

Density-functional study of charge disordering in $\text{Cs}_2\text{Au(I)Au(III)Cl}_6$ under pressure

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We demonstrate that density-functional theory can be used to study the charge-order/disorder transition in $\text{Cs}_2\text{Au(I)Au(III)Cl}_6$. The ground-state structure of this mixed-valence compound is reproduced with satisfactory accuracy, and a discontinuous phase transition is calculated to occur at about 6–10 GPa, in agreement with published experimental values. The precision of the calculations and of previously published experiments is insufficient to unambiguously determine whether the transition is from $I4/mmm$ to $P4/mmm$, or proceeds directly into a cubic phase with space group $Pm\bar{3}m$. Irrespective of the symmetry of the phase appearing at 6–10 GPa, the calculations show that the pressure-induced structural changes are accompanied by a charge disordering, and that all gold atoms are in the single-valence state, Au^{2+} , in the high-pressure phase.

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I. INTRODUCTION

During a “charge ordering transition” the electronic structure of a compound changes so that cations that had the same formal charge acquire different oxidation states and a mixed-valence compound results. Experimental and theoretical studies of such phase transitions are well suited to further our understanding of the relationship between structural, physical, and electronic properties.¹ Most studies of charge-ordering transitions are concerned with temperature-induced changes in the formal oxidation states of $3d$ -transition-metal ions, such as the Verwey transition in magnetite,² or the transitions in manganese oxides.³ While the driving forces of charge ordering may differ between compounds, it seems that charge ordering generally leads to a significant decrease in conductivity. For cases involving $3d$ -transition-metal cations the structural changes associated with the charge ordering are apparently small.

As ions with different formal charges have different ionic radii, it is also possible to induce changes in the ionic charges by pressure. This can be exploited in compressible compounds, as an applied pressure of only a few GPa will cause structural changes much larger than those available by a change of temperature. However, experimental studies of pressure-induced changes in mixed-valence compounds are usually problematic, as the identification of concomitant changes of structural and electronic properties is extremely difficult. Here, quantum-mechanical calculations can provide insight not made available by experiments. However, the most commonly used models for reasonably complex structures are based on density-functional theory, and it has been claimed that, at least, the conventional local spin density approximation cannot be used to study charge ordering.⁴

Here, we investigate pressure-induced changes in the mixed-valence compound $\text{Cs}_2\text{Au(I)Au(III)Cl}_6$, where several experimental results, although differing in detail, suggest

the occurrence of a phase transition leading to a structure in which all gold atoms have the same formal charge.⁵ $\text{Cs}_2\text{Au(I)Au(III)Cl}_6$ crystallizes at ambient conditions in a distorted tetragonal perovskite structure with space group $I4/mmm$.⁶ The structure is shown in Fig. 1.

The coordination of the symmetrically inequivalent gold atoms is peculiar to this structure.⁷ The Au(I) is 2+4 coordinated by chlorine, where the two Au(I)-Cl(1) bonds are 2.28 Å long, and the four Cl(2) atoms are 3.01 Å away. The Au(III) is 4+2 coordinated, where the four bonds to the co-

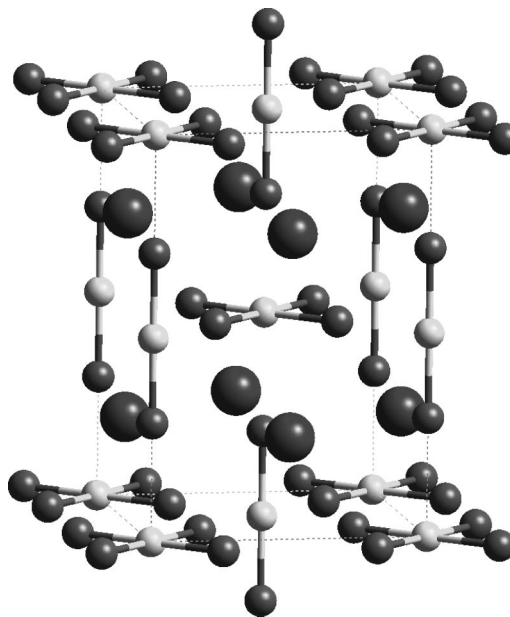


FIG. 1. The tetragonal structure of $\text{Cs}_2\text{Au(I)Au(III)Cl}_6$, stable at ambient conditions. The two symmetry-inequivalent gold atoms can be distinguished by their coordination: Au(I) shows a linear 2+4-coordinated geometry, while the Au(III) is in a planar 4+2 coordination.

