

## Photoinduced phase transition in a mixed-valence gold complex

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We have found a photoinduced phase transition (PIPT) in the mixed-valence (MV) gold complex  $\text{Cs}_2\text{Au}_2\text{Br}_6$  from the MV state (ambient pressure phase) to the single-valence (SV) phase (high-pressure phase) in the pressure region from 6.4 to 6.8 GPa. We have observed an accumulation of the photoirradiation effect of each pulse shot, and have ascribed it to stabilization of the photogenerated SV clusters due to the cooperative Jahn-Teller instability of  $\text{Au}^{2+}$  ions. The PIPT shows a distinct threshold behavior against the photon density as well as the shots number, which has been interpreted in terms of the critical nucleation of the photoinjected SV clusters. We further found that the phototransformed SV phase is not stable below 5.5 GPa, and changes into the former MV phase after a long dead time of  $\sim 10^4$  s.

One of the recent topics of solid state physics is to control the electronic and magnetic state of matters by light. In the past, electronic and magnetic states of several compounds, e.g., (In,Mn)As/GaSb,<sup>1</sup> cobalt-iron cyanide,<sup>2</sup> polydiacetylene,<sup>3</sup> polythiophene,<sup>4</sup> and Fe-based spin cross-over complex,<sup>5</sup> have been reported to be transformed to another state by photoirradiation. Among them, the  $\pi$ -conjugated polymer systems, i.e., polydiacetylene and polythiophene, show photoinduced phase change from a low-temperature (LT) to high-temperature (HT) states<sup>4</sup> as well as that from HT to LT states.<sup>3</sup> A characteristic feature of photoinduced phase transitions (PIPTs) of these polymer systems is existence of the critical photon density<sup>4,3</sup> below which no phase change is induced. We need more examples of materials that show definite PIPT to derive and understand the generic features of PIPTs.

Our strategy to search PIPT is to directly couple the photoexcitation with the electronic phase transition. For example, intense charge-transfer type excitations may trigger a melting of the charge-ordered state. Recently, Miyano *et al.*<sup>6</sup> has reported a photoinduced phase change from the charge-ordered insulating to conductive states in doped manganites  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  ( $0.3 \leq x \leq 0.5$ ),<sup>6</sup> although current seems to be essential for this phenomenon. Matsuda *et al.*<sup>7</sup> have found that photoexcited down spins destroy ferromagnetic spin ordering in films of doped manganites. Here, we have found a PIPT in the mixed-valence (MV) gold complex  $\text{Cs}_2\text{Au}_2\text{Br}_6$ , from the MV state to the single-valence (SV) phase in the pressure region from 6.4 to 6.8 GPa. In this system, the charge-transfer-type electron transfers between the valence-skipped Au sites directly convert the MV region into the SV region, and hence can induce a macroscopic MV-SV phase

transition. The present PIPT in gold complex shows a prominent *memory* effect, or accumulation of the photoirradiation effect of each pulse shot. This makes a sharp contrast with the PIPT in polythiophene,<sup>4</sup> in which the primary process is completed within the duration of the exciting laser pulse (5 ns).

A perovskitelike gold complex  $\text{Cs}_2\text{Au}_2\text{Br}_6$  shows a pressure-induced phase transition from MV to SV states.<sup>8,9</sup> In the MV state, the Au cations take two valence states, i.e.,  $\text{Au}^+$  (ten  $d$  electrons) and  $\text{Au}^{3+}$  (eight  $d$  electrons), forming linear  $\text{AuBr}_2^-$  and square  $\text{AuBr}_4^-$  molecules, respectively.<sup>10</sup> These two kinds of molecules form with pseudocubic crystal structure ( $I4/mmm$ ;  $Z=2$ ). Optical gap is characterized by the charge-transfer of a  $d$  electron from the  $\text{Au}^+$  to  $\text{Au}^{3+}$  sites.<sup>8</sup> Valence disproportion in the MV phase vanishes under hydrostatic pressures, and the SV state with  $\text{Au}^{2+}$  ions is realized. In Fig. 1 is shown the electronic phase diagram, determined by high-pressure Raman spectroscopy, against pressure and temperature.<sup>11</sup> The hatched region represents the bistable region, where both the MV and SV phases are stable and can be converted by an appropriate pressure process.

