Jahn-Teller effects in transition-metal compounds with small charge-transfer energy

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Abstract. We have studied Jahn-Teller effects in Cs$_2$Au$_2$Br$_6$, ACu$_3$Co$_4$O$_{12}$ (A=Ca or Y), and IrTe$_2$ in which the ligand $p$-to-transition-metal $d$ charge-transfer energy is small or negative. The Au$^+$/Au$^{3+}$ charge disproportionation of Cs$_2$Au$_2$Br$_6$ manifests in Au 4f photoemission spectra. In Cs$_2$Au$_2$Br$_6$ with negative $\Delta$ and intermediate $U$, the charge disproportionation can be described using effective $d$ orbitals constructed from the Au 5$d$ and Br 4$p$ orbitals and is stabilized by the Jahn-Teller distortion of the Au$^{3+}$ site with low-spin $d^8$ configuration. In ACu$_3$Co$_4$O$_{12}$, $\Delta$s for Cu$^{3+}$ and Co$^{4+}$ are negative and $Us$ are very large. The Zhang-Rice picture is valid to describe the electronic state, and the valence change from Cu$^{2+}$/Co$^{4+}$ to Cu$^{3+}$/Co$^{3+}$ can be viewed as the O 2$p$ hole transfer from Co to Cu or $d^9 + d^6 L \rightarrow d^9 L + d^6$. In IrTe$_2$, both $\Delta$ and $U$ are small and the Ir 5$d$ and Te 5$p$ electrons are itinerant to form the multi-band Fermi surfaces. The ideas of band Jahn-Teller transition and Peierls transition are useful to describe the structural instabilities.

1. Introduction
Insulating transition-metal compounds are classified into (i) Mott-Hubbard type insulators where Mott gap $E_G$ is mainly determined by Coulomb interaction $U$ between the transition-metal $d$ electrons and (ii) charge-transfer type insulators where $E_G$ is determined by charge-transfer energy $\Delta$ from the ligand $p$ state to the transition-metal $d$ state (Zaanen-Sawatzky-Allen scheme) [1, 2]. In transition-metal compounds with relatively large $\Delta$, orbital orderings can be described by the Jahn-Teller mechanism, in which lattice distortion removes the orbital degeneracy, and by the Kugel-Khomskii mechanism, in which the superexchange interaction $J \sim -2t^2/E_G$ ($t$: transfer integral, $E_G$: Mott gap) governs the spin-orbital orderings.

For example, in LaMnO$_3$ with $\Delta \sim 4$ eV, the Mn$^{3+}$ ion takes high-spin $d^n$ ($n = 4$) configuration and the MnO$_6$ octahedron is accompanied by Jahn-Teller distortion. The A-type antiferromagnetic state of LaMnO$_3$ can be described by the superexchange interaction between the high-spin $d^4$ states. On the other hand, there are some transition-metal compounds known to have negative $\Delta$. In particular, high valence transition-metal oxides such as NaCuO$_2$ and CaFeO$_3$ tend to have negative $\Delta$ [3, 4]. In CaFeO$_3$, Fe valence is formally 4$+$ and the Fe$^{4+}$ ion is expected to take high-spin $d^n$ ($n = 4$) configuration. However, CaFeO$_3$ with negative $\Delta$ takes $d^{n+1}L$ ($L$ represents a ligand hole) configuration instead of $d^n$ [5]. In such case, the Jahn-Teller instability expected for high-spin $d^4$ state can be avoided. Actually, CaFeO$_3$ does not exhibit Jahn-Teller distortion of FeO$_6$ octahedron and shows charge disproportionation with breathing distortion of FeO$_6$ octahedron [6].
In this article, we would like to discuss possible Jahn-Teller effects in negative-\(\Delta\) or small-\(\Delta\) transition-metal compounds including \(\text{Cs}_2\text{Au}_2\text{Br}_6\), \((\text{Ca},\text{Y})\text{Cu}_3\text{Co}_4\text{O}_{12}\) and \(\text{IrTe}_2\). As for \(\text{IrTe}_2\), the relationship between structural distortions and orbital orderings is analyzed on the basis of itinerant electron models considering band Jahn-Teller effect and Peierls instability. In perovskite-type \(\text{Cs}_2\text{Au}_2\text{Br}_6\) and \(\text{CaCu}_3\text{Co}_4\text{O}_{12}\), the Jahn-Teller effects tend to stabilize the \(\text{Au}^{2+}/\text{Au}^{3+}\) and \(\text{Cu}^{3+}/\text{Co}^{3+}\) valence states respectively, whereas the smallness of \(\Delta\) introduces additional charge and/or orbital instabilities.

