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Anharmonic effective pair potentials of gold under high pressure and high temperature

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Abstract

In order to examine the effect of pressure on the anharmonicity of Au, extended x-ray absorption fine-structure spectra near the Au L_3 edge were measured in the temperature range from 300 to 1100 K under pressures up to 14 GPa using large-volume high-pressure devices and synchrotron radiation. The anharmonic effective pair potentials of Au, $V(u) = au^2/2! + bu^3/3!$, at 0.1 MPa, 6 and 14 GPa have been calculated. The pressure dependence of the thermal expansion coefficients has also been evaluated. The reliability of the anharmonic correction proposed on the basis of the Anderson scale has been discussed.

1. Introduction

Gold (Au) has been widely used as a pressure marker for *in situ* x-ray experiments under high pressures and high temperatures because of its chemical stability and moderate compressibility. On the other hand, some problems inherent in this method of pressure calibration have been pointed out. It is reported that pressure determined by the equations of state (EOS) of Au proposed by different authors [1, 2] are not consistent in high-temperature regions. It has also been shown that discrepancies between the pressures determined using Au and other pressure markers become discernible at elevated temperatures [3]. In order to obtain the exact pressure and temperature in *in situ* experiments, it is most desirable to establish a reliable EOS for Au. The uncertainties of the EOS at high temperatures are mainly attributable to incorrect estimation of the effect of pressure on the thermal expansion in high-temperature and high-pressure regions. Extended x-ray absorption fine-structure (EXAFS) spectroscopy is a useful tool for clarifying the immediate environment around an absorbing atom. Analysis of the EXAFS Debye–Waller factor provides an anharmonic effective pair potential and can give detailed information about the anharmonicity of the thermal vibration of atoms [4]. In this

study, we determined the thermal expansion coefficients for Au by a high-temperature and high-pressure EXAFS technique. We also investigated the anharmonic interatomic potentials of Au by the cumulant expansion method under pressure up to 14 GPa and discussed the anharmonicity of Au under high-temperature and high-pressure conditions. We discussed the reliability of the Au calibration standard presented by Anderson *et al* [2].

2. Experiments and data analysis

High-pressure EXAFS measurements were carried out on bending magnet beamlines, BL01B1 and BL14B1, at SPring-8. A large-volume uniaxial press, the Paris–Edinburgh press [5], on BL01B1 and a cubic-type press, SMAP 180 [6], on BL14B1 were used for the pressure ranges below and above 6 GPa, respectively. Au foil 4 μm in thickness with a nominal purity of 99.95% was used. The Au foil was put in a BN sample chamber and encased in a pressure-transmitting medium made of a mixture of amorphous boron and epoxy resin (4:1 by weight ratio). A pair of graphite discs formed a furnace. The temperature in the pressure cell was monitored with a W97Re3–W75Re25 thermocouple without correction for the effect of pressure on the EMF. The nominal temperatures were kept within $\pm 0.5\%$ throughout the runs. The temperature difference between the hot junction of the thermocouple and the sample was within $\pm 0.5\%$. Generated pressure was estimated using a calibration curve based on a NaCl pressure marker [7, 8]. X-ray absorption spectra near Au L_3 edges were measured at temperatures from 300 to 1100 K under pressures of 0, 6, 9, 12 and 14 GPa. The incident x-ray beam was monochromatized by a Si(111) channel-cut monochromator. The x-ray beam was vertically focused by mirrors. The x-ray beam size was 0.3 mm (horizontally) and 0.2 mm (vertically). The intensities of the incident and transmitted x-rays were measured by ionization chambers filled with $Ar(15\%) + N_2(85\%)$ and $Ar(50\%) + N_2(50\%)$ gases, respectively. For the reference data at ambient pressure, EXAFS data collection was also performed at the XAFS station of BL10B of KEK-PF at temperatures from 300 to 1000 K. Details of the ambient pressure experiment are given elsewhere [4].