Single crystal of  $\text{Cs}_2\text{Au}_2\text{Br}_6$  was recrystallized from acetonitrile solution using an  $H$ -type double-test tube of glass. Detailed synthesis procedure is described in Ref. 9. In order to probe the photoinduced change on the volume ratio, we have adopted the Raman spectroscopy. Intensity of the Au-Br stretching mode is known to be proportional to relative volume of the MV state, i.e.,  $V_{\text{MV}}/(V_{\text{MV}}+V_{\text{SV}})$ , because the mode is deactivated in the SV state, where the  $\text{Br}^-$  ions are located at the centrosymmetric position.<sup>8</sup> High-pressure Raman measurements were performed using a dia-

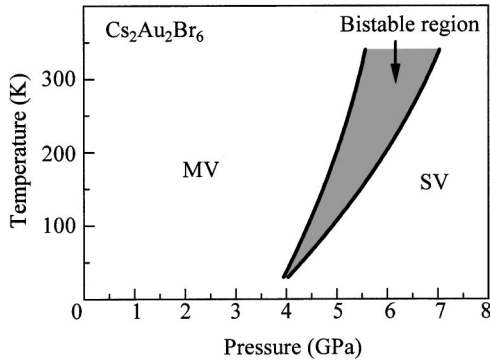


FIG. 1. Electronic phase diagram for  $\text{Cs}_2\text{Au}_2\text{Br}_6$  against pressure and temperature (cited from Ref. 11).

mond anvil cell and liquid paraffin as a pressure medium. A tiny crystal sample, 0.1 mm in thickness and  $0.2 \times 0.2 \text{ mm}^2$  in area (*ab* plane), was placed in the gasket hole (0.3 mm in diameter). Magnitude of the applied pressures were monitored with the luminescence of a small piece of ruby placed in the gasket hole. The probe laser power was kept below  $50 \text{ W/cm}^2$ . Scattered light was detected with a double monochromator equipped with a photon-counting system. The excitation light source is a dye-laser pumped by an Ex-cimer laser, whose pulse duration and frequency are  $\sim 20 \text{ ns}$  and  $\sim 10 \text{ Hz}$ , respectively.

Figure 2(a) shows Raman scattering spectra for  $\text{Cs}_2\text{Au}_2\text{Br}_6$  in the bistable region at 300 K. Before photoexcitation [upper spectra of Fig. 2(a)], the system is in the MV phase with the intense Au-Br stretching mode. The Raman signal completely disappears (middle spectra) after photoexcitation with 2000 pulse shots, due to the PIPT into the SV

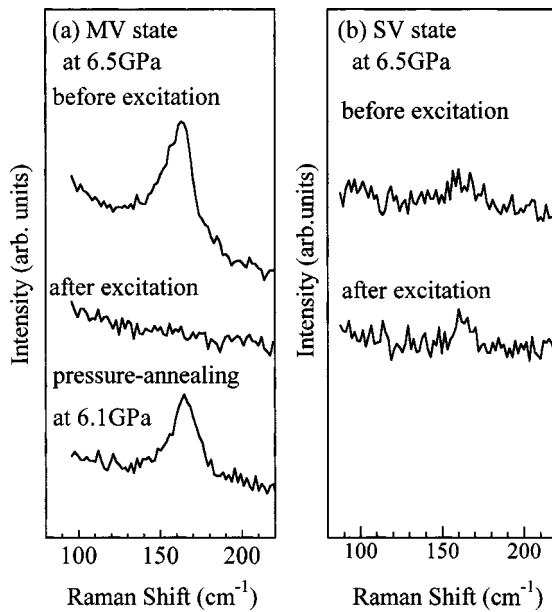


FIG. 2. Raman scattering spectra in the bistable region at 300 K for  $\text{Cs}_2\text{Au}_2\text{Br}_6$  before (upper spectra) and after (middle spectra) photoexcitation: Initial states are the MV (a) and SV (b) phases, respectively. Excitation energy  $E_{\text{exc}}$  is 1.9 eV and pulse duration is 20 ns. Photon density per pulse is  $3.6 \times 10^{16} \text{ cm}^{-2}$ . 2000 pulse shots are irradiated through the diamond window. The bottom spectrum was measured after pressure annealing.