ordinating Cl(2) atoms are 2.29 Å long, and the two Cl(1) are 3.15 Å away. The association of the fourfold coordination to Au(III) can be explained in terms of ligand-field theory, as for a d^8 electronic configuration only the $d_{x^2-y^2}$ orbital is energetically unfavorable, thereby favoring fourfold coordinated complex ions such as AuCl_4^- or PtH_4^{2-} with occupied d_{xz} , d_{yz} , d_{z^2} , and d_{xy} orbitals. The linear twofold coordination is often encountered in elements with ten d electrons, such as Cu(I), Ag(I), Au(I), or Hg(II) justifying the description of the electronic configuration in terms of the formal valence states. That gold ions in two different oxidation states coexist in $\text{Cs}_2\text{Au(I)Au(III)Cl}_6$ has been confirmed by x-ray photoelectron spectroscopy⁸ and ^{197}Au Mössbauer spectroscopy.^{9,10}

The pressure dependence of the structure was first investigated using x-ray diffraction by Denner *et al.*,⁶ who concluded that there was a transition into a tetragonal high-pressure structure with symmetry $P4/mmm$ at ≈ 5.2 GPa, where the Au-Cl distances had equal lengths. Kojima *et al.*¹¹ found from low-temperature x-ray diffraction measurements that at 12 GPa a second tetragonal phase appears, and that at low temperatures (< 100 K) the cubic phase does not appear in the pressure regime investigated, i.e., up to 14 GPa. At temperatures above 100 K a transition into the cubic phase occurred around 14 GPa. This is consistent with a recent room-temperature refinement that was interpreted as showing that a cubic phase appears at 12.5 GPa,¹² but no further details with respect to structural changes were given. In the cubic high-pressure phase all the Au-Cl bonds are symmetrically equivalent and there is only one oxidation state for the Au-ions, which formally are Au^{2+} . Mössbauer spectroscopy showed two different valence states of gold ions up to 6.8 GPa, the highest pressure studied.⁹ A study of the pressure dependence of the resistivity suggested a semiconductor-to-metal transition at around 6 GPa.¹³

Using a density-functional-theory-based model, we have investigated the pressure dependence of structural parameters and correlated them with the changes observed in a Mulliken population analysis. After describing the computational details, we will show that the approach used here is capable of reproducing the ground-state structure of this mixed-valence compound. We then describe the results of calculations addressing the influence of pressure and conclude with a discussion of the results obtained here.

II. COMPUTATIONAL DETAILS

The quantum-mechanical calculations performed here are based on density-functional theory (DFT). While DFT itself is exact,¹⁴ practical calculations require an approximation for the treatment of the exchange and correlation energies. Here we use the ‘‘generalized gradient approximation’’ (GGA).¹⁵ Results based on GGA calculations are generally in better agreement with experiment than those obtained with the local-density approximation.^{16–19}

Full-geometry optimizations of structures with several structural degrees of freedom are most efficiently performed if the stress tensor for a given configuration can be evaluated. This is most straightforward in the computational approaches

that use a basis set of plane waves to represent the charge density and electronic wave functions. For all calculations we used academic and commercial versions of the plane wave pseudopotential code CASTEP, which has been described elsewhere.^{20–22} We used ultrasoft pseudopotentials,^{23,24} with a maximum cutoff energy of the plane waves of 380 eV. In addition to the cutoff energy, only one further parameter determines the quality of the calculations, namely the density of points with which the Brillouin zone is sampled. Here, we use a sampling of reciprocal space such that distances between grid points are less than 0.05 \AA^{-1} . Two sets of full-geometry optimizations were performed, which differed in the initial space-group symmetry ($I4/mmm$ or $P4/mmm$). Full-geometry optimizations allow changes of structural parameters leading to higher space-group symmetries. After the final self-consistency cycle, the remaining forces on the atoms were less than 0.02 eV/\AA , and the remaining stress was less than 0.1 GPa. The present calculations are restricted to the athermal limit, in which temperature effects and zero-point motions are neglected.

While a DFT-based plane-wave/ultrasoft pseudopotential approach is well suited to study complex crystal structures, this efficient computational scheme lacks one appealing property of models based on localized basis sets, namely the possibility to express the computed charge density in terms of atomic orbitals and to compute partial charges and bond populations, as is commonly done in quantum chemistry. However, Sanchez-Portal *et al.*²⁵ showed that it is straightforward to describe the plane-wave wave functions we obtain using localized atomic pseudoorbitals. We used a Mulliken population analysis, as implemented for a plane-wave basis set by Segall *et al.*²⁶ It is generally acknowledged that population analyses only yield semiquantitative information, as the underlying crystal chemical concepts do not correspond to quantum-mechanical observables. However, the relative magnitude of bond populations and changes due to variations of the structural parameters induced, for example, by increasing pressure, can be monitored.

