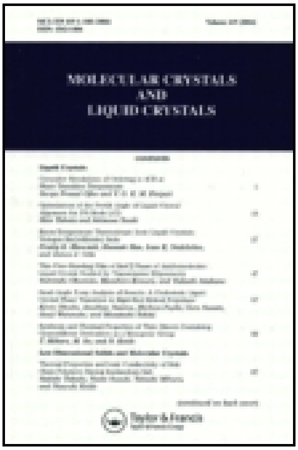

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Structural Phase Transition and Au Valence State of the Perovskite-Type Au Mixed-Valence Compounds $M_2Au_2X_6$(M = Rb, Cs; X = Cl, Br, I) Under High Pressure

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STRUCTURAL PHASE TRANSITION AND Au VALENCE STATE OF THE PEROVSKITE-TYPE Au MIXED-VALENCE COMPOUNDS $M_2Au_2X_6$(M=Rb,Cs;X=Cl,Br,I) UNDER HIGH PRESSURE

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Abstract We have investigated the structural P-T phase diagram, the Au valence state and the physical properties of $M_2Au_2X_6$ (M= Rb, Cs; X= Cl, Br, I) under high pressures. When the pressure is applied at room temperature, $Cs_2Au_2X_6$(X=Cl,Br,I) and $Rb_2Au_2I_6$ undergo a tetragonal-to-tetragonal phase transition at 11 GPa, 9 GPa, 5.5 GPa and 8.5 GPa, respectively. This transition is regarded as a band Jahn-Teller transition driven by the $Au^{I,III} \rightarrow Au^{II}$ transition, which was proven by the ^{197}Au Mössbauer spectroscopy under high pressure. The metallic cubic perovskite structure appearing under high pressures and high temperatures for all the title compounds, $M_2Au_2X_6$(M=Rb,Cs; X=Cl,Br,I) could be obtained as a metastable state at room temperature and ambient pressure. The Au valence states in the cubic phase are concluded to be Au^{II}.

INTRODUCTION

Since the discovery of high-Tc superconductors such as $La_{2-x}Ba_xCuO_4$[1] and $Ba_{1-x}K_xBiO_3$,[2] mixed valence systems having perovskite-type structure have become of great interest. For example, the valence state of Bi has been considered as an important factor for a comprehension of the physical properties of $BaPb_{1-x}Bi_xO_3$ system. The insulating state of the host compound $BaBiO_3$ is explained by the charge disproportionation of the Bi cations (IV into III and V) which couples to lattice deformation or the stabilization of a commensurate charge-density wave. According to recent theory,[3] an unusual superconductor due to the Bose condensation of bipolarons is expected under some electron-phonon coupling constant λ, while in the large limit of λ, a bipolaronic insulator occurs. The insulating $BaBiO_3$ is regarded as on-site bipolaron system where the bipolarons form a three-dimensional lattice and localize at the Bi^{III} site.

$Cs_2Au_2X_6$(X=Cl, Br and I) also have a mixed-valence system having perovskite-type structure, whose structure are shown in Fig. 1(a) and 1(b). Its structure consists of three-dimensional metal-halogen frameworks formed by elongated octahedra with Au^{III} and compressed octahedra with Au^{I} sharing their corners. Consequently, the breathing-mode-type distortion of AuX_6 octahedra is present in this system. These characteristic properties of crystal structure and mixed-valency are quite similar to those of $BaBiO_3$ which is the parent compound of the superconductors $Ba_{1-x}(K\text{ or }Rb)_xBiO_3$ and $BaPb_{1-x}Bi_xO_3$.

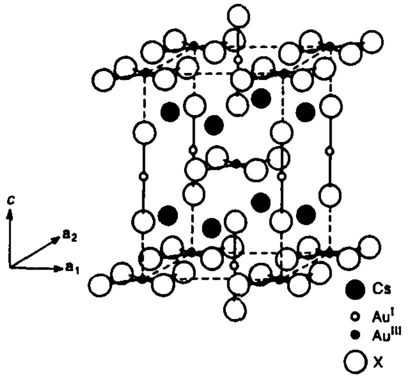

FIGURE 1(a) Crystal structure of $Cs_2Au_2X_6$(X=Cl,Br,I).

