Spin and orbital magnetic moments in perpendicularly magnetized Ni$_{1-x}$Co$_{2+y}$O$_{4-z}$ epitaxial thin films: Effects of site-dependent cation valence states

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We carried out x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) spectroscopy and investigated cation valence states and spin and orbital magnetic moments in the inverse-spinel ferrimagnet Ni$_{1-x}$Co$_{2+y}$O$_{4-z}$ (NCO) epitaxial films with the perpendicular magnetic anisotropy. We show that the oxygen pressure P$_{O2}$ during the film growth by pulsed laser deposition influences not only the cation stoichiometry (site-occupation) but also the cation valence state. Our XAS results show that the Ni in the Oh-site is in the intermediate valence state between +2 and +3, Ni$^{(2+\delta)^+}$ ($0<\delta<1$), whose nominal valence state (the $\delta$ value) varies depending on P$_{O2}$. On the other hand, the Co in the octahedral (Oh) and tetrahedral (Td) sites respectively have the valence state close to +3 and +2. We also find that the XMCD signals originate mainly from the Td-site Co$^{2+}$ (Co$_{Td}$) and Oh-site Ni$^{(2+\delta)^+}$ (Ni$_{Oh}$), indicating that these cation valence states are the key in determining the magnetic and transport properties of NCO films. Interestingly, the valence state of Ni$^{(2+\delta)^+}$ that gives rise to the XMCD signal remains unchanged independent of P$_{O2}$. The electronic structure of Ni$^{(2+\delta)^+}$ that is responsible for the magnetic moment and electrical conduction differs from those of Ni$^{2+}$ and Ni$^{3+}$. In addition, the orbital magnetic moment originating from Co$_{Td}$ is as large as 0.14 $\mu_B$/Co$_{Td}$ and parallel to the magnetization while the Ni$_{Oh}$ orbital moment is as small as 0.07 $\mu_B$/Ni$_{Oh}$ and is rather isotropic. The Co$_{Td}$ therefore plays the key role in the perpendicular magnetic anisotropy of the films. Our results demonstrate the significance of the site-dependent cations valence states for the magnetic and transport properties of NiCo$_2$O$_4$ films.
I. Introduction

Transition metals in oxides can have various valence states through orbital hybridization with oxygen, impacting various functional properties. For ternary spinel oxides, transition metals occupying tetrahedral and octahedral sites can have different valence states, leading to a variety of transport and magnetic properties. Evaluating cation valence states in spinel oxides and delineating their influence on physical properties are therefore important.

The inverse spinel oxide NiCo$_2$O$_4$[1-5] in which Co is in both tetrahedral (T$_d$) and octahedral (O$_h$) sites while Ni is in only the O$_h$ site, has been shown to have a variety of its properties, such as above-room-temperature ferrimagnetism[3,5], metallic electrical conduction[6-8], half-metallic properties[6,7], perpendicular magnetic anisotropy[9,10], and electrochemical activities [11-14]. These findings have revealed the potential application of this oxide for spintronic and electrochemical devices. Therefore, delineating correlations between cation valence states and functional properties in NiCo$_2$O$_4$ is crucial. Recently it has been shown that transport and magnetic properties of epitaxial films of this oxide strongly depend on their growth conditions[6,15-18]. Our resonant x-ray diffraction measurements[19] for films grown by pulsed laser deposition have also revealed that cation distribution (T$_d$- and O$_h$-site occupation of Co and Ni) in NiCo$_2$O$_4$ films vary depending on oxygen partial pressures (P$_{O_2}$) during film growth. Given that Co and Ni could accommodate various valence states (+2 and +3, for example), growth conditions such as P$_{O_2}$ would influence not only compositions but also valence states of Co and Ni, affecting films’ properties. It is therefore interesting to see correlations between cation valence states and physical properties of NiCo$_2$O$_4$ films grown under various P$_{O_2}$s.

In this study, we carried out x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) spectroscopy and investigated valence states and spin and orbital magnetic moments of Co and Ni in Ni$_{1-x}$Co$_{2+y}$O$_{4-z}$ (NCO) epitaxial films grown under a P$_{O_2}$ of 30mTorr,
50mTorr, and 100mTorr by pulsed laser deposition. We found that not only the Co and Ni site-occupations (the Co and Ni compositions) but also their valence states in the films vary depending on the P_{O2}. The NCO depositions under lower P_{O2} introduce larger amounts of Co^{2+} and Ni^{2+} into films, influencing their transport and magnetic properties. Furthermore, analyzing XAS and XMCD data quantitatively by the sum rules [20-22], we discuss the origin of the perpendicular magnetic anisotropy in the NCO films.