III. RESULTS

A. The structure at ambient pressure

The computed lattice parameters at 0 GPa are $a_{\text{calc}} = 7.6037 \text{ \AA}$, $c_{\text{calc}} = 11.251 \text{ \AA}$. They are therefore within +1.5% and +3.4% of the experimental values, $a_{\text{exp}} = 7.495(1) \text{ \AA}$ and $c_{\text{exp}} = 10.880(2) \text{ \AA}$, respectively.⁶ This is within the error typical for DFT-GGA calculations. Of much greater interest was the observation that the charge disproportionation between the symmetrically inequivalent Au atoms and the atomic arrangement mentioned above are well described. The bond lengths are given in Table I.

As can be seen from this list, the bond distances are systematically overestimated. This, however, is not problematic in the current discussion. The bond populations at zero pressure confirm the conventional crystal chemical point of view of the coordination, as the bond population for the long Au-Cl distances is very close to zero. Hence, the important features of the charge-ordered ground-state structure of $\text{Cs}_2\text{Au}_2\text{Cl}_6$ are correctly reproduced with conventional DFT/GGA calculations.

TABLE I. Observed [Denner *et al.* (Ref. 6)] and calculated interatomic distances of $\text{Cs}_2\text{Au(I)Au(III)Cl}_6$ at ambient conditions. At 50 GPa the predicted value is 2.24 Å for all Au-Cl distances.

	0 GPa			Bond pop. (<i>e</i>)
	Expt. (Å)	Calc. (Å)	% difference	
Au(I)-Cl(1)	2.28	2.314	+1.5	0.49
Au(I)-Cl(2)	3.01	3.018	+0.2	0.04
Au(III)-Cl(1)	3.15	3.311	+5.1	0.03
Au(III)-Cl(2)	2.29	2.359	+3.0	0.38

The tetragonal ($I4/mmm$) ground state has a DFT band gap of about 0.6 eV. Earlier all-electron augmented plane wave calculations for the experimentally observed tetragonal structure produced a band gap of about 1 eV in agreement with the present result.²⁷ The experimental value of 2.04 eV obtained by Liu *et al.*⁷ is larger due to the well-known DFT band-gap error.

B. High-pressure behavior

In the study of the pressure dependence of the structural parameters a set of calculations were carried out in which the structures initially had space-group symmetry $I4/mmm$. This allows the structure to distort in such a way that, at high pressures, it can assume space group $P4/mmm$ or $Pm\bar{3}m$. After each geometry optimization at the pressures investigated, we analyzed the symmetry of the relaxed structure. This analysis is not unambiguous, as the numerical uncertainty in the computed structural parameters has to be taken into account. Hence, an additional set of calculations were performed, with the initial space group chosen to be $P4/mmm$. Experience shows that energy differences of about 0.05 eV cannot be resolved reliably when comparing two sets of calculations employing different symmetries and a slightly different sampling of *k* space. This limits the precision with which the transition pressure can be predicted. Here, the enthalpy difference between the two sets of calculations decreases from 0.38 eV at zero pressure to less than 0.05 eV at 7 GPa, so the theoretical transition pressure is somewhere between 6–10 GPa.

The transition seems to be discontinuous, as there are discontinuities in the pressure dependence of the volume and of individual bond lengths (see below). However, at 10 GPa the difference between the *a*- and *c*-lattice parameters is only 0.004 Å, and hence it is also possible that in the athermal limit there is only one transition from $I4/mmm$ to $Pm\bar{3}m$. The enthalpy difference between a structure with space-group symmetry $Pm\bar{3}m$ and $P4/mmm$ is so small, and the structural parameters are so similar, that it is not possible to distinguish the two phases unambiguously. Thus the quantum-mechanical calculations cannot predict if there is only one transition from $I4/mmm$ to $Pm\bar{3}m$, or whether an intermediate phase with space-group symmetry $P4/mmm$ exists.