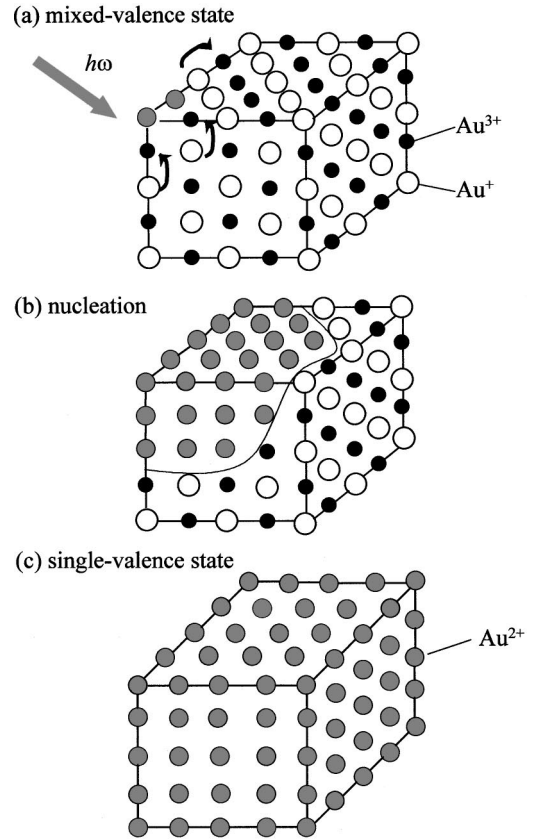


FIG. 3. Schematic structures of perovskitelike gold complex  $\text{Cs}_2\text{Au}_2\text{Br}_6$  for (a) mixed-valence (MV) state, (b) nucleation of the single-valence (SV) cluster after photoexcitation and (c) SV state.

phase. The excitation energy  $E_{\text{exc}}$  and photon density are 1.9 eV and  $3.6 \times 10^{16} \text{ cm}^{-2}$  per pulse, respectively. With this excitation condition, 80% Au atoms are excited into the  $\text{Au}^{2+}$  states per pulse (if we neglect relaxation of the *d* electrons). Disappearance of the Raman signal is not due to deterioration of the sample surface. In fact, the PIPT can be repeated several times with the same crystal. The bottom panel of Fig. 2(a) shows an example: The Raman signal nearly recovers after pressure-annealing procedure, that is, the pressure is released down to  $\sim 3 \text{ GPa}$  and then increased up to 6.1 GPa. The photoinduced phase transition of present system is one way, i.e., only from the MV to SV phases [see Fig. 2(b)]. This is perhaps due to the different electronic structures in each phase. In the MV phase, the spectral weight due to the charge-transfer-type excitation is dominated in the visible region.<sup>8</sup> The spectral weight, however, transfers into the infrared region in the highly conductive SV phase.

We show in Fig. 3 a schematic picture for the observed PIPT in the gold complex. In the MV state [Fig. 3(a)],  $\text{Au}^+$  and  $\text{Au}^{3+}$  states alternate three dimensionally. The photoirradiation, however, transfers *d* electrons from  $\text{Au}^+$  to  $\text{Au}^{3+}$  sites<sup>8</sup> and produces  $\text{Au}^{2+}$  pairs;  $\text{Au}^+ + \text{Au}^{3+} \rightarrow 2\text{Au}^{2+}$ . Such  $\text{Au}^{2+}$  pairs would form cluster states [see Fig. 3(b)] if the photon density were large enough. Here, we discuss phenomenologically nucleation processes of the phase transition. The first-order phase transition is known to be triggered when the clusters of the second (SV) phase grow up to the critical value  $r_c = 2\sigma/\Delta E$ , where  $\sigma$  and  $\Delta E$  are the surface

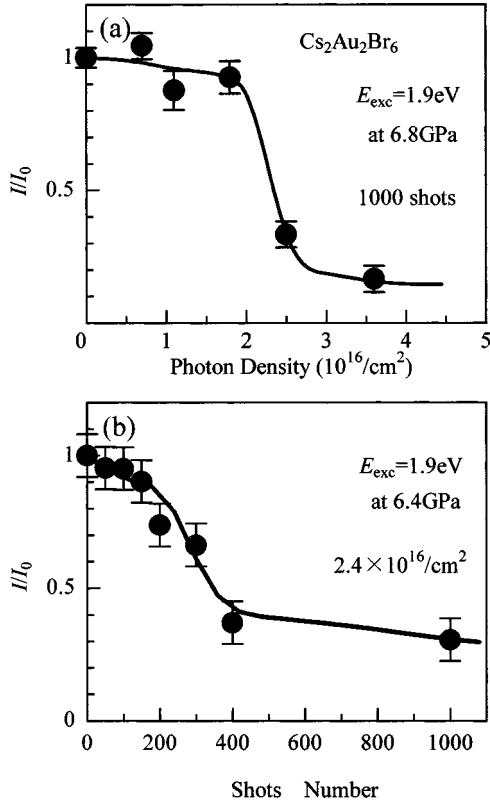


FIG. 4. (a) photon density and (b) shots number dependence of relative Raman intensity  $I/I_0$  of the Au-Br stretching mode, where  $I_0$  is the intensity before photoexcitation. The Raman mode is deactivated in the photogenerated SV phase.

