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High-pressure Raman scattering from hexagonal close-packed (HCP) metals Os and Re have been extended up to 200 GPa, and the pressure-dependent shear modulus C_{44} has been deduced from the Raman-active mode E_{2g}, which is generated from the adjacent vibration of atoms in hexagonal planes, providing the valuable information about the elastic properties for HCP metals under high pressure. Combined with the available data of HCP metals from previous works, a further study indicates that the C'_{44}/C_{44} ratio would be close to a constant value, 0.01, with increasing atomic number of metals. The results obtained from high-pressure Raman scattering will allow us to probe the elastic anisotropy of the HCP metals at very high pressure.

Keywords: hexagonal close-packed (HCP) metals, osmium, rhenium, high-pressure Raman scattering, shear modulus C_{44}

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1. Introduction

Hexagonal close-packed (HCP) osmium (Os) and rhenium (Re) are an important category of rare metals which belong to the platinoid 5d transition elements category with ultra-high density and cohesive energies at ambient pressure.[1–16] In the past decades, Os and Re metals have attracted an important attention due to the extensive scientific and engineering applications. In order to understand their exotic properties, the pressure parameter is considered as a fundamental thermodynamic variable. The effect of pressure on elastic properties of a metal is essential for understanding the mechanical stability. The elastic properties of metals under high pressure are desirable not only for material research itself,[17] but also because it may allow providing new insights into the fundamental effects of the high-pressure experiments on the atomic structure of solids and on possible variation of atomic distribution within crystal sublattices.

One of the interesting features of Os and Re materials is that they are able to retain the HCP phase (space group $P6_3/mmc$) upon very high applied pressure-values.[13,18–20] As shown in Fig. 1, the lattice of HCP metals comprises two atoms per unit cell (Fig. 1(a)). The only Raman-active E_{2g} mode in center of Brillouin zone (Fig. 1(b)), correlated with the shear vibration between different layers, provides direct information about the elastic properties (Fig. 1(c)). Noteworthy, C_{44} is the only elastic constant that could be measured in experiments as an independent modulus for HCP metals. Namely, the pressure dependence of the shear modulus C_{44} can be deduced from the Raman phonon frequency of the E_{2g} mode (Fig. 1(c)).

In group theory, each set of nuclei on sites of symmetry D_{3h} gives rise to six normal modes of zero wave vector $A_{2u}+B_{1g}+E_{1u}+E_{2g}$ depicted as irreducible representations. Among those modes, the doubly degenerate E_{2g} mode is Raman active, corresponding to vibrations of successive hexagonal planes against each other (Fig. 1(c)). The E_{2g} Raman mode reflects the shear vibration between different layers of atoms in HCP metals. By considering Os as a typical example, in Fig. 1(b), it is possible to notice its dispersion curves, which include six branches, and at high symmetry points Γ the acoustic and optical branches coincide. A phonon branch at the center of the Brillouin zone is a shear mode and the elastic shear modulus is related with the slope of the zone-center TO mode (Fig. 1). It is possible, therefore, for the vibration characters of HCP metals to be observed by Raman spectroscopy.

Due to the high reflectivity and strong background from the diamond-anvil cell (DAC) or gaskets, high-pressure Raman scattering signals acquired from metals were hard to be distinguished. To prevent specular reflection from being directed to the spectrometer and reduce the signal from the diamond, a lateral excitation technology (typical 35° incidence angle for the exciting radiation) was used in high-pressure Raman experiments on HCP metals, such as Be,[21] Fe,[22] Re[23] and Os.[24,25] The Raman scattering on the metals, however, are limited by the detection based on conventional experimental set-up. Up to now, high-pressure Raman scattering on the HCP Os and Re is only extended to 60 GPa[25] and 138 GPa,[26] respectively. There are far narrow pressure ranges that need to be investigated, and this implies that the influence of pressure upon HCP metals' elastic properties has

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not yet been unambiguously determined.

