Superexchange interaction revisited: the role of the A-site cations in ACuO₃ (A = Se, Te)

Beom Hyun Kim, Hongchul Choi and B I Min

PCTP, Department of Physics, Pohang University of Science and Technology, Pohang 790-784, Korea
E-mail: bimin@postech.ac.kr

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Abstract. To investigate the effects of A-site cations on the magnetic interaction in highly distorted perovskite ACuO₃ (A = Se, Te), we have set the microscopic Hamiltonian for the Cu–O–Cu–A cluster, taking into account the ŝp or ťp hybridization between A-š or A-p and O-2p orbitals. We have found that (i) the superexchange interaction of the simple Cu–O–Cu triad without considering the A-site effect is inadequate to explain the ferromagnetism of SeCuO₃, (ii) the ťp hybridization weakens the superexchange interactions and (iii) the ŝp hybridization induces the ferromagnetic superexchange interaction along the c-axis. We have also verified that the ŝp hybridization affects the magnetic interaction through anisotropic charge transfer energy shift in the Cu–O–Cu interaction path.

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1 Author to whom any correspondence should be addressed.
1. Introduction

The magnetism in transition metal oxides is closely correlated with structural properties, such as bond geometry, local crystal symmetry and Jahn–Teller (JT) distortion. Indeed, the empirical Goodenough–Kanamori–Anderson (GKA) rule \cite{1}–\cite{3} and the Kugel and Khomskii model \cite{4} have been successful in describing the magnetic interactions in transition metal oxides in relation to bond angle and orbital ordering. However, there are some cases that are not consistent with the prediction based on the above theoretical models. One typical example is the magnetic interaction in \( A\text{CuO}_3 \) (\( A = \text{Se}, \text{Te} \), which has a highly distorted perovskite structure (\( \text{Pbnm} \) space group) due to small ionic radii of Se and Te \cite{5}–\cite{7}.

Subramanian \textit{et al} \cite{7} reported that the magnetic ground state of \( \text{SeCuO}_3 \) changes when substituting Te for Se from the ferromagnetic (FM) to the antiferromagnetic (AFM) phase. They observed that the Cu–O–Cu bond angles increase from 122.3° to 123.1° along the \( c \)-axis (\( \phi_1 \)) and from 127.1° to 130.5° in the \( ab \)-plane (\( \phi_2 \)) (figure 1). Because a structural tuning of \( \phi_2 \) is much larger than \( \phi_1 \), they attributed the change in the magnetic state to the sign change of the magnetic interaction in the \( ab \)-plane by applying the GKA rule. They thus predicted that the magnetic ground state of \( \text{TeCuO}_3 \) would be the C-type AFM state, in which FM chains along the \( c \)-axis are coupled antiferromagnetically. However, subsequent electronic structure calculations \cite{8, 9}, as well as microscopic model analysis \cite{10}, showed that, going from \( \text{SeCuO}_3 \) to \( \text{TeCuO}_3 \), the magnetic interaction along the \( c \)-axis changes from FM to AFM, whereas the interaction in the \( ab \)-plane always remains FM. This implies that the A-type AFM state, in which FM layers in the \( ab \)-plane are coupled antiferromagnetically along the \( c \)-axis, is realized for \( \text{TeCuO}_3 \) rather than the C-type AFM state.

As shown in figure 1(a), 3 out of 12 surrounding oxygens around \( A \) in \( \text{ACuO}_3 \) are much closer to \( A \) than others, and so a structural unit of the \( AO_3 \) trigonal pyramid is formed. Such a structural character causes anisotropic bonding between \( A \) and three oxygens and induces nonbonded orbitals of \( A \) to appear along the empty corner of an \( AO_3 \) pyramid \cite{5, 11}. Moreover, the \( A–O \) distance is a bit smaller than the Cu–O distance, and accordingly strong hybridization between the orbitals of \( A \) and oxygen is expected to occur. For this reason, the hybridization effect between the orbitals of \( A \) and O is required to be taken into account to understand the physical properties of \( \text{ACuO}_3 \). In fact, Iñiguez and Yildirim \cite{8} showed that the magnetic ground state of \( \text{TeCuO}_3 \) is changed from the AFM to the FM phase by decreasing artificially the Te–O distance, and they suggested that the \( \tilde{s}p \) bonding between \( A–\tilde{s} \) and O-2p orbitals would play a role in switching the sign of the magnetic interaction in \( \text{ACuO}_3 \).