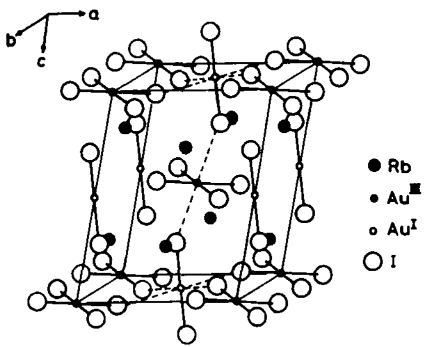

FIGURE 1(b) Crystal structure of $Rb_2Au_2X_6$(X=Br,I).

The purpose of this paper is to report the crystal structure, the Au valence state and the physical properties of $Cs_2Au_2X_6$, and to discuss the relationship between the crystal structure and the Au valence state.

EXPERIMENTAL

The structure analysis of these compounds was performed by energy-dispersive X-ray diffraction method using the high-temperature and high-pressure apparatus[4] with synchrotron radiation (SR) in the National Laboratory for High Energy Physics, Japan.

The electrical resistivity was measured for the single crystal of $Cs_2Au_2I_6$ by the standard dc four probe technique using a low-temperature and high-pressure apparatus[5] in the Institute of Solid State Physics, University of Tokyo, Japan.

The ^{197}Au Mössbauer spectroscopy under high pressure was measured using a Cu-Be clamp system with B_4C anvils.[6] A ^{197}Pt source with an activity of about 200 mCi was prepared at the Hahn Meitner Institute, Berlin during 24 h.

RESULT AND DISCUSSION

Fig. 2 shows the P-T phase diagram for $Cs_2Au_2X_6$(X=Cl, Br, I) and $Rb_2Au_2I_6$. In the case of $Cs_2Au_2X_6$, two kinds of tetragonal phases and a cubic phase exist.[7] In the case of $Rb_2Au_2I_6$, a monoclinic phase, three kinds of tetragonal phases and a cubic phase exist. The cubic phase appearing at high pressures and high temperatures could be obtained as a metastable state even at room temperature(r.t.) and ambient pressure(a.p.) for all the title compounds.

At r.t., $Cs_2Au_2Cl_6$, $Cs_2Au_2Br_6$ and $Cs_2Au_2I_6$ undergo a tetragonal-to-