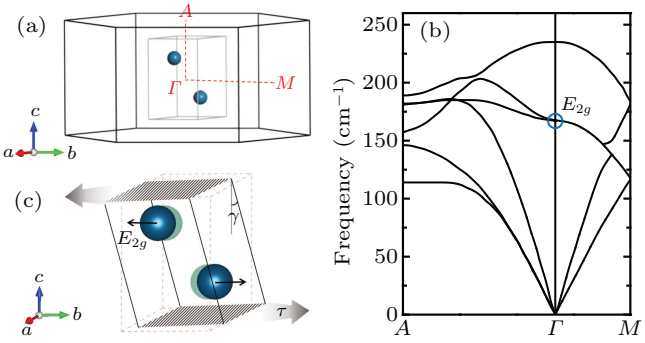


Fig. 1. (a) Brillouin zone of the HCP metal (space group $P6_3/mmc$), gray lines indicate the unit cell and blue balls indicate the metal atoms. The positions of representative high-symmetry points in the HCP Brillouin zone are plotted in red. (b) Typical phonon dispersion curves for the HCP metal (Os).[18] The circle points to the E_{2g} phonon mode at the center of the Brillouin zone. (c) The atomic displacement for the E_{2g} mode, and the ideal lattice model diagram of lattice shear stress. The uniaxial stress, τ, and the resulting normal strain, γ, have been labeled in the picture.

In this work, high-pressure Raman scattering from HCP metals Os and Re has been measured up to 200 GPa by using a DAC-based lateral excitation technology with 45° incidence angle for the exciting radiation,[27,28] and the shear modulus C_{44} has been deduced from the measured E_{2g} phonon frequency, which provides an independent experimental approach besides other methods, such as ultrasonic experiments[29,30] and theoretical calculations[4,31–34] to investigate the elastic property of the important platinoid 5d transition elements. More importantly, it is valuable to speculate their elastic properties for HCP metals under high pressure.[35]

2. Experimental details

We studied the elastic properties of Os and Re through high-pressure Raman scattering measurements using symmetric-type DACs for different pressure ranges in at least seven independent runs. To prevent specular reflection from being directed to spectrometer and reduce the signal from the diamonds, lateral excitation technology with 45° incidence angle for exciting radiation was used for our high-pressure Raman experiments.[27,28] High-pressure Raman spectra of HCP metals were measured by using a custom-built confocal micro-Raman system optical assembly with a 532-nm excitation solid-state laser (RGB Laser System Nova Pro) and an EMCCD detector (Andor Newton DU970P-UVB). The size of the pinhole of spatial filter that placed in front of a spectrometer (Andor Shamrock SR-303i-B) was 10 μm. The spectral resolution was within ±0.5 cm^{-1}, and the spatial resolution was within ±1 μm. The Raman system deviation had been corrected by employing a calibration method based on silicon wafer (520 cm^{-1}).

Ultrahigh-purity synthetic diamonds with culet sizes of 50–500 μm were used to reduce the background and scattering effect. High-purity (99.99% purity) poly-crystalline metal powder samples were loaded in the DAC chamber, and three different pressure-transmitting media (a 3:1 methanol–ethanol mixture (M/E), argon and nitrogen) were used to yield quasi-hydrostatic pressure condition. For lower pressures, comparative large culet diamonds adopted T301 steel as gasket with thickness of about 40 μm. For higher pressures, a rhenium gasket was preindented to thickness of 20–30 μm and drilled with a chamber hole in diameter of 20 μm. The pressure was then calibrated at room temperature by the fluorescence of ruby[36] and the high-frequency edge of diamond phonon.[37–39] The diameter of the Raman laser spot was ∼ 5 μm, which is smaller than the sample size (> 20 μm). This allowed to minimize the effect of the pressure gradient.

3. Results and discussion

Representative Raman spectra of HCP Os and Re at various pressures are shown in Fig. 2. Upon the quasi-hydrostatic compression, the blue shifts are observed on the pressure dependence curve of E_{2g} mode due to the increase of repulsive forces between adjacent atoms. From the consideration that the solidification of pressure transmitting medium inevitably occurs at no more than 15 GPa,[40,41] the observed broadening of Raman peaks at high pressures could attribute to the microscopic deviatoric stress under the nonhydrostatic compression.