energy and the difference in the free energy between two phases.<sup>12</sup> With increase of photon density, or shots number, the size  $r$  of the photogenerated SV clusters increases and reaches to the  $r_c$ . (Note that relaxation time of the photogenerated SV clusters is longer than the frequency of the laser pulse ( $=0.1$  s), because the PIPT of the present system shows shot number dependence [see Fig.4(b)].) Accordingly, the macroscopic MV-SV phase transition is triggered, as observed in Fig. 3(c).

Consistently with above arguments, the PIPT shows a threshold behavior against the excitation photon density and shots number. In Fig. 4 is shown relative Raman intensity  $I/I_0$ , where  $I_0$  is the intensity before photoexcitation, against (a) photon density (shots number is fixed at 1000) and (b) shots number (photon density is fixed at  $\sim 2.4 \times 10^{16} \text{ cm}^{-2}$ ). The  $I/I_0$  value represents the relative volume, i.e.,  $V_{MV}/(V_{MV} + V_{SV})$ , of the MV phase. In Fig. 4(a), the  $I/I_0$  value is nearly constant ( $\sim 1$ ) in the weak excitation condition, but suddenly drops down to  $\sim 0.2$  when the photon density exceeds the critical value ( $\sim 2 \times 10^{16} \text{ cm}^{-2}$ ). Similar threshold behavior is also observed in the shots number dependence of the  $I/I_0$  value [see Fig. 4(b)]: the intensity drops around 200–400 shots.

Thus observed *memory* effect, or accumulation of the photoirradiation effect of each pulse shot, is perhaps ascribed to the electron-lattice interaction inherent to the present system. Actually, the lattice constant  $c$  shrinks by  $\sim 1.6\%$  at the pressure-induced MV-SV phase transition, reflecting the Jahn-Teller instability of the  $\text{Au}^{2+}$  ions in the SV phase.<sup>9</sup>

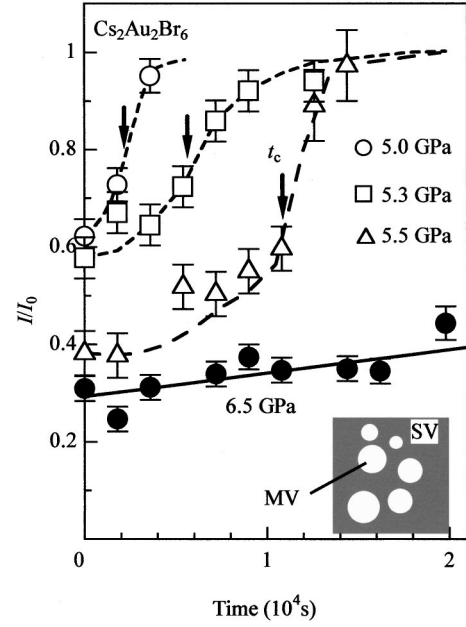


FIG. 5. Temporal evolution of the relative Raman intensity  $I/I_0$  of the Au-Br stretching mode. 300 pulse shots with photon density  $P=2.5 \times 10^{16} \text{ cm}^{-2}$  ( $E_{\text{exc}}=1.9$  eV) are irradiated at  $t=0$  s. Open symbols are the data obtained below the MV-SV phase boundary: circles, squares, and triangles are the data at 5.0, 5.3, and 5.5 GPa, respectively. Filled circles means that the data were obtained within the bistable region (at 6.5 GPa). Schematics shows shrinkage of the SV domains.

Such a strong Jahn-Teller instability inherent to the  $\text{Au}^{2+}\text{Br}_6$  octahedra could stabilize the photogenerated SV clusters in the sea of the MV region. This makes a sharp contrast with the PIPT in polythiophene,<sup>4</sup> in which the primary process is completed within the duration of the exciting laser pulse (5 ns).