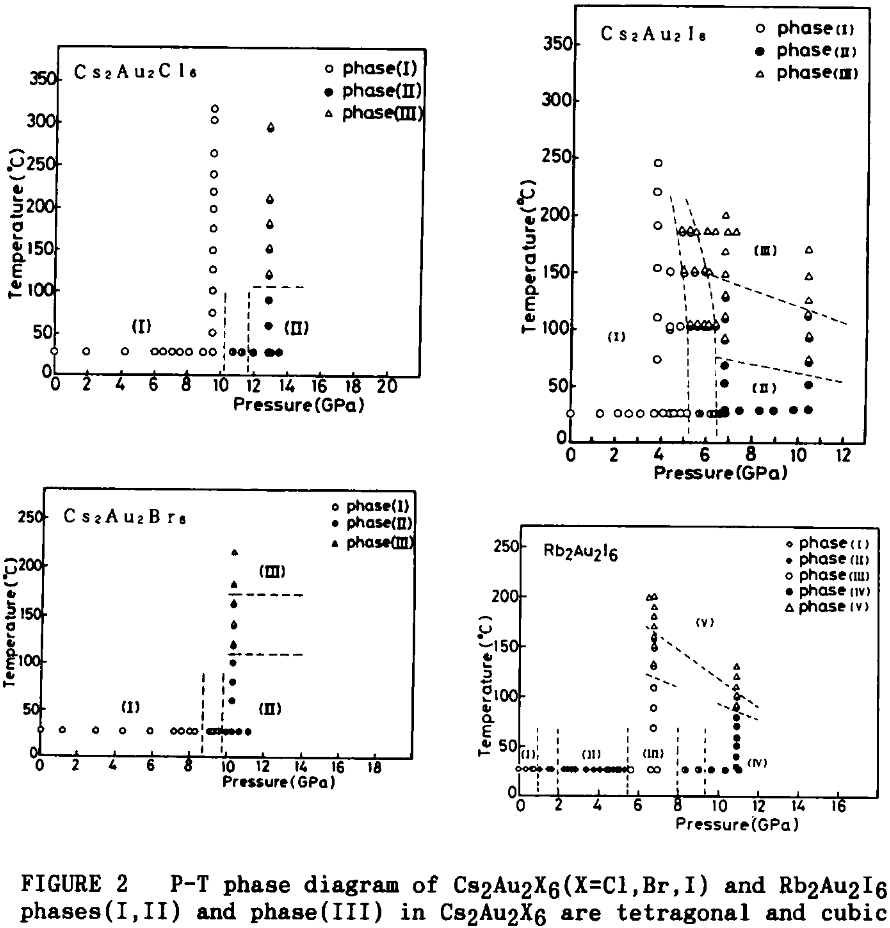

FIGURE 2 P-T phase diagram of $Cs_2Au_2X_6$(X=Cl,Br,I) and $Rb_2Au_2I_6$: phases(I,II) and phase(III) in $Cs_2Au_2X_6$ are tetragonal and cubic, respectively; phase(I), phases(II, III, IV) and phase(V) in $Rb_2Au_2I_6$ are monoclinic, tetragonal and cubic, respectively.

tetragonal phase transition at 11 GPa, 9 GPa and 5.5 GPa, respectively, whose values are beyond the pressure where the activation energy for the electrical resistivity becomes zero. The pressures where the activation energies become zero are 7.5 GPa, 7.2 GPa and 4.4 GPa, for $Cs_2Au_2Cl_6$, $Cs_2Au_2Br_6$ and $Cs_2Au_2I_6$, respectively.[8] Above the pressure where the activation energy becomes zero, the difference between the real oxidation states of Au^{I} and Au^{III} becomes quite small, which is proved by the fact that the (211) and (103) reflections, caused by the distortion of the bridging halogens from the midpoint between the Au^{I} and Au^{III} ions, are hardly detected in this pressure region. If the valence states of Au^{I} and Au^{III} finally become $Au^{II}(5d^9)$, the lowering in symmetry of AuX_6 octahedra should be caused by the Jahn-Teller effect.

As mentioned later, the tetragonal-to-tetragonal phase transition in $Cs_2Au_2X_6$ is regarded as a band Jahn-Teller transition driven by the $Au^{I,III}$ Au^{II} transition. In order to elucidate the Au valence transition, we have investigated to the ^{197}Au Mössbauer spectra of $Cs_2Au_2I_6$ under high pressures up to 12.5 GPa.[9]

As shown in Fig. 3, with increasing pressure, a gradual increase in the overlap of the doublets is observed due to a substantial increase of

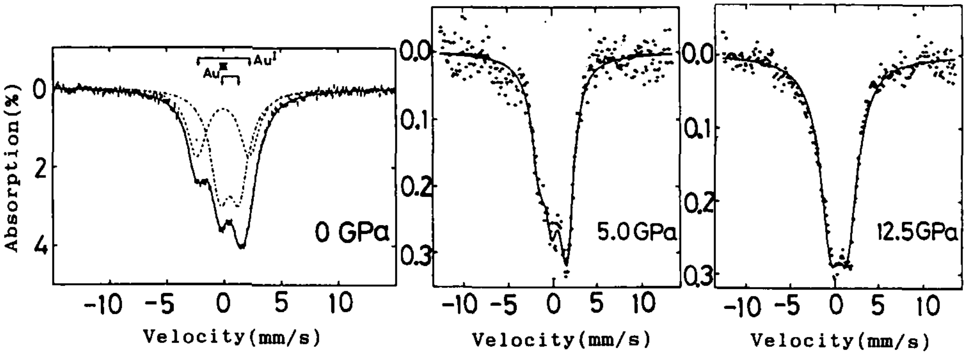

FIGURE 3 ^{197}Au Mössbauer spectra of $Cs_2Au_2I_6$ at a.p., 5.0 GPa, and 12.5 GPa.[9] The spectrum at a.p. shows clearly two overlapping doublets, which is typical for Cs_2Au_2X6 with distorted perovskite structure and $Au^{I,III}$ mixed valence system.

the isomer shift(IS) of Au^{I} and a less pronounced decrease of that of Au^{III} with increasing pressure. Finally, the ^{197}Au Mössbauer spectrum at 12.5 GPa shows only one electronic state for Au in $Cs_2Au_2I_6$. Therefore, the Au valence state of the tetragonal(II) phase in $Cs_2Au_2I_6$ is concluded to be Au^{II}, which is the first direct observation of the Au^{II} state in a relatively simple, primarily ionic compound.

Fig. 4 show the pressure dependence of the axial ratio $2^{1/2}a/c$ indicating the distortion of the tetragonal lattice for $Cs_2Au_2X_6$(X=Cl,Br,I) and $Rb_2Au_2I_6$. The cubic phase is realized at $2^{1/2}a/c$ = 1.0.

