Double perovskites \( (A_2BB'O_6) \), where \( A \) is a rare earth element, and \( B \) and \( B' \) are transition metal ions) have attracted much research interest because of their magnetism with potential application to spintronics [1–6]. A large magnetoresistance (MR) of ~42\% as well as a high Curie temperature of \( T_C \sim 410 \) K, has been reported for \( \text{Sr}_2\text{FeMoO}_6 \) [1]. This has stimulated researches into other double perovskite systems [2] including \( \text{Sr}_2\text{CrMO}_6 \) (where \( M = W, \text{Re}, \) or \( \text{Os} \) \) [3, 4] and \( \text{(La,Sr)}_2\text{CoIrO}_6 \) [5,6] with the aim to achieve a higher \( T_C \).

Microscopic analyses of the double perovskites have shown that the local spin moments in both the \( B \) and \( B' \) sites contribute to the magnetic moment [2]. Interestingly, ferromagnetic (FM) ordering can be stabilized in the \( B \) or \( B' \) ion sublattice, even though the interatomic distance between ions of the same atomic species is large (\( >4 \) Å). Such long-range interactions between the \( B \) sites have been explained as a consequence of inter-site spin interactions mediated by the exotic ions at the \( B' \) sites; i.e. the spin-selective orbital hybridization between the adjacent \( B \) and \( B' \) sites accounts for the preferential ordering of spins with respect to each other.

With cobaltite double perovskites, however, the magnetism may be more complicated. This is primarily due to the strong on-site many-body effects associated with the Co ions; The Co ions (Co\(^{2+}\), Co\(^{3+}\), or Co\(^{4+}\)) can have a high-spin (HS) state with...
a maximum number of spin-up electrons, a low-spin (LS) state with a minimum number of spin-up electrons, or an inter-
mediate-spin state. In particular, the energies of the HS and LS
states in Co$^{3+}$ are very close, so the occupation numbers, and
consequently, the net spin moments, can vary considerably with
temperature ($T$) [7, 8]. Hence, in principle, the cotailles require
more careful inspection in terms of the chemistry and the spin
states of Co ions than any other 3d transition metal oxides.

Here, we examine the local moments of Co ions and the
total magnetization of La$_2$CoMO$_6$ compounds, where $M$ = Ir or Pt. The local electronic structure of Co was investigated
using Co $L_{2,3}$-edge x-ray absorption spectroscopy (XAS), and
the magnetic properties were investigated using x-ray mag-
netic circular dichroism (XMCD). We found that the Co ions
had an HS configuration ($d^7$) with a valence of +2 at moderate
or low $T$’s for both samples. However, the magnetic properties
differed significantly; La$_2$CoIrO$_6$ was ferromagnetic at low
$T$’s, and La$_2$CoPtO$_6$ was almost paramagnetic. We analyzed
the orbital and spin moments in detail and demonstrated that
such dependence on composition can be explained in terms of
hybridization, as in other double perovskites.

An La$_2$CoIrO$_6$ (La$_2$CoPtO$_6$) polycrystalline sample was
prepared via solid-state synthesis from a stoichiometric mix-
ture of La$_2$O$_3$, IrO$_2$ (PtO$_2$), and Co$_3$O$_4$. The La$_2$O$_3$ was heated to
700 °C for two days, and the resulting La$_2$CoMIrO$_6$ ($M$ = Ir or
$M$ = Pt) phases were sintered at $T$’s in the range 900–1150 °C
for several days with intermediate grinding. Crystallographic
data for each specimen were obtained using powder x-ray
diffraction (XRD; Rigaku Miniflex2, Cu Kα radiation)
with $θ$ = 2$θ$ scans. The magnetic properties were character-
ized using a Quantum Design superconducting quantum
interference device (SQUID) in the range 2 K $\leq T \leq$ 300
K, and with magnetic fields in the range 0–5 T. XAS and
XMCD measurements were performed with circularly polarized
x-rays generated by an elliptically polarizing undulator at the 2A beamline in the Pohang Light Source.
Data were collected in total electron yield mode. For the
XMCD measurements, we used x-rays with fixed helicity
and alternated the direction of the external magnetic fields
($H$ = 8 kOe) to ensure a constant beam profile.