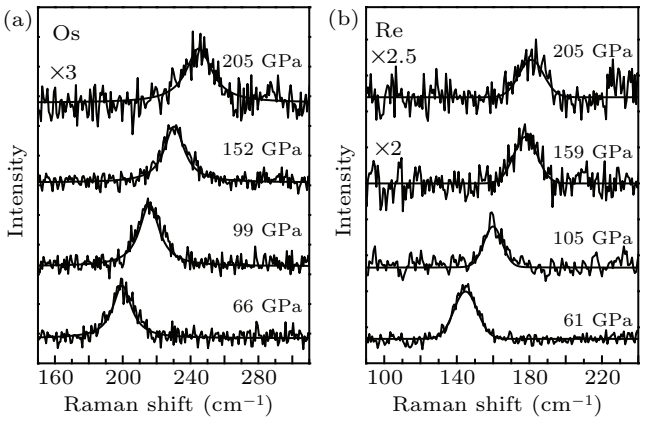


Fig. 2. The representative high-pressure Raman spectra spanning the pressure range covered of (a) Os and (b) Re, respectively. The solid lines are phenomenological fits (Lorentzians).

Figure 3(a) summarizes our experimental measurements of the high-pressure Raman scattering from HCP metals applied to Os and Re. As the pressure parameter was increased, the E_{2g} Raman frequency was found to monotonically increase. The softening of phonon can attribute to the pressure-dependent anharmonic effect.

A simplified physical model, as shown in Fig. 1(c), elucidates the relations of the E_{2g} Raman mode and the elastic constants C_{44}, which can be determined by the following equation:[42]

$$C_{44} = \frac{\tau}{\gamma} = 2\pi^2 m \left[\frac{\sqrt{3}c}{6a^2}\right] \omega^2, \tag{1}$$

where m is the atomic mass of HCP metal, a and c are the unit cell parameters, and ω is the measured frequency of the Raman phonon. In HCP metals, the elastic constant C_{44} can be defined as the ratio of the uniaxial stress, τ, exerted on a thin rod to the resulting normal strain, γ. By using the lattice parameters in Refs. [11,14], we can calculate the pressure dependence of the C_{44} of Os and Re up to 200 GPa, as shown in Fig. 3(a). Figure 3(b) shows the pressure-dependent shear modulus C_{44} deduced from the measured E_{2g} Raman phonon frequency. Here we note that C_{44}, calculated via Eq. (1) from high-pressure E_{2g} mode, can be fitted by two second-order polynomials,

$$C_{44}^{\mathrm{Os}} = 251.2 + 2.316P - 0.003P^2, \tag{2}$$

$$C_{44}^{\mathrm{Re}} = 132.6 + 1.401P - 0.002P^2. \tag{3}$$

Table 1 lists the elastic parameters for some typical HCP metals. With regard to the slope of the pressure dependence, elastic properties in HCP metals are suggested to be more complex and yield deviations of the first derivative of the elastic modulus, C'_{44}, from the theoretical curve. In theoretical calculation, in comparison to real lattice dynamics, ideal lattice vibrational models ignore the effect of crystalline defects, large binding energy of bonds and electronic shells, and next-nearest-neighbor interactions, leading to the discrepancies between the theoretical calculation and our Raman-dependent value. As for the discrepancies between the experimental data, this value is lower than that of ultrasonic experiments, partly because of the anisotropic deformation of a HCP metal under compression and the differences between the state of stress on all crystallographic planes.[22,35]

