First-principles electronic thermal pressure of metal Au and Pt

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Electronic thermal pressures (ETP's) of metal Au and Pt are predicted by first-principles electronic structure calculations based on the density functional theory in order to refine their thermal equations of state (EOS) which are frequently used as pressure scales in *in situ* high-pressure and high-temperature experiment. We find a large difference in the magnitude of ETP's for Au and Pt, which can be attributed to the different positions of the Fermi level. The ETP for Au is considerably smaller than it for Pt. The latter reaches 0.85 GPa at 2000 K, whereas the former is only 0.05 GPa at the same temperature. We also find a different temperature dependence of the ETP's of Au and Pt under high temperature, which arises from the different manner of thermal excitation. It is illustrated that the corrections of the ETP for known EOS of Au and Pt becomes substantially important with increasing temperature, and the ETP can perfectly compensate for the measured discrepancy of pressure values determined by previous EOS of Au and Pt.

I. INTRODUCTION

Metal Au and Pt are substantially important for high-pressure physics and the material science, because their temperature-pressure-volume (T-P-V) equations of state (EOS's) (Refs. 1–3) are most frequently used as pressure calibrants in *in situ* high-pressure and high-temperature experiments (e.g., Refs. 4–10). Their characteristic properties, namely, low rigidity and large chemical stability up to megabar conditions, are suitable for this special role.[11,12] However, some recent experimental studies have reported that the pressure values derived from these EOS's disperse in a wide range of pressure under high temperature condition. The Anderson's EOS of Au gives 1 GPa higher values than the Holmes' EOS of Pt at about 2000 K.[13] Such ambiguity in the pressure measurement is fundamental problem for the high-pressure science and the relevant refinement of these EOS's are therefore desired.[14–17]

The EOS of a metal constructed in the same way as that of an insulator, such as the Anderson's EOS of Au and the Holmes' EOS of Pt,[1,2] has an obvious deficiency itself, as pointed out in Refs. 18 and 19. Anderson's thermal EOS was constructed on the basis of a classical Debye model which is adaptable only for phonon. Holmes *et al.* intentionally neglected the electronic contribution to the thermal expansion, since it was small under low temperature condition such as room temperature. However, as is well known in metal, the contribution of the electronic degree of freedom to the thermal expansion becomes important with increasing temperature.[20,21] Since this effect was not taken into account in the known EOS's of Au and Pt, there is a possibility that they underestimated the value of pressure at high-T conditions where the electronic thermal pressure (ETP) becomes significant.

However, this contribution to the thermal expansion of metal Au and Pt and its pressure dependence have never been studied at all, to our knowledge. It has also never been clarified whether this effect is negligible or not under high-temperature and high-pressure conditions. Quantitative estimations are significantly important for pressure measure-

ments in *in situ* high-pressure and high-temperature experiments. In the present study, based on the electronic theory of metal and the electronic structure calculation method with the density functional theory,[22] we predict ETP's of gold and platinum and discuss the necessity for possible improvement of the known equations of state under high T-P conditions.

The pressure change due to the thermal excitation of electron, namely ETP, is given by[21]

$$P_{\text{th,el}}(V,T) = -\left(\frac{\partial \Delta f_{\text{el}}(V,T)}{\partial V}\right)_T. \qquad (1)$$

Here Δf_{el} is the thermal contribution to the electronic free energy density, represented as

$$\Delta f_{\text{el}}(V,T) = f_{\text{el}}(V,T) - f_{\text{el}}(V,T=0). \qquad (2)$$

The electronic free energy density is given by

$$f_{\text{el}}(V,T) = u_{\text{el}}(V,T) - T s_{\text{el}}(V,T), \qquad (3)$$

where u_{el} and s_{el} are the total electronic energy density and the entropy density, respectively. These quantities can be calculated by using the electronic density of states $n(\epsilon,V)$ as follows:

$$u_{\text{el}}(V,T) = \int_{-\infty}^{\infty} d\epsilon \, n(\epsilon,V) \epsilon f(\epsilon,T), \qquad (4)$$