Figure 1 shows powder XRD patterns of the La$_2$CoIrO$_6$
and La$_2$CoPtO$_6$ obtained at room temperature. The two
patterns are similar, which suggests that the crystal structures
were almost identical with similar lattice constants. This is
most probably due to the similar ionic radii of Ir$^{3+}$ and Pt$^{4+}$
(0.625 Å) [9]. Each of the reflection peaks was assigned according to a monoclinic crystal symmetry (P$2_1$/n) [10–12]
with lattice constants of $a \approx 5.58$ Å, $b \approx 5.67$ Å, and $c \approx 7.92$ Å
([10]). The crystal structure is shown in the inset of figure 1.
For both systems, the unit cell consisted of La$_2$CoMO$_6$ (where
$M$ = Ir or $M$ = Pt), in which the Co or M ions share the same
cation site in the perovskite structure, leading to an alternating
CoO$_6$ and MO$_6$ octahedra [13]. Rotation of the octahedral
oxygen coordination and buckling of octahedra are expected
[5, 13]. Recent studies of double perovskites have shown that
a significant charge reconstruction occurs among the cations
[6]. As will be shown later (see figure 3), we confirm that the valence
states of the cations in cobaltite double perovskites
are La$^{3+}$, Co$^{2+}$, and M$^{4+}$. It follows that inter-site interactions
between the Co$^{3+}$ ($d^7$) and M$^{4+}$ ($d^5$ for Ir and $d^6$ for Pt) ions
can be expected.

Despite the similarity in the crystal structure, La$_2$CoIrO$_6$
and La$_2$CoPtO$_6$ exhibited significantly different magnetic
properties. The $T$-dependence of the magnetization was obtained under zero-field cooling (ZFC) and field cooling
(FC), over a range of 2 $\leq T \leq$ 300 K with $H$ = 5 kOe, as shown
in figure 2(a). La$_2$CoIrO$_6$ exhibited a strong signature for fer-
romagnetic moment at low T, with a large contrast between the
FC and ZFC data, whereas La$_2$CoPtO$_6$ did not. This suggests
that La$_2$CoIrO$_6$ is ferromagnetic but La$_2$CoPtO$_6$ is almost par-
amagnetic with a very small ferromagnetic moment.

The inset shows the inverse of the magnetic susceptibility
$x_M$ as a function of $T$, which can be used to determine $T_C$.
The values of $T_C$’s estimated by extrapolating the maximum
gradient to the abscissa, were $T_C$ ~94 K for La$_2$CoIrO$_6$, whereas
$T_C$ < 50 K for La$_2$CoPtO$_6$. In the case of La$_2$CoIrO$_6$, a clear
step-like feature near $T = 100$ K validates the extrapolation
method. However, in the case of La$_2$CoPtO$_6$, it is hard to
choose an extrapolation point reliably, because the slope near
$T = 50$ K varies slowly. Therefore, we could obtain only an
upper bound of $T_C$ ~ 50 K for La$_2$CoPtO$_6$.

The lower $T_C$ of La$_2$CoPtO$_6$, as well as the weaker fer-
romagnetic signature, is indicative of strong suppression of the
magnetic moment. This contrast is highlighted by the mag-
etization curve as a function of $H$, shown in figure 2(b). The
magnetization measured at $T = 43$ K exhibits strong FM in
La$_2$CoIrO$_6$; however, the FM was significantly weaker for
La$_2$CoPtO$_6$ (by a factor of approximately 7). Therefore, we may
conclude that the FM moment was suppressed in La$_2$CoPtO$_6$.

The measured magnetization at $T = 43$ K was ~0.8 $\mu_B$ per
formula unit (f.u.) in La$_2$CoIrO$_6$ (see figure 2). In theory,
however, the nominal saturated spin moment should be 2 $\mu_B$/f.u.,
assuming antiferromagnetic (AFM) coupling of the high-spin
Co$^{3+}$ ($S = 3/2$) and Ir$^{3+}$ ($S_{\text{eff}} = 1/2$), or 4 $\mu_B$/f.u., assuming
FM coupling. This suggests that the measured magnetization