Our quantum-mechanical calculations allow a detailed analysis of the pressure-induced changes in the bond lengths

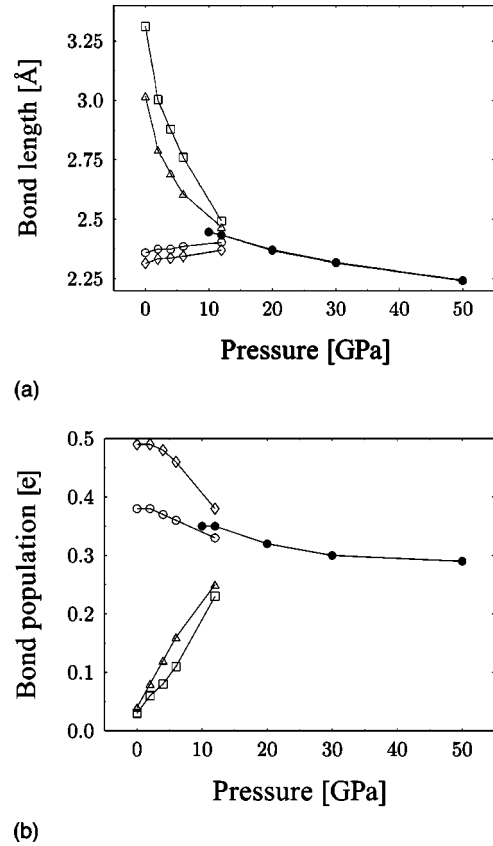


FIG. 2. Pressure-induced changes in interatomic distances (top) and in the bond population (bottom). Open symbols represent calculations for the structure with space-group symmetry $I4/mmm$. Diamonds: Au(I)-Cl(1), circles: Au(III)-Cl(2), triangles: Au(I)-Cl(2), squares: Au(III)-Cl(1). At 6–10 GPa a transition into a phase with space-group symmetry $Pm\bar{3}m$ occurs, the corresponding values are represented by filled symbols.

and the bond population as illustrated by Fig. 2. The strength of the long, very weak Au(I)-Cl(2) and Au(III)-Cl(1) bonds increases rapidly on compression. This causes a lengthening of the short Au-Cl bonds. The creation of a bond to an initially distant Au atom pulls the Cl atoms away from the Au atoms to which they were bound in the ground-state structure. The bond-population analysis confirms this interpretation. The bond population of the initially very weak long bonds increases, i.e., their covalent “character” increases, while the short strong bonds get less populated. In agreement with experiment²⁸ the Au-Cl bond lengths change discontinuously at the transition occurring at 6–10 GPa. The calculations show that this is also the case for the bond population. In the present case, the bond-population analysis is a very convincing confirmation of the description in terms of a 2+4 and 4+2 coordination for Au(I) and Au(III), respectively.

Changes in the atomic population have also been calculated, but the pressure-induced changes are too small to be analyzed unambiguously. The calculations clearly indicate that in the ground-state structure the charges between the symmetry inequivalent gold atoms differ (by about 0.15 *e*) and that they become equal at higher pressures. It seems that the major change in terms of orbital population occurs in the

Au $6p$ orbital, which becomes more populated under pressure. However, these changes cannot be reliably quantified and hence cannot be used to deepen our understanding of the changes in the bonding between the atoms.

The present calculations show that the band gap closes at about 2 GPa, noticeably lower than the value of 6 GPa obtained by Keller *et al.*¹³ from high-pressure resistivity measurements. However, due to the DFT band-gap error, a lower value for the semiconductor-metal transition is expected. Furthermore, it is not even clear whether the experimentally observed changes in transport properties under pressure are of purely electronic nature or involve other excitations in the system (e.g., bipolarons⁵). The present calculations imply that the semiconductor-metal transition is not associated with the structural phase transition into the cubic phase. This is consistent with the available experimental data, which also indicate that the structural phase transition is at higher pressures than the 6 GPa at which the resistivity becomes practically independent of pressure after decreasing by at least five orders of magnitudes in the pressure interval of 2–6 GPa.¹³

IV. SUMMARY AND DISCUSSION

Our calculations have successfully reproduced the structural details of the ground state of a mixed-valence compound. It had been proposed⁴ that the spurious self-interaction in DFT calculations would prevent the study of charge-ordered states. While this may be the case for compounds containing $3d$ -transition metal ions, such as magnetite, the successful calculation of the ground-state structure

of $\text{Cs}_2\text{Au}_2\text{Cl}_6$ shows that this is not generally the case and that the study of charge ordering does not always require a theory beyond standard DFT/GGA.