II. Experimental details

30-nm-thick Ni_{1-x}Co_{2+y}O_{4-z} (NCO) epitaxial films with (001) orientation were fabricated on (100) MgAl_2O_4 substrates and under various oxygen pressures (P_{O2}s) by pulsed laser deposition. All films studied here is under the substrate-induced compressive strain (0.4%). Previously we showed [19] that when films were grown at a fixed substrate temperature (350 °C), the P_{O2} affected the cation distribution (or the cation composition) in the films, influencing transport and magnetic properties. Details of results of basic characterization for grown NCO films, such as X-ray diffraction and magnetization measurements were provided in our previous report [19]. Briefly, by analyzing x-ray diffraction intensities near cations’ absorption edges, the T_d- and O_h-site-occupation of Ni (the amounts of Ni occupying the tetrahedral and octahedral sites) were determined to be 0.17 and 0.86 for the P_{O2}=30mTorr film, 0.17 and 0.92 for the P_{O2}=50mTorr film, and 0.12 and 0.98 for the P_{O2}=100mTorr film. As shown in Fig. 1a, the T_d-site-occupation of Ni is almost constant and independent of P_{O2}. On the other hand, the O_h-site-occupation of Ni increases with increasing P_{O2}. In addition, the films grown under the larger P_{O2} have the larger saturated magnetizations and the lower electrical resistivity (Fig. 1b). The ferrimagnetic transition temperature of the films grown under the larger P_{O2} also becomes higher, and the P_{O2} = 100mTorr film becomes a ferrimagnet below 400 K [19].
We carried out XAS and XMCD spectroscopy and characterized the NCO films grown under $P_{O_2} = 30, 50, \text{ and } 100 \text{ mTorr}$. Measurements were carried out at the beamlines BL25SU in SPring-8[23,24] and BL-16A in Photon Factory. XAS and XMCD datasets presented in this paper are those obtained from measurements in SPring-8. We note that the dataset acquired from measurements at the two beamlines were essentially the same. The XAS and MCD spectra were recorded at room temperature and under a 1.9 Tesla magnetic field applied at various angles $\theta_H$ with respect to the films’ surface. The incident x-ray beam is $10^\circ$ off the magnetic field direction. The energy resolution in XAS and XMCD spectra is $E/\Delta E=3000$. The XAS spectra for each helicity of the incident beam ($\mu^+$ and $\mu^-$) were obtained in the total electron yield mode and by averaging spectra taken under magnetic fields in opposite directions.

![Figure 1: PO2 dependence of (a) the tetrahedral (Td) and octahedral (Oh) site-occupations of Ni and (b) saturated magnetization and electrical resistivity in NCO epitaxial films. All data in the figures were taken at room temperature. The data in (a) were adopted from Ref. 19. We note that the cation site-occupation (cation composition) in the NCO film is defined as $(y_{Co-Td}x_{Ni-Td})(y_{Co-Oh}x_{Ni-Oh})O_4$. The Td- and Oh-site-occupations of cations were determined by assuming that $y_{Co-Td} + x_{Ni-Td} = 1$ and $y_{Co-Oh} + x_{Ni-Oh} = 2$.](image-url)
III. Results and Discussion

Figures 2a and 2b show the averaged Co and Ni $L_{2,3}$-edge XAS spectra $1/2(\mu^+ + \mu^-)$ for NCO films grown under $P_{\text{O}_2} = 30, 50,$ and $100$ mTorr, revealing $P_{\text{O}_2}$-dependent changes in the valence states of Co and Ni in the films. The data were taken under a 1.9 Tesla magnetic field normal to the films’ surface (the $\theta_H=0^\circ$ configuration). The incident beam is $10^\circ$ off the magnetic field direction $\theta_H$. In Co

![Graphs showing XAS and XMCD spectra](image)