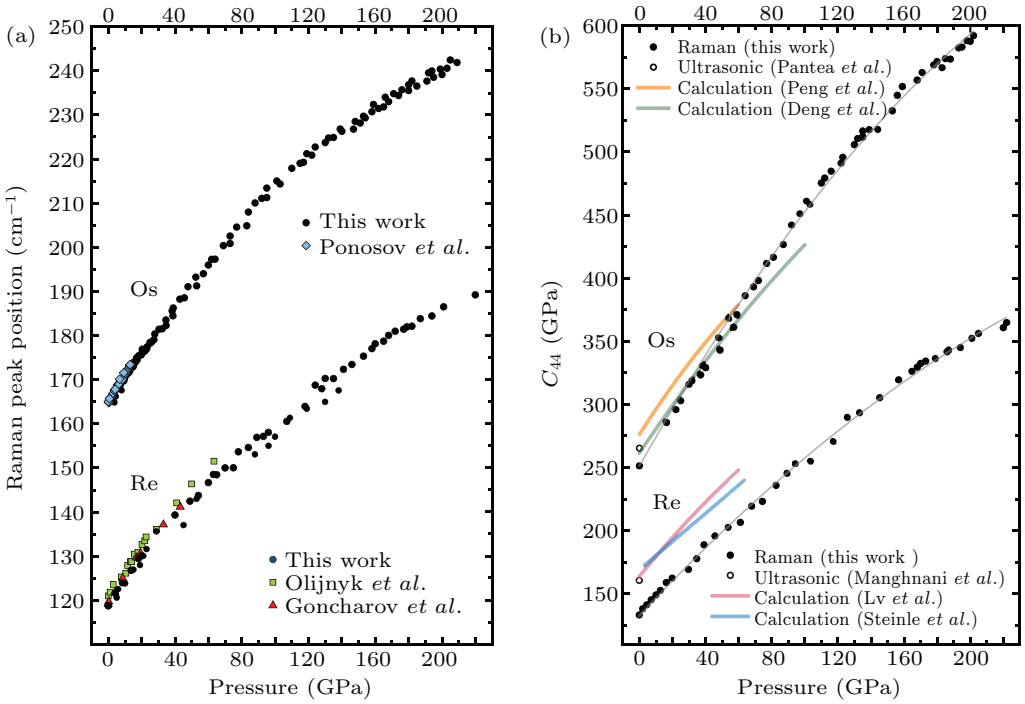


Fig. 3. (a) Pressure dependence of the E_{2g} Raman peak position of Os and Re, literature data (color symbols) are also shown for comparison. (b) Pressure dependence of the deduced elastic shear constant C_{44} of Os and Re, gray solid lines are guides to the eye (second order polynomials), open circles are the reported ultrasonic literature data at ambient pressure[29,30] and colored lines represent the theoretical calculated results.[31–34]

Table 1. Comparison of deduced and measured elastic constants for typical HCP metals.

hcp metals	P range (GPa)	ω_0 (cm^{-1})	B_0	B'	$C_{44}^{(0)}$ (GPa)	C'_{44}	$B_0/C_{44}^{(0)}$	$C'_{44}/C_{44}^{(0)}$	$\mathrm{d}(B_i/C_{44})/\mathrm{d}P$	Method
Os	0–202	160.99	399[11]	4.01[11]	251.2	2.32	1.59	0.92×10^{-2}	2.2×10^{-3}	Raman (this work)
	0		405.2		264.6		1.53			Ultrasonic[29]
Re	0–222	118.7	367[43]	4.64[43]	132.6	1.40	2.77	1.06×10^{-2}	4.6×10^{-3}	Raman (this work)
	0–21	120			133	1.1		0.83×10^{-2}		Raman[27]
	0–60	120.9			137.7	1.42		1.03×10^{-2}		Raman[25]
Be	0–0.42		360.3	5.43	160.5	1.49	2.24	0.93×10^{-2}		Ultrasonic[30]
	0–0.6		111	4.6	170.6	2.55	0.65	1.49×10^{-2}		Ultrasonic[44]
	0–23	457			110	1.65		1.50×10^{-2}		Raman[45]
	0–80	459	109.8	3.58	110.6	1.78	0.99	1.61×10^{-2}		Raman+XRD[21]
ε-Fe	22–152		165[46]	5.33[46]	114.7	1.30	1.44	1.11×10^{-2}		Raman[22]
	19–63	128.3			183.3	106	0.9	0.87×10^{-2}		Raman[23]
Ru	0–63	190.6	321[47]		180.8	1.9	1.78	1.05×10^{-2}		Raman[23]