The calculations have also correctly reproduced the occurrence of a phase transition at 6–10 GPa. This is consistent with experiment, where values between 5.2 GPa,⁶ 10 GPa,¹¹ and 12.5 GPa (Ref. 12) have been reported. However, the high-pressure behavior is not well understood and neither the experimental data nor the calculations allow us to determine unambiguously whether or not a phase with symmetry $P4/mmm$ occurs as an intermediate phase between the low pressure, $I4/mmm$, and the high pressure, $Pm\bar{3}m$, polymorphs. This is due to the very small difference in the structural parameters of the $Pm\bar{3}m$ and $P4/mmm$ polymorphs. Hence, the low-temperature energy dispersive measurements of Kojima *et al.*¹¹ may be viewed as indicative only. Comparisons of the theoretical results to data obtained from measurements of the phase-transition pressure at ambient temperature may be misleading as the sequence of high-pressure phases and transition pressures changes as a function of temperature.

The calculations clearly show that the structural changes and the electronic changes occur simultaneously. Specifically, the major change of the bond population of the Au-Cl bonds occurs at the 6–10-GPa phase transition and at higher pressures all gold atoms have a formal charge of +2. In principle, fast hopping of electrons between differently charged ions may lead to an intermediate formal charge. However, the current calculations represent a static state, and hence they confirm the disappearance of the mixed-valence state and the presence of Au^{2+} in CsAuCl_3 under pressure.

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¹M. Imada, A. Fujimori, and Y. Tokura, *Rev. Mod. Phys.* **70**, 1039 (1998).

²V. I. Anisimov, I. S. Elfimov, N. Hamada, and K. Terakura, *Phys. Rev. B* **54**, 4387 (1996).

³C. N. R. Rao, *J. Phys. Chem. B* **104**, 5877 (2000).

⁴V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, *J. Phys.: Condens. Matter* **9**, 767 (1997).

⁵N. Kojima, *Bull. Chem. Soc. Jpn.* **73**, 1445 (2000).

⁶W. Denner, H. Schulz, and H. D'Amour, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **35**, 360 (1979).

⁷X. J. Liu, K. Matsuda, Y. Moritomo, A. Nakamura, and N. Kojima, *Phys. Rev. B* **59**, 7925 (1999).

⁸H. Kitagawa, N. Kojima, and T. Nakajima, *J. Chem. Soc. Dalton Trans.* **1991**, 3121.

⁹J. Stanek, *J. Chem. Phys.* **76**, 2315 (1982).

¹⁰H. Kitagawa, N. Kojima, and H. Sakai, *J. Chem. Soc. Dalton Trans.* **1991**, 3211.

¹¹N. Kojima, M. Hasegawa, H. Kitagawa, T. Kikegawa, and O. Shimomura, *J. Am. Chem. Soc.* **116**, 11 368 (1994).

¹²N. Matsushita, H. Ahsbahs, S. S. Hafner, and N. Kojima, *Z. Kristallogr. Suppl.* **1998**, 187.

¹³R. Keller, J. Fenner, and W. B. Holzapfel, *Mater. Res. Bull.* **9**, 1363 (1974).

¹⁴P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).

¹⁵J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992).

¹⁶T. C. Leung, C. T. Chan, and B. N. Harmon, *Phys. Rev. B* **44**, 2923 (1991).

¹⁷B. Hammer, K. W. Jacobsen, and J. K. Nørskov, *Phys. Rev. Lett.* **70**, 3971 (1993).

¹⁸J. Goniakowski, J. M. Holender, L. N. Kantorovich, M. J. Gillian, and J. A. White, *Phys. Rev. B* **53**, 957 (1996).

¹⁹D. R. Hamann, *Phys. Rev. Lett.* **76**, 660 (1996).

²⁰M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, *Rev. Mod. Phys.* **64**, 1045 (1992).

²¹CASTEP User Guide (Molecular Simulations Inc., San Diego, CA, 1998).

²²V. Milman, B. Winkler, J. A. White, C. J. Pickard, M. C. Payne, E. V. Akhmatkaya, and R. H. Nobes, *Int. J. Quantum Chem.* **77**, 895 (2000).

²³D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).

²⁴G. Kresse and J. Hafner, *J. Phys.: Condens. Matter* **6**, 8245 (1994).

²⁵D. Sanchez-Portal, E. Artacho, and J. M. Soler, *J. Phys.: Condens. Matter* **8**, 3859 (1996).

²⁶M. D. Segall, R. Shah, C. J. Pickard, and M. C. Payne, *Phys. Rev. B* **54**, 16 317 (1996).

²⁷M. Shirai, *Synth. Met.* **56**, 3389 (1993).

²⁸H. Ahsbahs (private communication).