Other \( ABO_3 \) (\( B \) are transition metal elements) perovskites also have structural details similar to \( \text{ACuO}_3 \). Hence, the strong hybridization between \( A \) and O has been considered to investigate their electronic and magnetic properties \cite{5}, \cite{11}–\cite{14}. However, the microscopic treatment of this effect is far from complete.

In this study, we have performed a systematic study to explore the microscopic mechanism of the magnetic interaction in \( \text{ACuO}_3 \), considering not only structural specifications, such as Cu–O–Cu bond angle and orbital ordering, but also the \( A \)-site orbital contribution. Firstly, we have investigated the electronic structures of \( A \)-site ions in \( \text{SeCuO}_3 \) to inspect their hybridization behavior with other orbitals. Secondly, we have set the microscopic model for a Cu–O–Cu–A cluster and evaluated the magnetic exchange parameters with respect to the hybridization strength between orbitals of \( A \) and oxygen. As a result, we have demonstrated that the \( \tilde{s}p \)
hybridization between the occupied $\tilde{\text{A}}$-$\tilde{s}$ and the O-2p orbital plays a significant role in the magnetic interaction of the $\text{ACuO}_3$ system.

2. Electronic structure

To investigate the electronic properties of the $\text{A}$-site ion in $\text{ACuO}_3$ ($\text{A} = \text{Se, Te}$), we have performed the electronic structure calculation employing the full-potential augmented plane wave band method [15]. The generalized gradient approximation (GGA) [16] was used for the exchange-correlation potential. The density of states (DOS) and charge density difference (CDD) for the FM phase of $\text{SeCuO}_3$ are presented in figure 2. The CDD corresponds to the valence charge density of the crystalline solid after subtraction of the superposed atomic charge density of the valence electrons.

According to the DOS, figure 2 shows that FM $\text{SeCuO}_3$ has the insulating ground state with an energy gap of $\sim 0.3$ eV and the valence state of Cu ion is nearly 2+, consistent with existing band structure results [9, 10]. Focusing on the Se band, the 4$\tilde{s}$ band is fully occupied and shows a small band overlap with the oxygen 2p band. Its band center is about 9 eV lower than that of oxygen 2p. On the other hand, the unoccupied Se 4$\tilde{p}$ band is about 7 eV higher than the oxygen 2p band center. Strong mixing with the oxygen 2p band causes a small peak near $-6$ eV below the Fermi energy. This feature corroborates the strong hybridization between orbitals of Se and neighboring oxygens.

The CDD plot in the inset of figure 2 shows clearly the hybridization bonding property in $\text{SeCuO}_3$. An $\text{SeO}_3$ unit is known to produce the nonbonded Se lone-pair orbital, which is directed toward the apex of each trigonal pyramid [5, 11]. The CDD plot reveals that charges around Se ions are accumulated (red) on one side, but depleted (blue) on the other side, whereas those around oxygen ions are all accumulated. The distribution of positive CDD around Se ions,
which represents the formation of a nonbonded orbital, indicates that the lone-pair orbital is located toward the apex direction of trigonal pyramid. It thus results in an anisotropic pyramidal-shape bonding network. For A-type AFM TeCuO$_3$ too, we have obtained a similar band structure and confirmed the anisotropic nature of a strong hybridization between Te and oxygens.

3. The microscopic model

As discussed in figure 2, there exists a strong hybridization between the Se band and the O-2p band. This implies that oxygen states can be modified by A-site ions and accordingly the magnetic interaction mediated by oxygen can be changed in highly distorted perovskite ACuO$_3$. To understand the magnetic interaction in ACuO$_3$, we have considered the Cu–O–Cu–A clusters depicted in figure 1(b) and evaluated superexchange parameters in the framework of our previous study [17]. We have assumed that the ACuO$_3$ system follows the ideal $Pbnm$ structure to consider systematically the relation between the Cu–O–Cu bond angle and the local coordinates of two CuO$_6$ octahedra [18]. In this assumption, a Cu–O–Cu triad is described by the following Hamiltonian:

$$H_T = \sum_{i,\mu_1} \epsilon_{\mu_1} n_{\mu_1} + U_d \sum_{i,\mu_1,\nu_1} n_{\mu_1} n_{\nu_1} - J_d \sum_{i,\mu_1,\nu_1,\sigma} n_{\mu_1,\sigma} n_{\nu_1,\sigma} + \sum_{p} \epsilon_p n_p + U_p \sum_{p p'} n_p n_{p'}$$

$$- J_p \sum_{p p', \sigma} n_{p \sigma} n_{p', \sigma} + \sum_{i,\mu,\rho, \sigma} \tilde{t}_{\mu \rho} \sum_{\sigma} \tilde{c}_{\mu \rho, \sigma} \tilde{c}_{\sigma} + h.c.,$$

\[(1)\]
Table 1. Physical parameters employed for calculating the superexchange interaction in ACuO$_3$ systems. They are in units of eV. Because the electronic configuration of Cu$^{2+}$ is d$^9$, the charge transfer $\Delta$ is given by $E$(p$^5$d$^{10}$) − $E$(p$^6$d$^9$). According to Slater and Koster [19], the hopping integrals between O-2p and Cu-3d orbitals are expressed by two parameters $t_{pdr}$ and $t_{pdr}$ that follow the relation $t_{pdr} = -0.46t_{pdr}$ [20].

| $\Delta$ | 10$Dq$ | $\Delta_{JT}$ | $U_d$ | $J_d$ | $U_p$ | $J_p$ | $\epsilon_p$ | $t_{pdr}$ | $\Delta_i$ | $\Delta_p$ |
|---------|---------|-------------|-------|-------|-------|-------|------------|---------|---------|---------|
| 4.0     | 1.5     | 0.6         | 7.0   | 1.5   | 2.0   | 0.5   | 0.0        | -1.5    | 10.0    | 8.0     |

where $d_{i,\mu}^\dagger$ and $c_{p\sigma}$ are the creation operators of Cu 3d-electron with $\mu_i$ orbital and $\sigma$ spin states at i-site ($i = 1, 2$) and the annihilation operator of O 2p electron with p orbital and $\sigma$ spin states, respectively. Let the local coordinate of i-site Cu be $\{x_i, y_i, z_i\}$. Then it is convenient to describe $\mu_i$ orbitals by the basis $\{|x_iy_i, y_iz_i, z_ix_i, |\theta_i, |\theta_i + \pi\rangle\}$, where $|\theta_i\rangle$ is defined by $|\theta_i\rangle = \cos(\theta_i/2)|3z_i^2 - r_i^2\rangle + \sin(\theta_i/2)|x_i^2 - y_i^2\rangle$. $U_d$, $J_d$, $U_p$ and $J_p$ are Coulomb interaction parameters of 3d and 2p orbitals, respectively. The hopping parameters $t_{i^{\mu/p}}$ are evaluated as functions of the two $p$–d hopping parameters $t_{pdr}$ and $t_{pdr}$, according to Slater and Koster [19].

In order to investigate the effect of the hybridization between orbitals of A and oxygen ions, we have adopted the additional Hamiltonian

$$H_A = \sum_{\alpha\sigma} t_{\alpha\sigma} [c_{\alpha\sigma}^\dagger c_{\alpha\sigma} + \text{h.c.}],$$

where $c_{\alpha\sigma}^\dagger$ is the creation operator of the $\alpha$-site orbital with a $\sigma$ spin. Possible $\alpha$-site orbitals are occupied 4$s$ and empty 4$p$ orbitals in the case of SeCuO$_3$. According to Slater and Koster [19], the 4$s$ and 4$p$ orbitals are characterized by one ($t_{spo}$) and two ($t_{ppo}$ and $t_{ppr}$) parameters, respectively.

The physical parameters used in the superexchange calculation are provided in table 1. The charge transfer energy $\Delta$ is defined by $E$(3d$^{10}$2p$^5$) − $E$(3d$^9$2p$^6$). $\Delta_i$ and $\Delta_p$ are the charge transfer energies of the occupied $A$-$\tilde{s}$ and the empty $A$-$\tilde{p}$ orbital, respectively, e.g. for $A = $Se, $\Delta_i = E$(4$s^5$2p$^5$) − $E$(4$s^5$2p$^6$) and $\Delta_p = E$(4$p^5$2p$^5$) − $E$(4$p^6$2p$^6$). The distortion angle $\theta$, which represents the local JT distortion, and the occupied $e_g$ orbital state $|\theta\rangle$ are set in between 104° and 110° according to real ACuO$_3$ systems [7]. $\Delta_{JT}$ in table 1 corresponds to the JT splitting energy, which is defined by the energy difference between two $e_g$ orbitals, $|\theta\rangle$ and $|\theta + \pi\rangle$. $10Dq$ is the crystal field splitting between $t_{2g}$ and $e_g$ states of Cu.