$$s_{\text{el}}(V,T) = \int_0^T \frac{c_{v_{\text{el}}}(V,T)}{T} dT$$

$$= -k_B \int d\epsilon \, n(\epsilon,V)[f \ln f + (1-f)\ln(1-f)], \qquad (5)$$

where $f(\epsilon,T)$ is the Fermi-Dirac distribution function,

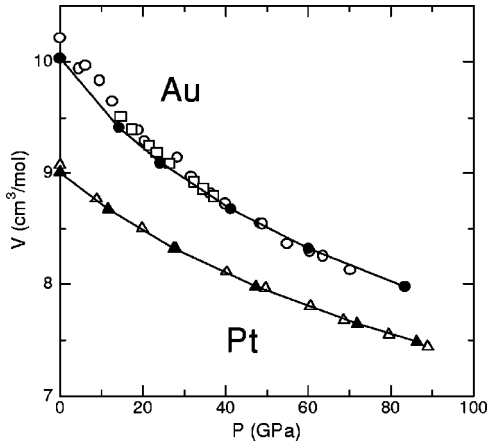$$f(\epsilon,T) = \frac{1}{e^{(\epsilon-\mu)/k_B T}+1}, \qquad (6)$$

FIG. 1. Calculated volumes of Au and Pt as a function of pressure (filled symbols). Experimental results are also shown by open symbols. Open circles, squares and triangles are from Refs. 29, 12 and 2, respectively.

k_B is the Boltzman constant, and $c_{v_{\mathrm{el}}}=(\partial u_{\mathrm{el}}/\partial T)_V$ is the electronic specific heat. Consequently, $P_{\mathrm{th,el}}(V,T)$ is obtained from $n(\epsilon)$, which can be calculated from the electronic structure.

II. CALCULATIONAL METHOD

In this study electronic structures of fcc-formed Au and Pt were calculated by the first-principles method within the density functional theory[22] and the local spin density approximation.[23] A Vosko-Wilk-Nasauir-type exchange-correlation potential[24] was applied. To calculate electronic structure, we adopted the *ab initio* full-potential linear muffin-tin-orbital (FP-LMTO) method[25] and a multiple-κ muffin-tin-orbital basis set.[26] We used three κ for valence electrons: $\kappa^2=-0.1$, -1.0, and -2.5 Ry were used for $6s$, $6p$, and $5d$ states. One more energy panel set $\kappa^2=-3.5$ Ry was added for the semicore $5p$ state. The core states were recalculated at each self-consistent iteration. It is known that the spin-orbit (SO) coupling of valence states is essential to describe the electronic structure with splittings and shifts of $5d$ bands in heavy metals.[27] In the present calculations the full-relativistic treatment for valence electrons was also performed to correctly include the SO coupling.

Charge densities, potentials and the envelope functions inside the muffin-tin spheres (MTS's) were expanded up to $l=8$. Densities and potentials at the interstitial region were expanded in the Fourier series with 6566 plane waves. In the interstitial region, basis functions were also expanded by plane waves up to a cutoff corresponding approximately to 60–90, 140–170, and 180–280 plane waves per s, p, and d orbital, respectively. The improved tetrahedron method[28] were used for the k-point sampling. We carefully checked to converge the energy eigenvalues with respect to the number of k points at small volume, because more k points are needed to maintain the same k-point density in Fourier space as at the large volume. A total of 376 k points were used in the irreducible wedge of the Brillouin zone. Through all calculations the MTS radius was settled to be 2.49 and 2.44 a.u.
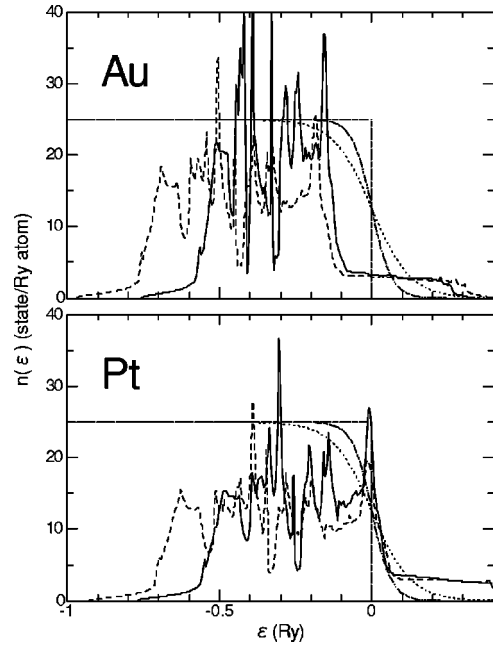