2. \(\text{Cs}_2\text{Au}_2\text{Br}_6\)

Perovskite-type \(\text{Cs}_2\text{Au}_2\text{Br}_6\) exhibits the charge disproportionation \(\text{Au}^{2+} + \text{Au}^{2+} \rightarrow \text{Au}^{+} + \text{Au}^{3+}\) \([7]\) as illustrated in Fig. 1(a). The \(\text{Au}^{+}\) and \(\text{Au}^{3+}\) sites take \(d^{10}(t_{2g}^6e^4_g)\) and low-spin \(d^8(t_{2g}^6e^2_g)\) configurations respectively. The \(\text{AuBr}_6\) octahedron with low-spin \(d^8\) configuration is expected to have Jahn-Teller instability in which the doubly degenerate \(e_g\) levels are split by the compression of the \(\text{AuBr}_6\) octahedron and the stabilized \(x^2 - y^2\) orbitals are occupied by the pair of electrons \([\text{Fig. } 1(\text{b})]\).

As shown in Fig. 1(c), the \(\text{Au} 4f\) core level peak of \(\text{Cs}_2\text{Au}_2\text{Br}_6\) is split into the \(\text{Au}^{+}\) and \(\text{Au}^{3+}\) components \([8]\). The energy difference between the \(\text{Au}^{+}\) and \(\text{Au}^{3+}\) components is \(\sim 2\) eV, and this situation of \(\text{Cs}_2\text{Au}_2\text{Br}_6\) is in sharp contrast to \(\text{CaFeO}_3\) in which the \(\text{Fe} 2p\) core level is hardly split in spite of the charge disproportionation of \(\text{Fe}^{3+}\) and \(\text{Fe}^{5+}\). In case of \(\text{CaFeO}_3\), the small (negative) \(\Delta\) and the large \(U\) provide the \(d^5\) ground state and, consequently, the charge disproportionation of \(\text{Fe}^{4+} + \text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{5+}\) corresponds to the configuration change of \(d^5L + d^5L \rightarrow d^5 + d^5L^2\). Therefore, the number of \(\text{Fe} 3d\) electrons as well as the energy of \(\text{Fe} 2p\) core level can be more or less same between the \(\text{Fe}^{3+}\) and \(\text{Fe}^{5+}\) sites. Namely, when \(\Delta\) is small and \(U\) is large, Zhang-Rice description of \(d^{n+1}L\) configuration is useful to describe the electronic state.

As for \(\text{Cs}_2\text{Au}_2\text{Br}_6\), a recent theoretical study shows that the \(\text{Au} 5d\) and \(\text{Br} 4p\) states are almost degenerate and the charge-transfer energy \(\Delta\) is negative \([10]\). If the \(d-d\) Coulomb interaction energy \(U\) for \(\text{Au} 5d\) is large, the charge disproportionation of \(\text{Au}^{2+} + \text{Au}^{2+} \rightarrow \text{Au}^{+} + \text{Au}^{3+}\) may correspond to the configuration change of \(d^{10}L + d^{10}L \rightarrow d^{10} + d^{10}L^2\). In such case, the Jahn-Teller instability at the \(\text{Au}^{3+}\) site is expected to be suppressed. However, the \(d-d\) Coulomb interaction energy \(U\) of \(\text{Cs}_2\text{Au}_2\text{Br}_6\) is not large enough and the hybridization between the \(d^9\) and \(d^{n+1}L\) states is substantial. In such case, effective \(d\) orbitals can be constructed from the \(\text{Au} 5d\) and \(\text{Br} 4p\) orbitals and the effective \(d\) orbitals accommodate the valence electrons. Therefore, the \(\text{Au}^{3+}\) site with low-spin \(d^9\) configuration should have strong Jahn-Teller instability. The charge disproportionation of \(\text{Cs}_2\text{Au}_2\text{Br}_6\) is stabilized by the Jahn-Teller effect of the \(\text{Au}^{3+}\) site. Here it should be noted that the \(\text{Au}^{+}/\text{Au}^{3+}\) state can be destroyed by moderate light illumination \([8]\). The light illumination probably disturbs the Jahn-Teller distortion and destabilizes the \(\text{Au}^{+}/\text{Au}^{3+}\) state.