Physical parameters such as $10Dq$, $\Delta_{JT}$, $J_d$, $\Delta_i$ and $\Delta_p$ can be estimated from the DOS results in figure 2, which are consistent with our choices in table 1. For $U_d$, the typical value ($U_d \approx 7$–8 eV) in cuprates is employed [21]. For $J_d$, considering that the GGA band calculation usually underestimates the Coulomb interaction parameters, we adopted the value of $J_d = 1.5$ eV that is in between the band calculation result $\sim 1.1$ eV and the atomic multiplet calculation result $\sim 1.6$ eV. We have checked that the reduction of $J_d$ tends to suppress the ab-plane FM interaction, but overall magnetic behaviors are really robust in the range of $J_d \approx 1.0$–1.5 eV.

In insulating ACuO$_3$ systems, electrons are nearly localized and so only the hopping between adjacent ions would give weak orbital overlaps. Then the ground state of the Cu–O–Cu–A cluster is mainly contributed by a Cu(3d$^9$)–O(2p$^6$)–Cu(3d$^9$)–A($s^2$ or $p^0$)
configurational state. For this reason, we have considered the restricted Hilbert space, in which states are overlapped with a Cu(3d⁹)–O(2p⁶)–Cu(3d⁹)–A(\tilde{s}² or \tilde{p}⁰) configurational state through off-diagonal elements of \( H \) and \( H^2 \). It is reminiscent of the fourth-order perturbation approximation in the hopping parameter \( t_{pd} \). Because the Hamiltonian has no spin-flip part, we have calculated the ground state energies of the FM (\( E_{↑↑} \)) and AFM (\( E_{↑↓} \)) cases separately.

Assuming that the magnetic energy is given by the Heisenberg type, \( E = 2 J \vec{S}_1 \cdot \vec{S}_2 \), the superexchange interaction parameters are calculated by the relation \( 4JS_2 = E_{↑↑} - E_{↑↓} \).

4. Magnetic interaction

Since \( ACuO_3 \) exhibits the C-type orbital ordering, its magnetic interaction would be similar to that of the perovskite manganite. In the \( ab \)-plane where the antiferro-orbital ordering appears, the FM interaction (\( J_{ab} \)) is dominant, whereas, along the \( c \)-axis having the ferro-orbital ordering, the AFM interaction (\( J_c \)) prevails. As the Cu–O–Cu bond angles (\( \phi_1 \) and \( \phi_2 \)) decrease with the distortion of GdFeO\(_3\) type, the magnitudes of two exchange parameters \( J_{ab} \) and \( J_c \) are reduced. This behavior is well described in figure 3. The magnetic structure of TeCuO\(_3\), whose bond angles \( \phi_1 \) and \( \phi_2 \) are estimated to be 123.5° and 130.5°, respectively, should be A-type AFM, because \( J_{ab} \) is negative and \( J_c \) is positive at those \( \phi_1 \) and \( \phi_2 \) (see purple arrows in figure 3). This finding does not agree with the magnetic structure proposed by Subramanian et al [7], but agrees with the results of the electronic structure calculations [8, 9] and the microscopic model calculation [10].

Note that both exchange parameters in figure 3 never change signs until \( \phi_1 \) and \( \phi_2 \) become as small as 110°, and so this result does not explain the FM ground state of ScCuO\(_3\) that has \( \phi_1 = 122.3° \) and \( \phi_2 = 127.1° \) (black arrows in figure 3). Of course, the FM ground state is possible when \( \phi_1 \) is smaller than about 100° [10]. But this value is far from \( \phi_1 \) of ScCuO\(_3\). Furthermore, as shown in figure 3, such a tendency is robust with respect to the variation in the
JT distortion angle $\theta$. $J_{ab}$ is more influenced by $\theta$ but it is always negative, whereas positive $J_c$ increases only slightly with varying $\theta$ from $104^\circ$ to $110^\circ$. This finding indicates that the superexchange interaction considering only the Cu–O–Cu bond angle and the orbital ordering pattern is not sufficient to describe the FM ground state of SeCuO$_3$ properly.