FIG. 2. Calculated DOS profiles $n(\epsilon)$ of Au and Pt at volumes V/V_0 of 1.0 (solid lines) and 0.8 (broken lines) with a Fermi distribution function $f(\epsilon,T)$. The maximum ordinate value of $f(\epsilon,T)$ is 1. The dot-dashed curve is $f(\epsilon,T=0\mathrm{K})$, the double-dot-dashed curve is $f(\epsilon,T=5000\ \mathrm{K})$, and the dotted curve is $f(\epsilon,T=10000\ \mathrm{K})$. The Fermi level is set to be 0 Ry.

for Au and Pt, respectively. The ground state equilibrium properties of zero-pressure volume (V_0), bulk modulus (B_0), and its pressure derivative (B_0') were determined by least-squares fitting to the E-V form of the third-order Birch-Murnaghan equation of state (BM-EOS).[29]

III. RESULTS AND DISCUSSION

Calculated volume compression curves shown in Fig. 1 with experimental results agree quite well with the experiments in wide pressure ranges up to near a megabar pressure. V_0, B_0, and B_0' determined by the BM-EOS are 10.03 (10.22) cm^3/mol, 182.1 (166.6) GPa, and 6.2 (5.5) for Au and 8.97 (9.08) cm^3/mol, 280.8 (266) GPa, and 6.1 (5.8) for Pt, respectively, where the experimental values[30,2] are given in parentheses. Though calculated V_0 and B_0 are approximately 2% smaller and 10% larger than the room-temperature experimental results, these trends are systematically seen in the local-density-approximation calculations without the lattice thermal energy of finite temperature.

Calculated density of states (DOS) profiles $n(\epsilon)$ for Au and Pt at $V/V_0=1$ and 0.8 are shown in Fig. 2 with a Fermi function $f(\epsilon,T)$. These are schematically explained by the highly frequent d dominant part within the low, smooth, and wide s dominant part. Moreover, the $5d$ parts are clearly divided into three parts. This is characteristic in the DOS including SO coupling, while the partition in the $5d$ DOS without SO coupling is broader. Figure 2 indicates that
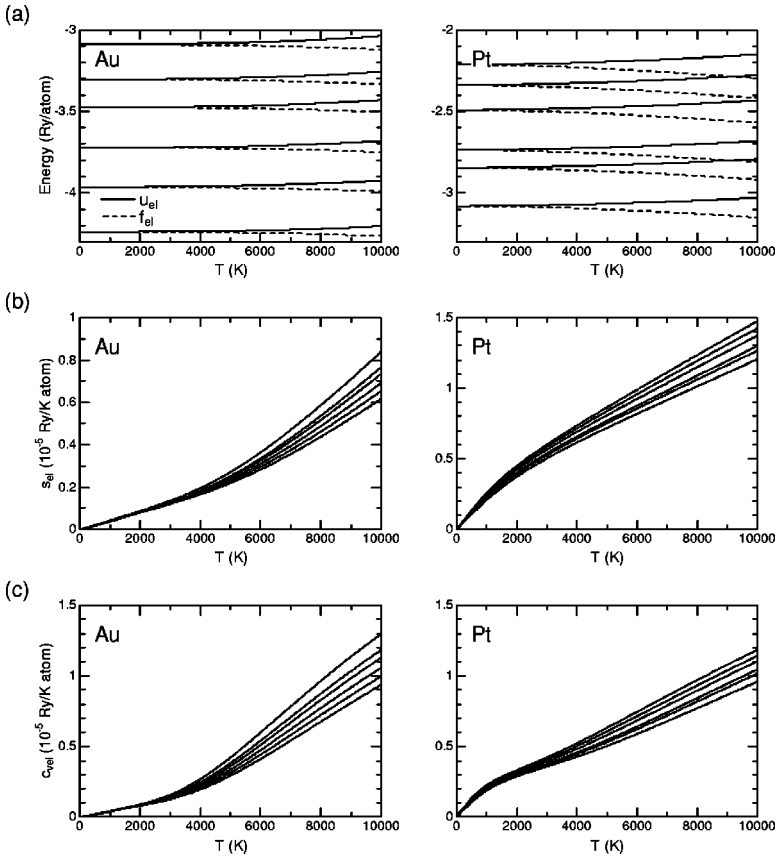
FIG. 3. Temperature dependencies of the total electronic energy density u_{el} and free energy density f_{el} (a), entropy density s_{el} (b), and electronic specific heat $c_{v_{el}}$ (c) at six volumes which correspond to the filled symbols shown in Fig. 1. The lower plot is the result at higher compression (smaller volume).