It is worth noting that there is no direct dependency between the zero-pressure bulk modulus, B_0, and the zero-pressure shear modulus, $C_{44}^{(0)}$, but the ratio of bulk modulus to shear modulus (B/C_{44}) reflects the ductility and fragility of matter. B/C_{44} of HCP Os is observed an increase from about 1.59 at $P = 0$ GPa (this value differs by 3.8% of the results reported by Pantea *et al.*[29]) to 2.13 with increasing pressure to 200 GPa. For Re, this value increases from about 2.75 to 3.83. $B_0/C_{44}^{(0)}$ and its first derivative of the pressure dependence, $\mathrm{d}(B_i/C_{44})/\mathrm{d}P$, are listed in Table 1. According to the empirical critical value 1.75, by dividing the character of resistance to plastic deformation and fracture, the parameters of above HCP metals are found to be in good agreement with their inherent properties (e.g., this value for diamond is 0.77). The slope $\mathrm{d}(B_i/C_{44})/\mathrm{d}P$ for Os averaged over the pressure range is about 2.2×10^{-3} (first-order fitting), which is much approximate with $\mathrm{d}(B_i/C_{44})/\mathrm{d}P = 4.6\times10^{-3}$ for Re. This points to the pronounced ductile property of Re under pressure, and might show up the identical tendency for both Os and Re in the evolution of lattice structure.

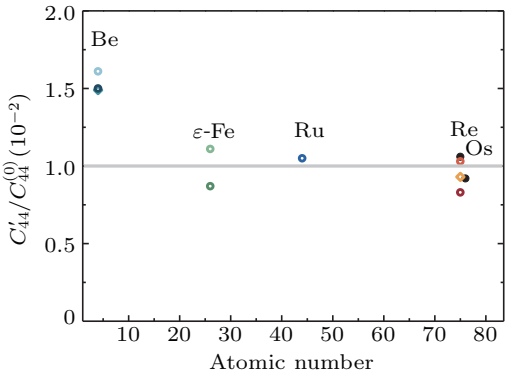


Fig. 4. The ratio of normalized elastic constant, C_{44}, and its first derivative, C'_{44}, as a function of atomic number for the typical HCP metals. The full circles are our data. The open diamonds and circles are the data obtained from ultrasonic[29,30] and Raman measurements in the literature,[21–23,25,27,44,45] respectively.

In this work, the shear modulus C_{44} and the pressure slope C'_{44} for HCP Os and Re have been deduced from the acquired high-pressure Raman data. We notice that there is a positive correlation between C_{44} and C'_{44} for the HCP metals (Table 1). The ratio of C'_{44} to $C_{44}^{(0)}$ reflects the elastic property of a metal, covering the range from 0.8×10^{-2} to 1.6×10^{-2} for those mentioned elements. As shown in Fig. 4, this value is approximately equivalent to 0.01 with the increase of the atomic number, which means to a positive correlation between C_{44} and C'_{44} upon compression. The association of high value at ambient pressure and the comparatively strong increase under compression of the elastic parameter hints on a potential law about this important group of metals. The differences of the elastic properties between those HCP metals are probably attributed to the completion of the unlike valence electron configuration (for example s→d) transfer under high pressure, which even leads to electronic topological transition.[11] Thus, the consistence of the elastic properties might imply to the similar high-pressure behavior for those HCP metals.

4. Conclusions

In summary, we have extended the direct measurements of phonon vibration frequency of E_{2g} and the information on C_{44} up to the 200 GPa pressure range for HCP Os and Re. In order to describe properly the elastic behavior of Os and Re at high pressure, the second-order polynomial fit was used with elastic modulus and their pressure slope. A high B/C_{44} associated with better ductility for HCP Os and Re was discussed. Finally, hints of a coincident ductility properties for HCP metals on compression have also been explored in this work. In an attempt to determine unambiguously the positive correlation between the elastic shear constant C_{44} and its slope C'_{44} under high pressure, future work will focus on the investigation of vibrational dynamics for other HCP metals.

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