![Figure 1](image-url)
Figure 2. The magnetization of La$_2$CoIrO$_6$ and La$_2$CoPtO$_6$ polycrystalline samples as a function of (a) $T$ and (b) $H$. The inset in (a) shows the inverse of the susceptibility (i.e. $1/\chi$), which was used to determine $T_C$. In the case of La$_2$CoIrO$_6$, a clear signature of a ferromagnetic moment was observed, with a large contrast between the field cooled (FC) and zero-field cooled (ZFC) regimes, with $T_C \approx 94$ K. For La$_2$CoPtO$_6$, however, such behavior was not observed, and only a slight increase in the magnetization at very low $T$’s was seen. The vertical dashed line in (b) indicates the temperature ($C \approx 94$ K) whereas it vanished almost completely at $T = 43$ K (significantly higher than $T_C$), the spectra $T = 43$ K and $300$ K. Linearly polarized x-rays were used. For comparison, the spectrum of CoO is also shown. For both samples, the lineshapes were almost identical to the spectrum of CoO, which suggests that HS Co$^{2+}$ was dominant, even at room temperature. (c) XMCD data for La$_2$CoIrO$_6$ and (d) XMCD data for La$_2$CoPtO$_6$. Circularly polarized x-rays with alternating magnetic fields of $H = \pm 8$ kOe were used. The XMCD lineshapes of La$_2$CoPtO$_6$ almost coincides with that of La$_2$CoIrO$_6$, which suggests almost identical local electronic structure of the Co$^{2+}$ ions. For La$_2$CoIrO$_6$ almost coincides with that of La$_2$CoIrO$_6$, which suggests the involvement of another many-body state in Co$^{2+}$. In contrast, the spin moment varied significantly with $T$ and with composition. Figures 3(c) and (d) show the $T$-dependence of the XMCD spectra for the two samples. We used circular polarization and measured the difference in the absorption intensity between $H = +8$ kOe and $H = -8$ kOe. For La$_2$CoIrO$_6$, the XMCD was clearly observed at $T = 43$ K (below $T_C$) whereas it vanished almost completely at $T =$

Figure 3. The Co $L_{2,3}$-edge XAS spectra of (a) La$_2$CoIrO$_6$ and (b) La$_2$CoPtO$_6$ at 43 K and 300 K. Linearly polarized x-rays were used. For comparison, the spectrum of CoO is also shown. For both samples, the lineshapes were almost identical to the spectrum of CoO, which suggests that HS Co$^{2+}$ was dominant, even at room temperature. (c) XMCD data for La$_2$CoIrO$_6$ and (d) XMCD data for La$_2$CoPtO$_6$. Circularly polarized x-rays with alternating magnetic fields of $H = \pm 8$ kOe were used. The XMCD lineshapes of La$_2$CoPtO$_6$ almost coincides with that of La$_2$CoIrO$_6$, which suggests almost identical local electronic structure of the Co$^{2+}$ ions. For comparison, the spectrum of CoO is also shown. For both samples, the lineshapes were almost identical to the spectrum of CoO, which suggests that HS Co$^{2+}$ was dominant, even at room temperature. (c) XMCD data for La$_2$CoIrO$_6$ and (d) XMCD data for La$_2$CoPtO$_6$. Circularly polarized x-rays with alternating magnetic fields of $H = \pm 8$ kOe were used. The XMCD lineshapes of La$_2$CoPtO$_6$ almost coincides with that of La$_2$CoIrO$_6$, which suggests almost identical local electronic structure of the Co$^{2+}$ ions.
reflecting a weaker local spin moment, which is consistent with the magnetization data shown in figure 2.

The lineshapes of the low-T XMCD spectra in figure 3(d) were similar to those shown in figure 3(c), despite the reduced amplitude. This suggests that the weak magnetism in La$_2$CoPtO$_6$ does not result from an evolution of the electronic structure; rather, the HS state dominates for both La$_2$CoIrO$_6$ and La$_2$CoPtO$_6$, but the spin orientations among different Co$^{2+}$ ions were less coherent for La$_2$CoPtO$_6$. Therefore, inter-site spin interactions, rather than competition between local many-body states, are significant in determining the magnetic properties of this system.

