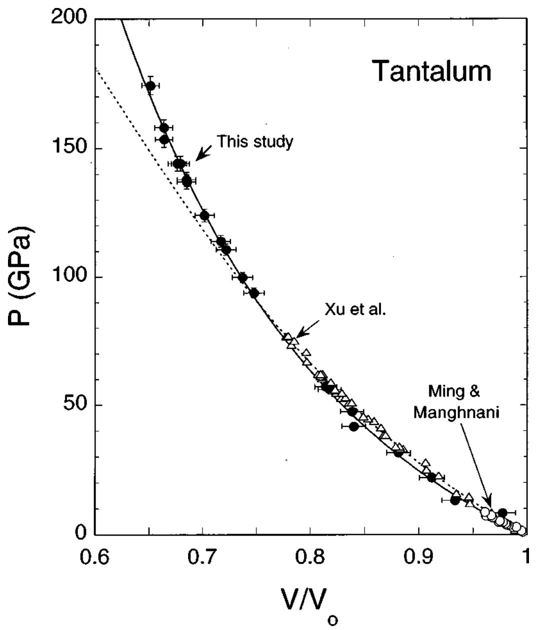

FIG. 2. Static pressure-volume data of tantalum. The solid circles with error bars represent the present data; whereas, open circles and triangles represent the earlier x-ray results from Refs. 15 and 13, respectively. Solid and dotted curves are, respectively, the Birch-Murghanan fits to the present and earlier results in Ref. 13.

range of this study. Compression data of Ta obtained in this work are summarized in Table II. We used molar volume of Ta, $V_0=10.865\ \mathrm{cm}^3/\mathrm{mol}$ at ambient conditions,[1,25] in reasonable agreement with the extrapolated value 10.920 $\mathrm{cm}^3/\mathrm{mol}$ of our high-pressure data within 0.5%. The equation of state for Ta is then obtained by fitting the measured compression data to a third-order Birch-Murnaghan equation,

$$P(\mathrm{GPa})=(3/2)B_{0T}[(V/V_0)^{-7/3}-(V/V_0)^{-5/3}]\{1-(3/4)(4-B')\times[(V/V_0)^{-2/3}-1]\}. \quad (1)$$

We obtained $B_{0T}=194.7\pm4.8$ GPa and $B'=3.4\pm0.1$. Figure 2 compares this result with the previous static compression data.[13,15] Note that the data by Xu *et al.*[13] estimate a systematically higher pressure than the current result at a given volume. For comparison, we fit the data by Xu *et al.*[13] to the same equation (1) and obtain a substantially larger $B_{0T}=231$ GPa but smaller $B'=2.5$ than the current data. Clearly, the EOS fit of Xu's data[13] softens very rapidly with pressure and estimates substantially lower pressures than the current results above 100 GPa (Fig. 2). On the other hand, the data by Ming and Manghnani[15] agree rather well with our data, although those are limited to only 8.7 GPa. The present result constrains B' better than the previous ones in a substantially extended pressure range. Using the present $B'=3.4$, the data by Xu *et al.* yield $B=208$ GPa (better but still 7% higher than ours).

Table III compares EOS data of Ta obtained from this and other earlier studies. Note that the current data $B_{0T}=194.7$ GPa agrees well with both ultrasonic results $B_{0S}=190$ to 196 GPa.[7–12] The ultrasonic velocity measurements provide adiabatic bulk modulus B_S which can be related to isothermal bulk modulus B_T by

$$B_T=B_S/(1+\alpha\gamma T), \quad (2)$$

where α, γ, and T represent, respectively, the thermal-expansion coefficient, Grüneisen parameter, and temperature in *K*. $\gamma_0=1.639$ for tantalum using the thermodynamic relation, $\gamma=\alpha B_S/\rho C_P$, $\alpha=1.95\times10^{-5}\ \mathrm{K}^{-1}$,[26] $C_P=1.40\times10^{-1}$ J/g/K,[26] and $B_S=196$ GPa.[11] Then the ultrasonically measured $B_{0S}=190-196$ GPa is converted to $B_{0T}=189-195$ GPa. These values are in good agreement with the current result $B_{0T}=194.7\pm4.8$ GPa and, thus, it appears that $B_{0T}=230$ GPa by Xu *et al.*[13] is too high.

In conclusion, we have determined an EOS for Ta in an extended pressure range more than twice the previous ones,[13–15] using a third-order Birch-Murnaghan fit with $B_{0T}=194.7$ GPa and $B'=3.4$. It agrees well with the previous ultrasonic results. This work confirms that the bcc phase of

TABLE III. Comparison of B_0 and B' of Ta.

B_0 (GPa)[a]	B'	Method	References
196		Ultrasonic	Bolef (Ref. 7)
192		Ultrasonic	Featherston and Neighbour (Ref. 8)
190		Ultrasonic	Soga (Ref. 9)
194		Ultrasonic	Leisure *et al.* (Ref. 10)
196	3.79	Ultrasonic	Katahara *et al.* (Ref. 11)
195		Ultrasonic	Sarrao *et al.* (Ref. 12)
211		Local-density approximation (LDA)	Wu *et al.* (Ref. 16)
198		LMTO-LDA	Wu *et al.* (Ref. 16)
203	4.3	LMTO-GGA	Söderlind and Moriarty (Ref. 6)
206	2.76	x-ray (4.5 GPa)[c]	Vaidya and Kennedy (Ref. 14)
194(7)[b]	3.8	x-ray (8.7 GPa)[c]	Min and Manghnani (Ref. 15)
213(3)[b]	2.5(0.1)[b]	x-ray (77 GPa)[c]	Xu *et al.* (Ref. 13)
194.7(4.8)[b]	3.4(0.1)[b]	x-ray (174 GPa)[c]	Present work

[a]All ultrasonic results represent adiabatic moduli, whereas the others are isothermal.
[b]The value in parenthesis presents the uncertainty.
[c]The value in parenthesis represents the maximum pressure of the measurements.

Ta is indeed stable to 174 GPa. It also shows that Ta is soft with relatively low values of B and B'. $B'=3.4$ of Ta is substantially smaller than 5.5 of Au; whereas, $B_{0T}=194.7$ GPa of Ta is only 14% higher than $B_{0T}=167$ GPa of Au. In fact, the B' of Ta is relatively low in comparison with other bcc, fcc, and hcp metals, all of which typically range between 4 and 6.[27] Tungsten has relatively low $B'=4.0$ but very high $B_{0T}=308$ GPa.[27,28] Therefore, Ta is considered to be a pressure standard of higher accuracy.

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