Let us take into account the effect of $A$ cations on the Cu–O–Cu superexchange interaction. In the ideal $Pbnm$ structure in figure 1(a), $A$–O distance ($d_A$) decreases with lowering the $\phi$ and becomes smaller than the Cu–O distance ($d_0$) when $\phi_1$ and $\phi_2$ are less than $132.8^\circ$ and $136.5^\circ$, respectively (see figure 4(a)). In real systems, $d_A/d_0$ for $A$–$O1$ is about 0.84 for $J_{ab}$ for different $\hat{p}$-site positions of real materials show a small shift from (0, 0, 0.25) to (0, 0, 0.25). In our calculation, we have taken into account a small $A$-site shift ($\Delta x = 0.040, \Delta y = 0.060$) that produces theoretical $d_A/d_0$s close to experimental $d_A/d_0$s and so $d_A$s at $\phi = 180^\circ$ in figure 4(a) are not $\sqrt{2} d_0$ but 1.4–1.6$d_0$.

**Figure 4.** (a) Bond angle dependence of the $A$–O distance ($d_A$) for the ideal $Pbnm$ structure. $A$–$O1$ and $A$–$O2$ are as a function of $\phi_1$ and $\phi_2$, respectively. Squares and circles denote experimental values of $d_A/d_0$ ($A$–$O1$) for SeCuO$_3$ and TeCuO$_3$, respectively. (b) The bond angle dependence of $t_{\bar{a}p\sigma}/t_{pd\sigma}$ ($\bar{a} = \bar{5}$ or $\bar{p}$) for given $t_{\bar{a}p\sigma0}$ values. Squares and circles refer to theoretical values of $t_{\bar{a}p\sigma}/t_{pd\sigma}$ for SeCuO$_3$ and TeCuO$_3$ in [8]. (c) Bond angle dependence of $J_c$ and (d) that of $J_{ab}$ for different $\bar{p}$-site bond strengths with given parameters in table 1.

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SeCuO$_3$ (square in figure 4(a)) and 0.93 for TeCuO$_3$ (circle in figure 4(a)) \cite{5, 6}, which are close to the values for the ideal $Pbnm$ structure. Smaller $d_{\parallel}$ induces stronger hybridization between the outermost occupied $A$-$s$ or unoccupied $A$-$p$ and O-2p orbitals, and its strength overwhelms the pd hybridization between Cu-3d and O-2p orbitals. In fact, according to the tight-binding calculation \cite{8}, the $sp$ hybridization is five or six times larger than the pd hybridization.

Therefore, we have investigated the effect of the hybridization between orbitals of $A$ and O on exchange parameters $J_{ab}$ and $J_c$. In the calculation, we have assumed $t_{\bar{a}p\sigma} \propto d^{-1}_{\parallel} (\bar{a} = \bar{s}$ or $\bar{p})$ and $t_{\bar{p}p\sigma} = -0.25 t_{\bar{a}p\sigma}$, following Harrison’s relation \cite{20}. If the bond strength for $d_{\parallel} = d_0$ is $t_{\bar{a}p\sigma 0}$, $t_{\bar{a}p\sigma}$ is given by $t_{\bar{a}p\sigma} = t_{\bar{a}p\sigma 0}(d_{\parallel}/d_0)^{-2}$. Figure 4(b) provides bond angle-dependent behaviors of $t_{\bar{a}p\sigma}/t_{\bar{p}d\sigma}$ for some $t_{\bar{a}p\sigma 0}$ values.

Figures 4(c) and (d) show the effect of the $pp$ hybridization on $J_{ab}$ and $J_c$. The magnitudes of both $J_{ab}$ and $J_c$ decrease monotonically with increasing $pp$. However, $J_c$ is still positive down to $\phi_1 = 110^\circ$, and so no magnetic transition from the AFM to the FM state takes place, even with strong $pp$ hybridization. This means that unoccupied $A$-$p$ states can modify the strengths of two exchange parameters, but cannot change the magnetic ground state. Thus, to explain the FM state in SeCuO$_3$, the additional effect should be invoked.