3. \((\text{Ca},\text{Y})\text{Cu}_3\text{Co}_4\text{O}_{12}\)

In A-site ordered perovskite \(\text{AA}'_3\text{Br}_4\text{O}_{12}\), the three quarters of A sites are occupied by Jahn-Teller active \(\text{Cu}^{2+}\) or \(\text{Mn}^{3+}\) ions and the \(\text{BO}_6\) octahedra are tilted to stabilize the \(\text{Cu}^{2+}\) or \(\text{Mn}^{3+}\) ions with the pseudo-square planar coordination as shown in Fig. 2(a). Recently, \(\text{ACu}_3\text{Co}_4\text{O}_{12}\) (\(A=\text{Ca}\) or \(\text{Y}\)) has been synthesized using high pressure synthesis and the transport study has revealed that \(\text{CaCu}_3\text{Co}_4\text{O}_{12}\) is metallic and \(\text{YC}_3\text{Co}_4\text{O}_{12}\) is insulating \([11]\). However, if \(\text{Cu}\) valence is +2, then \(\text{Co}\) valence is expected to be +4 in \((\text{Ca},\text{Y})\text{Cu}_3\text{Co}_4\text{O}_{12}\) and +3.75 in \((\text{Y})\text{Cu}_3\text{Co}_4\text{O}_{12}\). Since the \(\text{Cu}\) and \(\text{Co}\) ions have integer number of 3d electrons with relatively large \(U\), \(\text{CaCu}_3\text{Co}_4\text{O}_{12}\) is expected to be a Mott insulator. On the other hand, if \(\text{Cu}\) is formally +3, then \(\text{Co}\) valence is +3.25 in \((\text{Ca},\text{Y})\text{Cu}_3\text{Co}_4\text{O}_{12}\) and +3 in \((\text{Y})\text{Cu}_3\text{Co}_4\text{O}_{12}\), which is consistent with the experimental result. Since \(\Delta\)s of \(\text{Cu}^{3+}\) oxides and \(\text{Co}^{4+}\) oxides tend to be negative, ligand
Figure 1. (a) Au$^+/\text{Au}^{3+}$ charge disproportionation of Cs$_2\text{Au}_2\text{Br}_6$. (b) Electronic configurations of the Au$^+$ and Au$^{3+}$ sites. (c) Au 4$f$ photoemission spectrum of Cs$_2\text{Au}_2\text{Br}_6$.

Figure 2. (a) Crystal structure of ACu$_3\text{Co}_4\text{O}_{12}$. (b) Cu 2$p$ photoemission spectra for A = Ca and Y compared with that of CaCu$_3\text{Ti}_4\text{O}_{12}$. (c) Co 2$p$ photoemission spectra for A = Ca and Y compared with those of LaCoO$_3$ and SrCoO$_3$[13].

(O 2$p$) hole should be considered explicitly in order to understand the electronic structure of ACu$_3\text{Co}_4\text{O}_{12}$.

Figure 2(b) shows the Cu 2$p$ photoemission spectra of CaCu$_3\text{Co}_4\text{O}_{12}$ and YCu$_3\text{Co}_4\text{O}_{12}$ which are compared with that of CaCu$_3\text{Ti}_4\text{O}_{12}$. The Cu 2$p$ binding energy of CaCu$_3\text{Co}_4\text{O}_{12}$ and YCu$_3\text{Co}_4\text{O}_{12}$ is similar to that of Cu$^{2+}$ ($d^9$) state in CaCu$_3^{2+}\text{Ti}_4\text{O}_{12}$. The Cu 2$p$ binding energy reflects the number of Cu 3$d$ electrons. Therefore, if Cu is formally 3+, the Cu ion should take $d^5L$ configuration instead of $d^9$. In Fig. 2(c), the Co 2$p$ photoemission spectra of CaCu$_3\text{Co}_4\text{O}_{12}$ and YCu$_3\text{Co}_4\text{O}_{12}$ are compared with those of LaCo$^{3+}\text{O}_3$ and SrCo$^{4+}\text{O}_3$[13]. The position and the shape of the charge-transfer satellite of CaCu$_3\text{Co}_4\text{O}_{12}$ and YCu$_3\text{Co}_4\text{O}_{12}$ are very similar.
Figure 3. (a) Crystal structure of IrTe$_2$, electronic configuration and expected Jahn-Teller splitting for Ir$^{4+}$, and expected Fermi surface change due to band Jahn-Teller effect. (b) Valence-band photoemission spectra above and below the structural transition. (c) Calculated density of states with and without orbital order due to band Jahn-Teller effect.