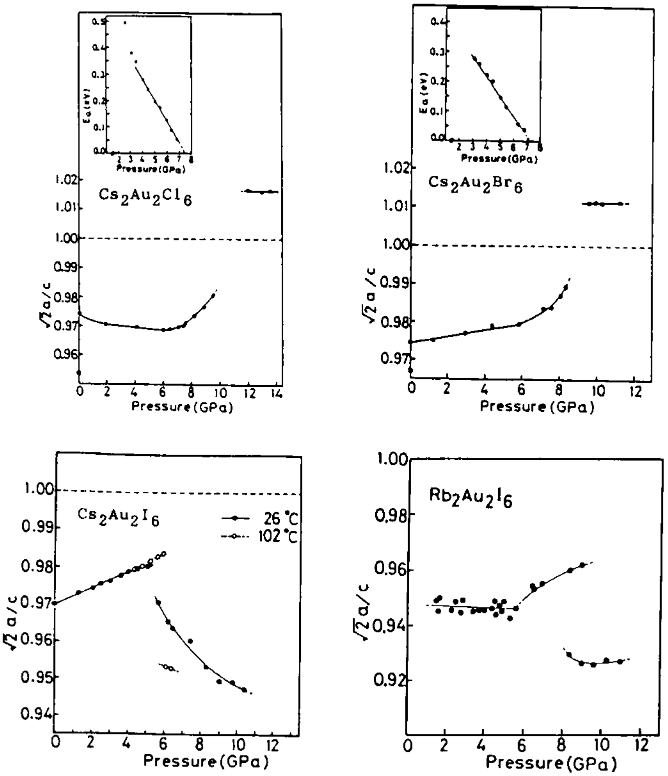

FIGURE 4 Pressure dependence of the axial ratio $2^{1/2}a/c$ of $Cs_2Au_2X_6$ and $Rb_2Au_2I_6$.

In the case of $Cs_2Au_2I_6$, when the pressure is applied at r.t., $2^{1/2}a/c$ increases from 0.969 to 0.980 with increasing pressure up to about 5.5 GPa. However, it drops abruptly from 0.980 to 0.970 at about 5.5 GPa. $Rb_2Au_2I_6$ undergoes two kinds of tetragonal-to-tetragonal transitions at 5 GPa and 8.5 GPa, respectively. The abrupt drops in $2^{1/2}a/c$ at 5.5 GPa in $Cs_2Au_2I_6$ and at 8.5 GPa in $Rb_2Au_2I_6$ are attributed to the band Jahn-Teller transition caused by the realization of the Au^{II} valence state.

Above the transition pressure, $2^{1/2}a/c$ of $Cs_2Au_2I_6$ is smaller than 1.00 and it decreases with pressure. On the other hand, $2^{1/2}a/c$ of $Cs_2Au_2X_6$(X=Cl and Br) is larger than 1.00 and it remains almost unchanged. Therefore, in the second tetragonal phase, the AuI_6 octahedra of $Cs_2Au_2I_6$ are "elongated", contrary the AuX_6 octahedra of $Cs_2Au_2X_6$(X=Cl and Br) are "compressed".

Considering the distortion of the AuX_6 octahedra, the HOMO in the second tetragonal phase is the half-filled $5d_{z^2}$ band and the half-filled $5d_{x^2-y^2}$ band for $Cs_2Au_2X_6$(X=Cl and Br) and $Cs_2Au_2I_6$, respectively. Therefore, it is considered that the second tetragonal phase in $Cs_2Au_2X_6$(X=Cl and Br) behaves as a one-dimensional conductor, while that in $Cs_2Au_2I_6$ behaves as a two-dimensional conductor. In fact, we have confirmed that the second tetragonal phase in $Cs_2Au_2I_6$ behaves as a two-dimensional conductor under high pressures and low temperatures.[10]

Next, we investigate the relationship between the tetragonal-to-

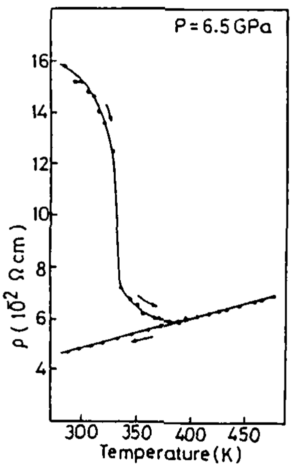

FIGURE 5 Temperature dependence of the resistivity of $Cs_2Au_2I_6$ at 6.5 GPa. The sample was first heated up to 470 K, then cooled down to r.t.[11]