Now we have considered the effect of the $sp$ hybridization on $J_c$ and $J_{ab}$. Even though the band mixing between $A$-$s$ and O-2p orbitals looks rather small, strong $sp$ hybridization is estimated in the tight-binding model \cite{8}. Figures 5(a) and (b) show the modification of magnetic interactions $J_c$ and $J_{ab}$ with respect to the change in $sp$ hybridization. Most prominent in figure 5(a) is the realization of FM $J_c$ for small $\phi_1$. The change in the magnetic interactions is not notable for $t_{\bar{s}p\sigma 0} < 3.0$ eV. However, with increasing $t_{\bar{s}p\sigma 0}$ further, the FM region appears and the critical angle, where the sign of $J_c$ is reversed, becomes close to $\phi_1$ of SeCuO$_3$. It is coincidental that the in-plane FM interaction $J_{ab}$ is much strengthened near the critical angle, as shown in figure 5(b). It is seen in figure 5(a) that, for $t_{\bar{s}p\sigma 0} = 4.5$ eV, $J_c$ is changed from about 3.8 to $-2.8$ meV when $\phi_1$ varies from 123.5$^\circ$ to 120.5$^\circ$. Also, in figure 5(b), $J_{ab}$ is seen to be in between $-2.0$ and $-1.6$ meV when $\phi_2$ varies from 130.2$^\circ$ to 127.1$^\circ$. These values are consistent with calculated exchange parameters based on the band structures of ACuO$_3$ \cite{8, 9}.

**Figure 5.** Bond angle dependence of (a) $J_c$ and (b) $J_{ab}$ for different $\bar{s}p\sigma$ bond strengths with given parameters in table 1. The inset in (b) shows the magnetic phase diagram for $\phi_1 = 122.33^\circ$ corresponding to $\phi_1$ of SeCuO$_3$. 

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Figure 6. (a) Bond angle-dependent behavior of the PTHW for different types of hybridization with A-site ions. (b) $J_c$ as a function of $\Delta \epsilon_x$ that corresponds to the energy difference between oxygen 2p$_x$ and other 2p orbitals. The inset in (a) presents the PTHW for different $\Delta \epsilon_x$.

Besides $t_{\tilde{p}p\sigma}$, the charge transfer energy $\Delta \tilde{\epsilon}$ also affects $J_{ab}$ and $J_c$. Because an electron in the occupied $\tilde{s}$ state can hop into the empty O-2p states easily for small $\Delta \tilde{\epsilon}$, the FM region will be broadened with decreasing $\Delta \tilde{\epsilon}$. The inset in figure 5(b) presents the magnetic phase diagram for $\phi_1 = 122.33^\circ$ as functions of $t_{\tilde{p}p\sigma}$ and $\Delta \tilde{\epsilon}$. It is evident that the strong $\tilde{s}p$ hybridization modifies largely the superexchange interaction, and proper values of $t_{\tilde{p}p\sigma}$ and $\Delta \tilde{\epsilon}$ cause its sign to be reversed and stabilize the FM interaction.

When the charge transfer energy $\Delta$ is similar to or smaller than the on-site Coulomb energy, the charge transferred states with oxygen 2p holes can play an important role in the magnetic interaction. We have investigated the relation between the $\tilde{s}p$ or $\tilde{p}p$ hybridization and oxygen 2p hole states. For this purpose, we introduce the projected 2p hole weight (PTHW) that refers to the weight of one or two O-2p hole states in the collapsed state obtained by projecting the ground state of a Cu–O–Cu–A cluster on the subspace where A-site configuration is $\tilde{s}^2$ or $\tilde{p}^0$. Figure 6(a) presents the bond angle-dependent behavior of PTHW. PTHW is useful to examine the effective change of the O-2p hole weight in the Cu–O–Cu cluster due to the hybridization with A-site orbitals. Without the hybridization, the PTHW along the c-axis is nearly constant and the weight for the AFM case is always a little larger than that for the FM case. The difference becomes nearly zero with decreasing $\phi_1$. By contrast, with the hybridization, the PTHW shifts up or down depending on the A-site orbitals. For the $\tilde{p}p$ hybridization, the PTHW decreases monotonically, and the difference between the FM and AFM cases becomes reduced similarly to the prior case of no hybridization. For the $\tilde{s}p$ hybridization, however, the weights of both the FM and AFM cases increase rapidly near the critical angle, and their magnitudes are reversed. Note that, according to the second-order perturbation theory, the weight coefficient of charge transferred states is approximately proportional to $-t_{pd}/\Delta$. This implies that the $\tilde{s}p$ hybridization causes the charge transfer energy $\Delta$ of 2p hole states to be effectively lowered, whereas the $p\bar{p}$ hybridization gives rise to an opposite effect$^3$.