to LaCoO$_3$ indicating that Co valence is close to +3 for A=Ca and Y. The combination of Cu 2p and Co 2p spectra shows that the Cu valence is formally +3 and the Co valence is +3 in YCu$_3$Co$_4$O$_{12}$ consistent with the fact that YCu$_3$Co$_4$O$_{12}$ is insulating and CaCu$_3$Co$_4$O$_{12}$ is metallic. The valence change from Cu$^{2+}$/Co$^{4+}$ to Cu$^{3+}$/Co$^{3+}$ can be viewed as the O 2p hole transfer from Co to Cu or $d^5 + d^6L \rightarrow d^0L + d^6$ [12]. Since $\Delta$ is small and $U$ is large in the late 3d transition-metal oxides, the Zhang-Rice description or ligand hole description becomes valid.

4. IrTe$_2$
Both $\Delta$ and $U$ tend to decrease in going from oxides to chalcogenides [4]. Some transition-metal chalcogenides such as CuIr$_2$S$_4$ exhibit exotic phase transitions originating from the orbital degeneracy of transition-metal $d$ orbitals [14, 15]. Among them, IrTe$_2$ shows a structural phase transition at $\sim 270$ K which is probably due to Ir 5$d$ orbital order [16]. Recently, it has been found that Pt doping suppresses the static orbital order, and the superconductivity is induced around the quantum critical point for the orbital or bond order [17]. Valence-band photoemission spectrum of IrTe$_2$ is shown in Fig. 2(a). Across the orbital or bond order temperature, the spectral weight at -0.1 eV is suppressed instead of that at the Fermi level. The spectral weight suppression is reproduced by the calculation with $\Delta \sim 1$ eV which is relatively small among various transition-metal chalcogenides such as NiS and FeS.
The Ir 4f photoemission spectra reported by Ootsuki et al. indicates that the low temperature phase of IrTe$_2$ is accompanied by weak modulation of Ir 5d electron density [18]. The charge modulation or charge density wave can be induced by Fermi surface nesting due to the orbital order (orbitally-induced Peierls effect) [19]. Actually, the calculated Fermi surfaces show this tendency as shown in Fig. 3(a). Without the orbital order, the Fermi surfaces of the Ir 5d bands are made up from the Ir 5d $yz$, $zx$, and $xy$ orbitals and have the six-fold symmetry as expected from the trigonal structure. Under the compression along b-axis and the orbital order, the Fermi surface is calculated to be quasi-one-dimensional with Ir 5d $yz$ character. Such quasi-one-dimensional Fermi surface is expected to have instability to charge or spin density wave.

5. Concluding remarks
We have discussed Jahn-Teller effects in Cs$_2$Au$_2$Br$_6$, ACu$_3$Co$_4$O$_{12}$ (A=Ca or Y), and IrTe$_2$ in which the ligand p-to-transition-metal d charge-transfer energy is small or negative. In IrTe$_2$, both $\Delta$ and $U$ are small and the Ir 5d and Te 5p electrons are itinerant to form the multi-band Fermi surfaces. In such case, the ideas of band Jahn-Teller transition and Peierls transition are valid to describe the structural instabilities. In Cs$_2$Au$_2$Br$_6$, $\Delta$ is negative and $U$ is intermediate. In such case, the Au$^{2+}$/Au$^{3+}$ charge disproportionation can be described using effective “d orbitals” constructed from the Au 5d and Br 4p orbitals. The Au$^{3+}$ site with low-spin d$^9$ configuration undergoes the Jahn-Teller distortion. As for ACu$_3$Co$_4$O$_{12}$, $\Delta$s for Cu$^{3+}$ and Co$^{4+}$ are negative and the Zhang-Rice picture is valid to describe the electronic state. The valence change from Cu$^{2+}$/Co$^{4+}$ to Cu$^{3+}$/Co$^{3+}$ can be viewed as the O 2p hole transfer from Co to Cu or $d^9 + d^{6}L \rightarrow d^{9}L + d^{6}$.

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