**Figure 2:** (a, b) Averaged XAS and (c, d) normalized XMCD spectra for NCO films grown under $P_{\text{O}_2} = 30, 50$ and $100$ mTorr. The spectra were in the energy region around (a,c) Co and (b,d) Ni $L_{2,3}$-edge absorptions. The measurements were carried out at room temperature and under a 1.9 Tesla magnetic field normal to the films’ surface (the $\theta_H=0^\circ$ configuration). The incident beam is $10^\circ$ off the magnetic field direction $\theta_H$. The insets in parts (a) and (b) show expanded views of the Co and Ni-$L_3$ edge absorption peaks.
$L_3$-edge XAS spectra (Fig. 2a), the pre-edge structure around 777.2 eV is pronounced with higher intensity, and the hump structure around 778.8 eV is slightly broader for films grown under lower $P_{O_2}$. On the other hand, the peak intensities at 780.2 eV are almost constant and independent of $P_{O_2}$. Based on reference spectra of Co oxides such as CoO and EuCoO$_3$[18,25,26], the pre-edge structure (around 777.2 eV) is characteristic for Co$^{2+}$ octahedrally coordinated by oxygen. The hump (around 778.8 eV) arises from both octahedrally and tetrahedrally coordinated Co$^{2+}$. On the other hand, the peak at 780.2 eV originates from the Co$^{3+}$ in either tetrahedral or octahedral oxygen coordination. Therefore, the observed $P_{O_2}$-dependent changes in Co $L_3$-edge XAS spectra indicates that for the film grown under $P_{O_2} = 100$ mTorr and having the cation site-occupation closer to the stoichiometric, the Td- and Oh-site Co (referred to as Co$_{Td}$ and Co$_{Oh}$, respectively) dominantly have the +2 and +3 valence states, respectively. We also point out that as revealed by our resonant x-ray diffraction measurements (Fig. 1a), the film grown under the lower $P_{O_2}$ has the larger site-occupation of Co$_{Oh}$ while the Co$_{Td}$ site-occupation remains almost unchanged against $P_{O_2}$. The additionally introduced Co$_{Oh}$, which substitutes the Oh-site Ni, in the films grown under the lower $P_{O_2}$ have the +2 valence states. We note that spectral shape around the Co $L_2$-edge absorption is known to be less dependent on the valence state (+2 or +3). Therefore, the Co $L_2$-edge XAS peak at 794.6 eV exhibit no obvious $P_{O_2}$ dependence.

The Ni $L_{2,3}$-edge absorption spectra in Figure 2b also depend on $P_{O_2}$. The peak positions of the Ni $L_3$-edge absorptions for the films grown under higher $P_{O_2}$ shift toward the higher-energy side. Concomitantly, the shoulder structures associated with the Ni $L_2$-edge absorptions (around 870.3 eV) are less pronounced for the larger-$P_{O_2}$ films. These observations indicate that Ni in the Oh-site is in the intermediate valence state between +2 and +3, Ni$^{(2+\delta)+}$ ($0<\delta<1$). We note that the $L_3$-edge peak position for the $P_{O_2} = 30$ mTorr film (853.1 eV) is almost identical to the $L_3$-edge peak position characteristic of the Ni$^{2+}$ octahedrally coordinated by oxygen (~853 eV) [18,27,28]. In addition, the Oh-site-occupation of Ni in the film decreases with decreasing $P_{O_2}$ [19]. The $P_{O_2}$-dependent shifts of the Ni
$L_3$-edge absorption peaks, therefore, indicate that growing films under lower $P_{O_2}$ leads not only to the decrease in the $O_h$-site-occupation of Ni but also to the lowering of its valence state. The Ni valence state for the $P_{O_2} = 30$ mTorr film is closer to +2. By reproducing the experimentally observed Ni XAS spectra based on reference spectra of Ni$^{2+}$ and Ni$^{3+}$ $L$-edge absorptions, the Ni nominal valence state for the $P_{O_2} = 100$ mTorr film is estimated to be about +2.5 ($\delta \sim 0.5$) [29]. The observed changes in the valence states of Co and Ni imply that the oxygen contents in NCO films also vary depending on $P_{O_2}$ and that larger amounts of oxygen vacancies are accommodated in films grown under lower $P_{O_2}$ [29].

The $P_{O_2}$-dependent changes in the Co and Ni valence states impact on magnetic properties as revealed by XMCD spectroscopy. Figures 2c and 2d respectively show the Co and Ni $L_{2,3}$-edge XMCD spectra for the $P_{O_2} = 30, 50$, and 100 mTorr films. The XMCD signals ($\Delta \mu = \mu^+ - \mu^-$) are observed in both Co and Ni absorption edges for all the films. While the signal intensities depend on $P_{O_2}$, the whole spectral shapes and the peak positions remain almost unchanged independent of $P_{O_2}$. Both Co and Ni XMCD peaks for the films grown under larger $P_{O_2}$ have higher intensities, indicating that both spin magnetic moments of Co and Ni are larger for films having the larger magnetization.