$^3$ We assumed that the pd hopping strength is independent of the bond angle. According to [8], the pd hopping strength of SeCuO$_3$ can be about 10% smaller than that of TeCuO$_3$. But such a small difference is insufficient to increase the 2p hole weight to two to three times larger.
In the Cu–O1–Cu interaction path depicted in figure 1(a), the displacement vector between A and O1 is along the a-axis. Then the hybridization between the A-š and O-2p, orbitals, whose lobe is directed to the a-axis, will be much stronger than others. Combining this fact with the finding of effective shift of ∆ in figure 6(a), one expects that a system in which a p, orbital has a different energy from others by Δε, would exhibit behaviors similar to figure 5(a). Figure 6(b) shows J, for various Δε, . Indeed, positive Δε, produces the FM interaction of J, . Here, positive Δε, means the reduction in Δ for p, orbital. Thus figure 6(b) indicates that the anisotropic reduction in the charge transfer energy ∆ can stabilize the FM interaction. Moreover, the inset in figure 6(a) shows that the PTHW for positive Δε, also increases with decreasing bond angle and their magnitudes of FM and AFM cases are reversed near the critical bond angle. It is thus clear that the effect of the šp hybridization on charge transferred states is equivalent to that of positive Δε, .

Further, we have found that the geometry of the Cu–O–Cu–A cluster is crucial to stabilize the FM interaction. As an example, we have considered an artificial Cu–O–Cu–A cluster where the A–O displacement is perpendicular to the Cu–O–Cu plane. In this case, the magnetic interaction along the c-axis is found to be almost inert against the šp hybridization. This behavior is related to the type of oxygen 2p orbital which bonds with the A-š orbital. Because the O-2p orbital that performs the strong šp hybridization is perpendicular to the Cu–O–Cu plane, its bonding with Cu 3d orbitals is too weak to give a significant contribution to the superexchange interaction. In the same context, it is verified that, if the p, orbital is shifted by Δε, instead of p, , the Cu–O1–Cu system does not exhibit the FM stabilization. Based on these findings, one can construct a new scenario on the role of the šp hybridization. When an A-site ion is located in a position where the A–O displacement is included in the Cu–O–Cu plane and bisects the Cu–O–Cu bond angle, the strong šp hybridization can give rise to a maximal effect in modifying the magnetic interaction and stabilizing the FM interaction.

In the case of Jab, the PTHW for the FM case is always larger than that for the AFM case, and their values are nearly constant (∼ 0.1). But when Jab becomes enhanced suddenly for large šp (figure 5(b)), the PTHW also increases abruptly. This indicates that the behavior of Jab with respect to the šp hybridization is also understandable in view of the effective reduction in the charge transfer energy.

In contrast to the šp hybridization, the šp hybridization just suppresses the PTHW. One might expect that an electron in the oxygen 2p orbital can hop into unoccupied A-š orbitals easily and so the oxygen 2p hole weight grows up. In actuality, total 2p hole weight (TTHW) of the Cu–O–Cu–A cluster increases with including the šp hybridization and becomes two to three times larger than that of the nonhybridized case. However, the TTHW increment does not bring about the PTHW increment, because an unoccupied A-š orbital can increase the O-2p hole weight by overlapping not only with the charge transferred states but also with the nontransferred states, for which no charge transfer between Cu-3d and O-2p orbitals takes place. If the O-2p hole contribution of nontransferred states prevails, the effective shift of the charge transfer energy, which is determined by the energy difference between the charge transferred and nontransferred states, would be positive. As a consequence, the enhancement of effective charge transfer energy reduces the magnitudes of Jab and J, , as seen in figures 4(c) and (d).