We obtained the orbital and spin moments in Co$^{2+}$ using the XMCD sum rules [16, 17] and the procedures described in [18–20]. The value of the orbital moment $m_{\text{orb}}$ was deduced directly from the sum rule, while that of the spin moment $m_{\text{spin}}$ was done by multiplying a theoretical correction factor of 1.1 for Co$^{2+}$ ([20]). In the procedures, the $m_{\text{orb}}$'s and $m_{\text{spin}}$'s are calculated from the $L_3$- and $L_2$-edge peak areas measured after compensating the saturation effect and subtracting the weak incoherent higher-energy backgrounds. This process minimizes the possible experimental artifact caused by the saturation of signals from the thick powder specimens. The measured $m_{\text{spin}}$ and $m_{\text{orb}}$ (and consequently, $m_{\text{tot}}$) may contain errors from several experimental and theoretical origins as shown in the table. The experimental origins include incomplete circular polarization of x-rays, magnetocrystalline anisotropy, or inaccuracy in determining the integrated intensity [19]. We estimate these could contribute the errors of up to ~10%. The theoretical origins are from uncertainty in determining the number of $d$ electrons and in determining the correction factor to obtain the $m_{\text{spin}}$'s. The number of $d$ electrons can differ by ~10% depending on charge transfer, and the correction factor can by 5–10% of the central values in the case of Co$^{2+}$ HS [20]. Therefore, we took the maximal value (20%) to estimate the total error to be up to ~30%.

The $m_{\text{orb}}$'s and $m_{\text{spin}}$'s at $T = 43$ K are listed in table 1, together with the sum ($m_{\text{tot}}$) and the ratio ($m_{\text{orb}}/m_{\text{spin}}$). Overall, the moments for La$_2$CoIrO$_6$ were small, which suggests very weak FM ordering, whereas those for La$_2$CoPtO$_6$ were appreciable. This contrast is consistent with that in the magnetization data (figure 2). The ratio $m_{\text{orb}}/m_{\text{spin}}$ highlights the significance of the orbital angular momentum. We found $m_{\text{orb}}/m_{\text{spin}} = 0.58$ for both systems, which is larger than, for example, that of Fe$^{2+}$ in Fe$_2$O$_4$ (0.18; [21]) and Mn$^{2+}$ in (Ga,Mn)As (~0.037; [22]). This clearly indicates a considerable unquenched orbital moment, leading to the possibility of a substantial distortion of the octahedral symmetry of the oxygen coordination [23].

It should be noted that even in La$_2$CoIrO$_6$, the measured $m_{\text{tot}}$ for Co$^{2+}$ 3d (~0.48 $\mu_B$) is much smaller than the nominal value for the spin moment in the HS Co$^{2+}$ (3 $\mu_B$). As discussed above, this may be the result of partially aligned Co spins due to non-collinear magnetism [5, 6] with the moderate magnetic fields ($H < 10$ kOe). The net magnetic moment in La$_2$CoIrO$_6$ measured by SQUID is approximately ~0.8 $\mu_B$ at $T = 43$ K (see figure 2(a)). According to Kolchinskaya et al [6], the 5d magnetic moment in the Ir$^{4+}$ ion is readily saturated to ~0.38 $\mu_B$ even with the moderate magnetic field. Provided that the total magnetic moment (including paramagnetic one) in Ir$^{4+}$ is mostly contributed by the 5d orbital state and the magnetism in La$_3^+$ or O$^{2-}$ ions is negligible, the AFM coupling [2, 5, 6] between the Co$^{2+}$ and Ir$^{4+}$ (pseudo)spins should result in a magnetic moment in Co$^{2+}$ of approximately $+1.2$ $\mu_B$/f.u. Therefore, the $m_{\text{tot}}$ for Co$^{2+}$ 3d measured by XMCD is only ~40% of the total magnetic moment in Co$^{2+}$. This implies that the magnetic contribution from Co $sp$ orbital states should be also substantial, as is observed in the Co K-edge XMCD measurement [6].

As with other double perovskites, spin–spin interactions between neighboring Co$^{2+}$ and $M^{4+}$ ($M = \text{Ir or } M = \text{Pt}$) can be described by a hybridization mechanism [4, 24], which dictates that orbital hybridization or virtual electron hopping between the two cations lowers the hybridized electron state so as to stabilize a given spin state. Figure 4(a) shows an energy level diagram for the orbital hybridization assuming FM coupling, and figure 4(b) shows a similar energy level diagram assuming AFM coupling. In the HS state of Co$^{2+}$ with an octahedral crystal field, two spin-down electrons occupy the $t_{2g}$ level below the Fermi energy, whereas five spin-up electrons occupy the $t_{2g}$ and $e_g$ levels far below the Fermi energy (not shown), resulting in a total $S = 3/2$ spin-up state. For Ir$^{4+}$, single electrons occupy the $j_{\text{eff}} = 1/2$ level beneath the Fermi energy, and the other four electrons occupy the $j_{\text{eff}} = 3/2$ states (not shown), resulting in a total $J_{\text{eff}} = 1/2$ (pseudo) spin-up state. In Pt$^{4+}$, two electrons occupy both $j_{\text{eff}} = 1/2$ levels, resulting in a $J_{\text{eff}} = 0$ state.