Interestingly, the Co $L_3$-edge XMCD signals are enhanced at 779 eV where the x-ray absorptions of the $T_d$- and $O_h$-site Co$^{2+}$ occur, and their magnitudes become larger for the films grown under the larger $P_{O_2}$ whose $O_h$-site-occupation of Co$^{2+}$ is smaller. In addition, the $O_h$-site Co$^{3+}$ should be in the low spin state with $S = 0$ [1,4,18], and no contribution of Co$_{Oh}$ to the XMCD signal is expected. Therefore, the observed $P_{O_2}$ dependence of the Co XMCD signal implies that the spin magnetic moments in the $T_d$-site Co$^{2+}$ ($S = 3/2$) dominantly contribute to the signal. The Ni $L_3$-edge XMCD signal in Fig. 2d also becomes larger for the films grown under the larger $P_{O_2}$ and having the $O_h$-site Ni with the higher intermediate valence state. While the observed spectral shape of the Ni XMCD signals resembles that characteristic of octahedrally coordinated Ni$^{2+}$ [30], it is unlikely that the Ni$^{2+}$ in the $O_h$-site, which has the $S = 1$ configuration, give rise to XMCD signal. The $O_h$-site-
occupations of Ni$^{2+}$ is larger for the films grown under the lower $P_{O_2}$ while their Ni XMCD signals are largely suppressed (Fig. 2d). We also note that the energy positions of Ni XMCD signals are constant independent of $P_{O_2}$, which is in contrast to the $P_{O_2}$-dependent variations of the nominal valence of Ni (Figure 2b). These observations indicate that the Ni having the intermediate valence state, Ni$^{(2+\delta)^+}$ is the key for the spin magnetic moment. The electronic structure of Ni$^{(2+\delta)^+}$ that gives rise to the XMCD signal differs from those of Ni$^{2+}$ and N$^{3+}$.

Our XAS and XMCD results highlight the significance of the $T_d$-site Co (Co$_{T_d}$) and $O_h$-site Ni (Ni$_{O_h}$) as the keys that determine the magnetic and transport properties of NCO films. Recent first-principles calculations showed that the density of states at the Fermi level in stoichiometric NCO consists of spin-down electrons of the Ni$_{O_h}$, leading to the half-metallic electronic structure [6,7]. Importantly, when the $O_h$-site Ni has the intermediate valence state (higher than +2), its $e_g$ orbitals are partially unoccupied, and conduction carriers are provided. Given the half-metallic electronic structure in NCO, the delocalization of the conduction carriers should preferably align the spin magnetic moments in each $O_h$ and $T_d$ sub-lattice. It is worth pointing out that reducing the Ni site-occupation and lowering its valence state results in localization of the conduction carriers, and thus the spin magnetic moments in the films with lowered electrical conduction are more difficult to be aligned. Therefore, the films grown under the larger $P_{O_2}$ have the lower electrical resistivity and the larger magnetization (Fig. 1).

We also note that the signs of the Co and Ni XMCD signals are opposite each other, which is further confirmed from the magnetic field dependences of Co and Ni $L_3$-edge XMCD signals in Figure 3. For all films, the Co and Ni signals in the positive magnetic field regions are negative and positive, respectively, indicating that the spin magnetic moments of the Co$_{T_d}$ and Ni$_{O_h}$ align in the anti-parallel manner. The hysteresis behavior of the signals against the magnetic field sweep direction becomes prominent for the films grown under the larger $P_{O_2}$, and the remnant values of both Co and
Ni signals at zero magnetic field also become larger. These observations are in close agreement with the fact that the films grown under the larger P\textsubscript{O2} have the larger magnetization and the higher ferrimagnetic transition temperature [19].

We further evaluate spin and orbital magnetic moments originating from the Ni\textsubscript{Oh} and Co\textsubscript{Td} quantitatively and investigate how these cations contribute to the orbital magnetic moments that determine the perpendicular magnetic anisotropy in the films. Figure 4 shows the Co and Ni L\textsubscript{2,3}-edge XMCD spectra and their integrated ones obtained with the $\theta_H=0^\circ$, $40^\circ$, and $80^\circ$ configurations. The inset of the figure schematically shows the measurement configuration including the magnetic field angle $\theta_H$. The Co L\textsubscript{3}-edge XMCD peak intensities and the integrated XMCD signals decrease with increasing $\theta_H$. In contrast, while the Ni XMCD signals and their integrated intensities slightly vary against the change in $\theta_H$, no clear relationships between the signal variations and $\theta_H$ are seen. Given that the value obtained by integrating the $L_2$ and $L_3$ XMCD peaks is proportional to the orbital magnetic moment according to the sum rules [20-22], the $\theta_H$ dependence observed in the Co and Ni XMCD signals implies that the orbital magnetic moment of Co is anisotropic whereas that of Ni is rather

Figure 3: Magnetic field dependence of (a) Co L\textsubscript{3}- and (b) Ni L\textsubscript{3}-XMCD peak intensity for NCO films grown under P\textsubscript{O2} = 30, 50 and 100mTorr. The data were collected in the $\theta_H=0^\circ$ configuration and with the incident x-ray energy fixed to be 779.0eV for the Co L\textsubscript{3}-XMCD signal and 853.5eV for the Ni signal.
symmetric, indicating that the Co plays the dominant role in determining the magnetic anisotropy in NCO.