$n(\epsilon)$'s of Au and Pt and trends of their volume dependence are very similar. However, the positions of the Fermi level are essentially different. That is, the Fermi level exists in the higher part of the $6s$ part above the $5d$ part in Au, it crosses the upper part of the $5d$ part in Pt. Such a difference corresponds to the fulfilled or unfilled d state in the electronic configurations of Au and Pt atom.

The total electronic energy density u_{el}, free energy density f_{el}, and the entropy density s_{el} at several volumes are shown in Figs. 3(a) and 3(b) as a function of temperature. The electronic specific heat $c_{v_{el}}$ is also shown in Fig. 3(c). It is indicated that temperature dependencies of the entropy densities and specific heats of Au and Pt change at a few thousand K with different tendency. Those of Au increase at ~ 4000 K, whereas those of Pt decrease at ~ 1500 K. These differences can be understood from $n(\epsilon)$ plots in Fig. 2. In Au, the excitation from a d state which has a large density of states increases at a sufficiently high temperature, but in Pt the excitation to the s state which has a small density of states increases under high temperature. Thus the temperature dependence of the excitation energy shifts to larger and smaller in Au and Pt, respectively.

We comment on a more simple calculational way of the ETP, which is based on the so-called Sömmerfeld expansion of electronic free energy, and uses only the density of states at the Fermi level.[31,20] Prudent care is necessary to use this method because this is only valid under the sufficiently low temperature condition where the state of thermal excitation is unchangeable. Such an overly rough way clearly never conducts the opposite high-temperature behavior of entropy and

specific heat of Au and Pt (Fig. 3), since it is caused by the excitation of electrons different from ones at the Fermi level. The total density of states is therefore indispensable to predict the detail temperature dependence of the ETP.

In Fig. 4 the thermal contributions to the electronic free energy density Δf_{el} are shown up to 10000 K at intervals of 1000 K with their linear least-square fittings. The volume dependence of Δf_{el} of Au is smaller than those of Pt, since the s part of the DOS is insensitive to volume, whereas the d part is sensitive to volume (Fig. 2). The good regression by linear fitting in Fig. 4 indicates that the ETP does not depend on volume in the given volume ranges. The temperature dependence of Δf_{el} is also smaller in Au, since the behavior of s_{el} is reflected to Δf_{el}.

By means of these results ETP's are calculated as a function of temperature, as shown in Fig. 5. We find that the ETP increases with increasing temperature and reaches over a gigapascal at thousands of K. Therefore, when the known EOS's of Au and Pt, which do not take ETP's into account, are used as pressure calibrants at sufficiently high temperature, the corrections of the ETP's must be adapted. However, Fig. 5 shows the large difference between ETP's of Au and Pt. At 2000 K the ETP of Pt becomes 0.85 GPa, which is not clearly negligible. On the other hand, the ETP of Au is remarkably smaller, and even at a higher temperature of 4000 K it is only 0.26 GPa. This difference in the ETP's of the two metals is essentially caused by the position of the Fermi level, namely, s or d nature of the top of the valence electron.

The present results mean that the Anderson's EOS of Au is not significantly changed by the correction of the ETP up
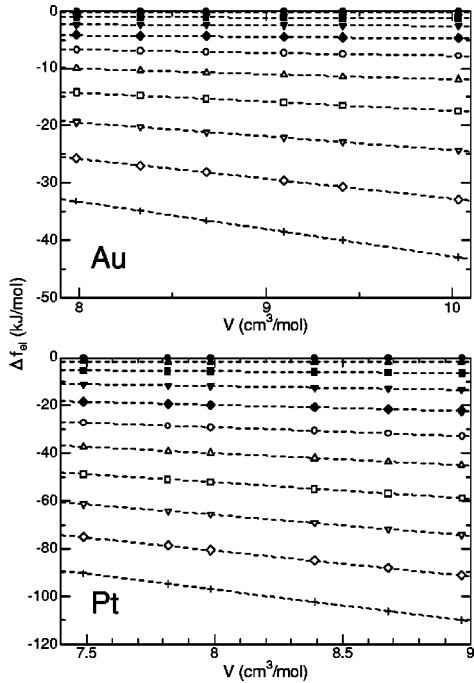
FIG. 4. Volume dependencies of the thermal contribution to the electronic free energy density Δf_{el} at 11 temperatures from 0 to 10000 K at intervals of 1000 K. The lower plot is the result at higher temperature. Dashed lines are the linear fittings at each temperature.