For FM coupling (see figure 4(a)), only the spin-down states are unoccupied in Co$^{2+}$, so hybridization can occur only for spin-down electronic states. For this reason, the $j_{\text{eff}} = 1/2$ state in Ir$^{4+}$ cannot hybridize with the Co $t_{2g}$ state, whereas the (pseudo) spin-down state of Pt$^{4+}$ can in the case of the FM coupling. Conversely, with AFM coupling (see figure 4(b)), only the spin-up states are unoccupied in Co$^{2+}$, so hybridization

| Compound       | $m_{\text{orb}}/\mu_B$ | $m_{\text{spin}}/\mu_B$ | $m_{\text{tot}}/\mu_B$ | $m_{\text{orb}}/m_{\text{spin}}$ |
|----------------|-------------------------|--------------------------|-------------------------|----------------------------------|
| La$_2$CoIrO$_6$| 0.18 ± 0.04              | 0.31 ± 0.09               | 0.48 ± 0.13             | -0.58                            |
| La$_2$CoPtO$_6$| 0.04 ± 0.04              | 0.06 ± 0.02               | 0.10 ± 0.06             | -0.58                            |
can occur for spin-up electronic states. Thus, both the Ir$^{4+}$ and Pt$^{4+}$ $j_{eff}$ states can hybridize with the Co $t_{2g}$ state in the case of the AFM coupling. Therefore, it follows that in La$_2$CoPtO$_6$, only AFM coupling is allowed to stabilize the ferromagnetic ordering, whereas in La$_2$CoIrO$_6$, both couplings are allowed with equal probability, so a net zero moment is expected.

This suggests that the Ir$^{4+}$ ions, which intervene in the network of Co$^{2+}$ ions, can induce FM order within the Co$^{2+}$ ion sublattice. According to the model described above, strong inter-site orbital hybridization is essential for stabilization of the FM ordering in the sublattice. Because the hybridization strength should depend on the dispersion and symmetry of the orbitals, mainly electrons occupying shallow levels will determine the magnetic coupling. It is well known that, although shallow, the $j_{eff}$ state is localized due to strong spin-orbit coupling. This will result in weak hybridization and consequently weak control over the spin orientations of nearby Co$^{2+}$ ions. This may explain the small magnetic moment of Co and the persistent increase with an increasing external magnetic field.

In conclusion, control over the magnetism of La$_2$CoMO$_6$ by replacing $M = $ Ir$^{4+}$ with $M = $ Pt$^{4+}$ was evidenced by the magnetization and XMCD measurements. This was explained in terms of orbital hybridization of the unoccupied minority-spin state in Co$^{2+}$ and the occupied $j_{eff}$ state in Ir$^{4+}$/Pt$^{4+}$. FM ordering in the Co$^{2+}$ sublattice in La$_2$CoPtO$_6$ was stabilized owing to the AFM-coupled Ir$^{4+}$ $j_{eff} = 1/2$ $\leftrightarrow$ Co $t_{2g}$ state, whereas such magnetic ordering was absent in La$_2$CoIrO$_6$ because of the absence of a preferential spin orientation in the hybridized state. The dominance of the Co$^{2+}$ HS state, even at 300 K, suggests that inter-site spin interactions are more important than many-body on-site interactions in determining the magnetic properties of La$_2$CoIrO$_6$.

Figure 4. Energy level diagrams of the hybridization mechanism in the double perovskites. Orbital hybridization between the HS Co$^{2+}$ ($d^{7}$) and Ir$^{4+}$($d^{5}$)Pt$^{4+}$($d^{5}$) (a) assuming ferromagnetic (FM) coupling and (b) assuming antiferromagnetic (AFM) coupling. For La$_2$CoIrO$_6$, the FM coupling is forbidden, while only the AFM coupling is allowed. AFM ordering between Co$^{2+}$ and Ir$^{4+}$ was responsible for the ferromagnetism. For La$_2$CoPtO$_6$, both the FM and AFM couplings are allowed, so the net orbital/spin moments of Co$^{2+}$ are expected to vanish.

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We refer to the references provided in the text. Here are some examples:

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