As mentioned earlier, the effect of the šp bonding on ACuO3 was suggested by Iñiguez and Yildirim [8]. In their analysis, however, the role of šp hybridization was simply restricted to the reduction of the effective pd hopping. That is, its effect suppresses the magnitude but cannot change the sign of the superexchange interaction. Hence they assumed an additional but
seemingly artificial FM direct exchange interaction that is induced by the intersite exchange Coulomb interaction between two facing Cu-d orbitals or between Cu-d and O-p orbitals, and concluded that the competition between the constant FM direct exchange and the varying superexchange due to the \( \tilde{s}p \) hybridization would give rise to the magnetic transition of \( A\text{CuO}_3 \) systems. For the intersite exchange interaction parameters, they adopted typical values of cuprates such as \( \text{Ca}_2\text{CuO}_3 \) and \( \text{Sr}_2\text{CuO}_3 \), for which the direct exchange interaction (\( K \)) was estimated to be 10–30 meV [22]. Note, however, that Cu–O distances along the \( c \)-axis of \( A\text{CuO}_3 \) (2.06–2.09 Å) are considerably longer than those of the above conventional cuprates (1.89–1.96 Å). Then the \( K \) value of \( A\text{CuO}_3 \) is expected to be much smaller than that of conventional cuprates, and the direct exchange effect in \( A\text{CuO}_3 \) would be much weaker. In contrast, in our analysis, the \( \tilde{s}p \) hybridization could bring about the anisotropic change of the charge transfer energy as well as the reduction of the \( pd \) hopping. Moreover, it not only suppresses the magnitude but also reverses the sign of the superexchange interaction. Thus the artificial intersite exchange interaction is not necessary to stabilize the FM interaction in \( A\text{CuO}_3 \). Nevertheless, it is hard at the moment to determine which scenario is more relevant in real \( A\text{CuO}_3 \) systems. There is no concrete experimental or theoretical evidence to justify physical parameters such as \( \Delta\epsilon_p \) and \( K \) in \( A\text{CuO}_3 \). More precise determination of physical parameters and more information on the relation between structural change and magnetism are required. Investigation of the pressure effect on magnetic properties of \( A\text{CuO}_3 \) is desirable to test the relevant mechanism.

The proposed mechanism of superexchange interaction exploiting the anisotropic shift of the charge transfer energy can be applied to any magnetic insulator of perovskite \( ABO_3 \) type, in which the charge transfer energy is relatively smaller than the on-site Coulomb repulsion and the hopping-mediating anions bond strongly with nonmagnetic cations. \( ABO_3 \) magnetic insulators with \( B = \text{Co, Ni} \) and Cu belong to the former kind of group, whereas those with nonmagnetic cations, such as \( A = \text{Se and Te} \), belong to the latter. Thus typical candidates are \( ABO_3 \) systems with \( A = \text{Se, Te} \) and \( B = \text{Mn, Co, Ni} \) [5]. When the \( A \) cation is replaced from Se to Te, the bond angle change of these systems is only about 5\( ^\circ \). But the Neel temperature (\( T_N \)) is enhanced by about 20–50\%. To understand this feature, we think that not only the change of bond angle and the \( pd \) hopping but also the charge transfer energy shift proposed in the present study should be taken into account properly, as in \( A\text{CuO}_3 \).

5. Conclusion

We have investigated the effects of hybridization of \( A \)-site orbitals on the magnetic interactions in highly distorted \( A\text{CuO}_3 \) (\( A = \text{Se, Te} \)). Band mixing between \( \tilde{s} \) and \( \tilde{p} \) orbitals of the \( A \) and oxygen \( 2p \) orbital is viewed with the help of the electronic structure calculation for \( A\text{CuO}_3 \) (\( A = \text{Se, Te} \)). Using the microscopic model that includes the effect of \( \tilde{s}p \) or \( \tilde{p}p \) hybridization, we have found that the simple Cu–O–Cu superexchange interaction model that considers only the orbital ordering and the bond angle change is inadequate to explain the transition from the AFM to the FM state in \( A\text{CuO}_3 \), as \( A \) is substituted from Te to Se. We have provided a new mechanism where the \( \tilde{s}p \) hybridization gives rise to an anisotropic change in the effective charge transfer energy, which stabilizes the FM interaction along the \( c \)-axis. On the other hand, the \( pp \) hybridization weakens both magnetic exchange parameters \( J_{ab} \) and \( J_c \), but does not induce the transition from the AFM to the FM state for the bond angles relevant for \( A\text{CuO}_3 \).
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