3. EXAFS data analysis

The EXAFS interference function, $\chi(k)$, was extracted from the measured absorption spectra following a standard procedure [9] (k denotes the wavenumber of the photoelectrons): $k = [2m(E - E_0)/\hbar^2]^{1/2}$. $\chi(k)$ was normalized using McMaster coefficients according to an EXAFS workshop report [10]. In quantitative analyses we carried out a Fourier-filtering technique and used a nonlinear least-squares fitting method, comparing the observed $\chi_{exp}(k)$ and calculated $\chi_{calc}(k)$. Details of the analysis are given elsewhere [11]. We considered pairs of atoms interacting via a central-field potential $V(r)$, where r is the distance between two atoms. Upon defining u as the deviation of the bond length from r_0, $V(u)$ is expressed as

$$V(u) = \frac{1}{2!}au^2 + \frac{1}{3!}bu^3 + \frac{1}{4!}cu^4 \tag{1}$$

where $u = r - r_0$. Here we adopt the anharmonic potential model up to third-order terms because the parameter c is proved to be negligible by the present analysis. The linear thermal expansion coefficient α_l and the net thermal expansion $a(T) = \langle r - r_0 \rangle$ are also obtained from [12].

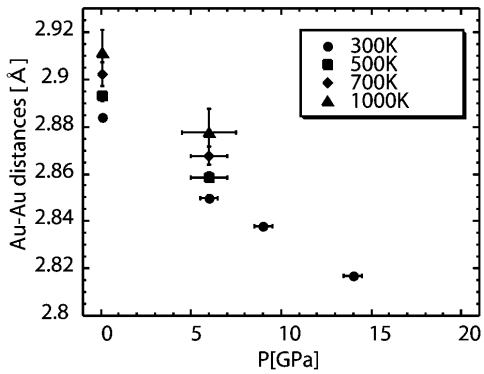

Figure 1. Pressure dependence of the first-nearest-neighbour distance in Au at high temperature.

Table 1. The Au pressure scale evaluated from EXAFS experimental results. Pressure (GPa) versus the first-nearest atomic distances of Au (Å).

P (GPa)	300 K	500 K	1000 K	1500 K	2000 K
0.1	2.884	2.894	2.920	2.952	2.988
1	2.878	2.888	2.914	2.944	2.978
2	2.873	2.882	2.908	2.937	2.969
3	2.868	2.877	2.902	2.930	2.960
4	2.863	2.872	2.896	2.923	2.951
5	2.858	2.867	2.890	2.916	2.942
6	2.853	2.862	2.885	2.909	2.934
7	2.849	2.859	2.888	2.921	2.959
8	2.844	2.853	2.874	2.895	2.917
9	2.839	2.848	2.869	2.889	2.908
10	2.835	2.843	2.863	2.882	2.900
11	2.831	2.839	2.858	2.876	2.892
12	2.826	2.834	2.853	2.870	2.884
13	2.822	2.830	2.848	2.863	2.876
14	2.818	2.826	2.843	2.857	2.868
15	2.814	2.822	2.839	2.851	2.860
16	2.810	2.818	2.834	2.845	2.852
17	2.806	2.814	2.829	2.840	2.845
18	2.803	2.810	2.825	2.834	2.837
19	2.799	2.806	2.820	2.828	2.830
20	2.795	2.803	2.816	2.823	2.823

4. Results

The first-nearest atomic distances up to 14 GPa and 1000 K obtained from the present EXAFS experiments are shown in figure 1 and table 1. The errors of the Au–Au distances are around 1%. The interatomic distances in the extended pressure and temperature region up to 20 GPa and 2000 K are also listed in table 1. Details will be discussed later. The anharmonic effective pair potentials obtained for Au under 0.1 MPa, 6 GPa and 14 GPa are shown in figure 2.

The anharmonic effective pair potential coefficients a and b in equation (1) are calculated to be 3.80 eV Å^{-2} and -7.6 eV Å^{-3}, 3.95 eV Å^{-2} and -6.5 eV Å^{-3}, 4.17 eV Å^{-2} and -5.7 eV Å^{-3} at 0.1 MPa, 6 GPa and 14 GPa, respectively. The potential coefficient a increases by about 4% at 6 GPa and 10% at 14 GPa indicating that potential widths become narrower on compression as shown in figure 2. The potential changes affect the vibrations of atoms.