TABLE I. Calculated electronic thermal pressure of Au and Pt. Units are given in GPa.

T (K)	Au	Pt	T (K)	Au	Pt
0	0.00	0.00	2600	0.09	1.31
100	0.00	0.01	2700	0.10	1.39
200	0.00	0.02	2800	0.10	1.47
300	0.00	0.04	2900	0.11	1.56
400	0.00	0.06	3000	0.12	1.64
500	0.00	0.08	3100	0.19	1.73
600	0.00	0.11	3200	0.19	1.82
700	0.00	0.14	3300	0.19	1.91
800	0.01	0.17	3400	0.20	2.01
900	0.01	0.21	3500	0.20	2.11
1000	0.01	0.25	3600	0.21	2.20
1100	0.01	0.29	3700	0.22	2.31
1200	0.02	0.34	3800	0.23	2.41
1300	0.02	0.39	3900	0.25	2.52
1400	0.02	0.45	4000	0.26	2.63
1500	0.03	0.51	4100	0.28	2.73
1600	0.03	0.57	4200	0.30	2.85
1700	0.03	0.63	4300	0.32	2.96
1800	0.04	0.70	4400	0.34	3.08
1900	0.04	0.77	4500	0.37	3.20
2000	0.05	0.85	4600	0.39	3.32
2100	0.06	0.95	4700	0.42	3.44
2200	0.06	1.01	4800	0.45	3.57
2300	0.07	1.09	4900	0.48	3.70
2400	0.07	1.16	5000	0.52	3.82
2500	0.08	1.23			

to a few thousand K. It is incompatible with the earlier expectation,[18,19] which inferred that the measured discrepancy of pressure values by Au and insulator pressure scales at ~2000 K could be explained by the ETP. However, the difference between the ETP's of Au and Pt at 2000 K, which is 0.8 GPa, can perfectly compensate for the measured discrepancy between pressure values derived from the Anderson's EOS of Au and Holmes' EOS of Pt (Ref. 13). Moreover, Hirose *et al.* showed that pressure values determined by other transition metals W and Mo also deviate from pressure by Au with a similar degree of Pt. It can be considered that these deviations are also caused by a neglect of the ETP, since W and Mo have the unfilled valence *d* band as Pt, and their ETP's should be similar to that of Pt.
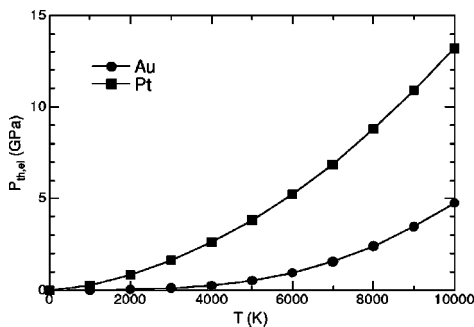
IV. CONCLUSION

The electronic thermal pressures (ETP's) of metal Au and Pt are predicted by a full relativistic version of the first principles FP-LMTO method to refine their known *T-P-V* EOS. We find that the corrections of ETP's to previous EOS's become indispensable with increasing temperature. However, their pressure dependencies are quite small. Moreover, the contribution of electrons to the thermal expansion of Au is significantly smaller than that of Pt, resulting from the difference in nature of the top of the valence electron. It is concluded that the pressure difference measured by *in situ* high-temperature and high-pressure experiments using the pressure scale of Au and other transition metals can be compensated for by the ETP.

APPENDIX

We give the specific values of calculated ETP up to 5000 K at intervals of 100 K in Table I. This table is useful for corrections of the ETP for the known EOS.

FIG. 5. Electronic thermal pressures $P_{th,el}$ of Au and Pt as a function of temperature.

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