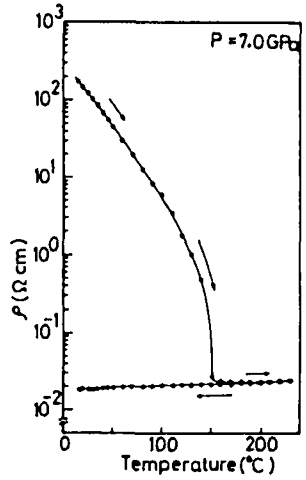

FIGURE 6 Temperature dependence of the resistivity of $Rb_2Au_2I_6$ at 7.0 GPa. The sample was first heated up to 510 K, then cooled down to r.t.

cubic transition and the behavior of the resistivity. According to our resistivity measurement of $Cs_2Au_2I_6$ under high pressures,[11] $Cs_2Au_2I_6$ undergoes a pressure-induced semiconductor-to-metal transition at P = 4.5 GPa and T = r.t. Moreover, as shown in Fig. 5,[11] when the temperature is increased at 6.5 GPa, the resistivity decreases and a steep drop occurs at about 330 K and then it increases linearly above about 400 K, which implies that $Cs_2Au_2I_6$ has two metallic phases and the second metallic phase appears at P = 6.5 GPa and T~330 K. Comparing the behavior of the resistivity with the X-ray diffraction profiles in the vicinity of the tetragonal-to-cubic phase transition, the drastic resistivity drop at about 330 K and the linear increase in the resistivity above 400 K are attributed to the beginning and the end of the tetragonal-to-cubic phase transition, respectively. In the cooling process, the resistivity decreases linearly with temperature cooled down to r.t., which implies that the second metallic phase(phase (III)) can be stable at P = 6.5 GPa and T = r.t. Moreover, this metallic phase could be obtained as a metastable phase at r.t. and a.p. by decreasing temperature and pressure after increasing pressure up to 6.5 GPa and temperature up to 470 K.[11]

Fig. 6 shows the resistivity of $Rb_2Au_2I_6$ as a function of temperature at 7.0 GPa. The steep drop in the resistivity at about 420 K is due to the tetragonal(III)-to-cubic transition. As shown in Fig. 6, the metallic cubic phase is stable at 7.0 GPa and r.t. in the cooling process. Moreover, this metallic phase could be obtained as a metastable phase at r.t. and a.p.

Fig. 7 shows the temperature dependence of the resistivity of the metastable cubic phase in $Cs_2Au_2I_6$. The sample was first heated up to 470 K at 7.5 GPa, then cooled down to 4.2 K. As shown in

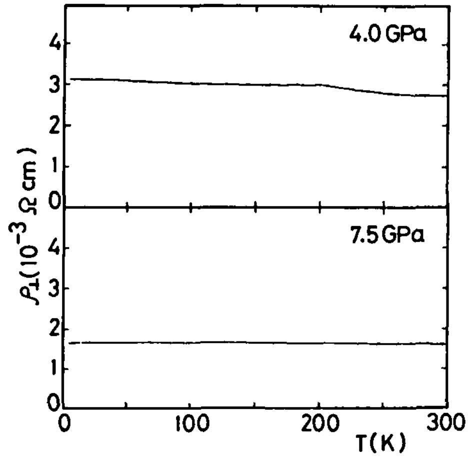

FIGURE 7 Temperature dependence of the resistivity of the metastable cubic phase in $Cs_2Au_2I_6$.

Fig. 7, the resistivity of the metastable cubic phase remains unchanged between r.t. and 4.2 K at both 7.5 GPa and 4.0 GPa.

From the resistivity measurements up to 8 GPa and down to 4.2 K, a superconducting transition has not been observed for $Cs_2Au_2I_6$. Recently, Varma proporsed a theoretical model with negative U effect, which gives insulating behavior near the half-filling band and superconductivity further from the half-filling band in agreement with the properties of $BaPb_{1-x}Bi_xO_3$ and $Ba_{1-x}K_xBiO_3$.[12] From this model, the chemical decoration such as the replacement of Cs or Au with Ba or Pt might be necessary for the research on high-Tc superconductivity.

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