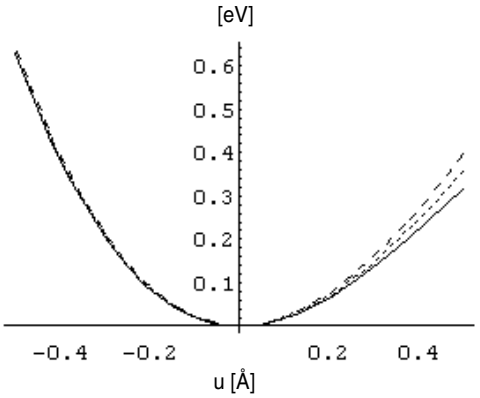

Figure 2. Anharmonic effective pair potentials of gold under 0.1 MPa (solid curve), 6 GPa (0.1, dotted curve), 14 GPa (0.3, dotted curve) at 300 K.

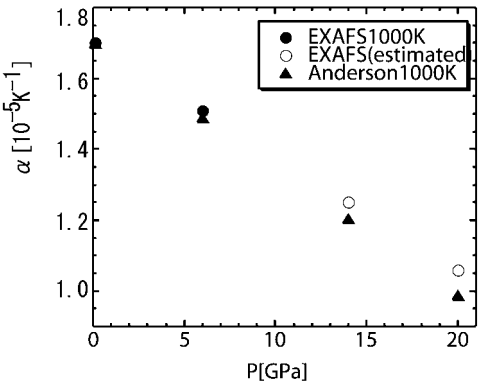

Figure 3. The pressure dependence of the thermal expansion coefficients around 1000 K. Closed circles, open circles and closed triangles represent α_l obtained from EXAFS experiments, extrapolation of experimental data and Anderson's EOS, respectively.

The linear thermal expansion coefficients α_l can be derived from EXAFS parameters [12] and are calculated at 300, 500 and 1000 K under pressure. The thermal expansion coefficients, α_l, have the tendency of becoming smaller linearly with the increase of pressure in this region. At 14 GPa, α_l falls by 26% from 300 to 1000 K relatively. In comparable calculations, α_l calculated from the EOS proposed by Anderson *et al* [2] changes by 28% under the same conditions [13].

5. Discussion

We discuss the reliability of the Anderson scale by examining the location of the post-spinel (Mg_2SiO_4 spinel = MgO perovskite + MgO periclase) boundary in the Earth's mantle. The boundary determined by *in situ* diffraction study using the Anderson scale [14] is situated at 20.5 GPa and 2100 K, which is ∼2 GPa lower than the earlier estimates. Recent studies [15, 16] show that the discrepancy is due to the error in the Anderson scale. Figure 3 shows the pressure dependence of the thermal expansion coefficients around 1000 K. There are discrepancies between the results from the EXAFS experiments and Anderson's EOS, and they become larger with the rise of pressure.

Using the present data, we estimate the interatomic distances of Au around 20 GPa and compare them with those calculated from the Anderson scale. The interatomic distances up to 20 GPa below 1000 K are estimated by extrapolating the pressure dependence of the thermal expansion coefficients. The interatomic distances at 1500 and 2000 K are calculated by extrapolating the temperature dependences of the atomic distances assuming that no melting occurs. The calculated atomic distances in the extended pressure and temperature region are shown in table 1. At 20 GPa and 1000 K, our calculations yield 2.816 Å (details of the calculations are given in [12]). However, 2.816 Å in the Anderson scale corresponds to 18.5–19 GPa. This result suggests that the Anderson scale underestimates the pressure dependence of the anharmonicity. At 20 GPa and 2000 K, though errors caused by our extrapolation may be large, the difference in pressure between the present calculations and the Anderson scale is about 3 GPa. If the post-spinel boundary given by Irifune *et al* [14] is moved by 2 GPa to higher pressure, it shows good agreement with the earlier estimates. EXAFS studies of Au or

other pressure markers in extended pressure and temperature ranges promise to give the more correct EOS.

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