Effect of the electron-lattice interaction can be seen in the recovery process from the photogenerated SV phase under pressures below 5.5 GPa. The photogenerated SV phase is not stable in this pressure region (see Fig. 1), and changes into the stable MV phase. In Fig. 5 is shown temporal evolution of the Raman intensity  $I/I_0$  after photoexcitation with 300 pulse shots at  $t=0$  s. The open and closed symbols mean that the crystal is in the MV and bistable regions, respectively. Photoexcitation at  $t=0$  s reduces the  $I/I_0$  value, indicating transition into the SV phase. At 5.5 GPa near below the MV-SV phase boundary, the  $I/I_0$  value slightly increases from  $\sim 0.4$  at  $t=0$  s to  $\sim 0.5$  at  $t=1 \times 10^4$  s, and then discontinuously jumps up to  $\sim 1$ . Here, let us define the critical time  $t_c$  as the time where  $I(t)/I_0$  becomes  $[1 + I(t=0)/I_0]/2$ . Photogenerated SV domains divides the MV phase into parts, as schematically shown in the inset of Fig. 5. The large lattice distortion around the MV-SV phase boundary prevents the MV cluster from spreading, and causes the long dead time  $t_c$ . The cluster size finally reaches to  $r_c$  at  $t_c$ , and the SV-MV phase transition is triggered. Slight increase of the  $I/I_0$  value seen for  $t < t_c$  may reflect growth of the MV clusters (see Fig. 5). With further decrease of pressure, the MV phase becomes more stable ( $\Delta E$  increases) and hence  $r_c (=2\sigma/\Delta E)$  becomes smaller. Conse-

quently, the recovery process is much accelerated:  $t_c \sim 0.5 \times 10^4$  s at 5.3 GPa and  $t_c \sim 0.2 \times 10^4$  s at 5.0 GPa.

In summary, we have found a photoinduced phase transition (PIPT) in the mixed-valence (MV) gold complex  $\text{Cs}_2\text{Au}_2\text{Br}_6$ , from the MV state to the single-valence (SV) phase in the pressure region from 6.4 to 6.8 GPa. In this system, the charge-transfer type excitation directly creates the SV clusters in the sea of the MV phase, and would trigger the phase transition if the size exceeded the critical radius

$r_c$ . The observed memory effect, or accumulation of the photoirradiation effect of each pulse shot, suggests that the electron-lattice interaction is the key for the present PIPT in the mixed-valence gold complex.

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<sup>1</sup>S. Koshihara, A. Oiwa, M. Hirasawa, S. Katsumoto, Y. Iye, C. Urano, H. Takagi, and H. Munekata, Phys. Rev. Lett. **78**, 4617 (1997).

<sup>2</sup>O. Sato, T. Iyoda, A. Fujishima, and K. Hashimoto, Science **272**, 704 (1996).

<sup>3</sup>S. Koshihara, Y. Tokura, K. Takeda, and T. Koda, Phys. Rev. Lett. **68**, 1148 (1992).

<sup>4</sup>N. Hosaka, H. Tachibana, N. Shiga, M. Matsumoto, and Y. Tokura, Phys. Rev. Lett. **82**, 1672 (1999).

<sup>5</sup>A. Mino, Y. Ogawa, and S. Koshihara, Mol. Cryst. Liq. Cryst. **314**, 107 (1998).

<sup>6</sup>K. Miyano, T. Tanaka, Y. Tomioka, and Y. Tokura, Phys. Rev.

Lett. **78**, 4257 (1997); K. Ogawa, W. Wei, K. Miyano, Y. Tomioka, and Y. Tokura, Phys. Rev. B **57**, R15 033 (1998).

<sup>7</sup>K. Matsuda, A. Machida, Y. Moritomo, and A. Nakamura, Phys. Rev. B **58**, R4203 (1998); K. Matsuda *et al.* (unpublished).

<sup>8</sup>X. J. Liu, K. Matsuda, Y. Moritomo, A. Nakamura, and N. Kojima, Phys. Rev. B **59**, 7925 (1999).

<sup>9</sup>N. Kojima, M. Hasegawa, H. Kitagawa, T. Kitagawa, and O. Shimomura, J. Am. Chem. Soc. **116**, 11 368 (1994).

<sup>10</sup>J. C. M. Tindemans-v Eijndhoven, and G. C. Verschoor, Mater. Res. Bull. **9**, 1667 (1974).

<sup>11</sup>X. J. Liu, Y. Moritomo, A. Nakamura, and N. Kojima, J. Chem. Phys. **110**, 9174 (1999).

<sup>12</sup>J. S. Langer, Ann. Phys. (N.Y.) **41**, 108 (1967).