To quantitatively evaluate orbital and spin magnetic moments, we applied the sum rules to the XAS and XMCD spectra obtained at various $\theta_H$ and calculated the moments. We note that the Co XMCD signals mainly originate from the Co$_{Td}$ dominantly having the +2 valence state while none of the Co$_{Oh}$ contribute to the magnetic moment. The number of electrons in 3d orbitals, $n_{3d}$, for Co is thus assumed to be 7 (corresponding to Co$^{2+}$). Taking into account that the energy position of the Ni $L_3$-edge XMCD peak is close to that of the Ni $L_3$-edge absorption peak for the $P_{O2}$=100mTorr film as shown in the inset of Figure 2b, we assume that the Ni valence state that dominantly contributes to the XMCD signal is +2.5 and the $n_{3d}$ for Ni is 7.5. Figure 5 shows the $\theta_H$ dependence of the spin and orbital magnetic moments of Co$_{Td}$ and Ni$_{Oh}$ in the NCO films grown under $P_{O2}$ = 30, 50, and

![Figure 4](image)

Figure 4: (a) Co $L_{2,3}$- and (b) Ni $L_{2,3}$-XMCD spectra and their integrated intensity for the $P_{O2}$ = 100mTorr film. The spectra were measured with the magnetic field angle $\theta_H$ of 0, 40, and 80 degrees. The measurement configuration is shown in the inset of the figure.
100mTorr. As expected from the $P_{O_2}$-dependence of the XMCD signals (Figs. 2 and 3), the spin magnetic moments of both Co$_{Td}$ and Ni$_{Oh}$ in the films grown under the larger $P_{O_2}$ become larger.

Both Co$_{Td}$ and Ni$_{Oh}$ spin magnetic moments are $\theta_H$-dependent with their maximums at $\theta_H = 0^\circ$. In addition, the orbital magnetic moments of Co$_{Td}$ and Ni$_{Oh}$ are $P_{O_2}$-dependent, and their trends follow those of the $P_{O_2}$-dependence of the spin magnetic moments. For both Co$_{Td}$ and Ni$_{Oh}$, the orbital and spin moments have the same sign. Thus, the orbital and spin moments are parallel aligned in each T$_d$ and O$_h$ sub-lattice. Importantly, the Co$_{Td}$ orbital magnetic moment is $\theta_H$-dependent and is maximized at $\theta_H = 0^\circ$ while the Ni$_{Oh}$ orbital magnetic moment is almost $\theta_H$-independent. For the $P_{O_2} = 100$ mTorr film whose perpendicular magnetic anisotropy energy is largest among the films investigated in this study [19], the Co$_{Td}$ orbital moment is as large as $0.14\mu_B$/Co$_{Td}$ while the Ni$_{Oh}$ one is as small as $0.07\mu_B$, indicating that the Co$_{Td}$ play the dominant role in determining the perpendicular anisotropy and

Figure 5: Magnetic field angle dependence of spin and orbital magnetic moments ($m_{spin}$ and $m_{orb}$) originating from the T$_d$-site Co (Co$_{Td}$) and the O$_h$-site Ni (Ni$_{Oh}$) in NCO films grown under $P_{O_2}$ = (a) 100, (b) 50 and (c) 30 mTorr. The filled squares and circles are for the $m_{spin}$ from the Co$_{Td}$ and Ni$_{Oh}$, respectively. The open squares and circles are for the $m_{orb}$ from the Co$_{Td}$ and Ni$_{Oh}$, respectively. Errors in the spin and orbital magnetic moments of Ni$_{Oh}$ are estimated from the possible variation of $n_{3d}$, i.e. $7 < n_{3d} < 8$. In (c), the errors in the Ni moments are not included in the figure because they are relatively small (smaller than the marker sizes).
that the contribution of the Ni\textsubscript{Oh} to the magnetic anisotropy is less dominant. This observation is in agreement with the recent theoretical investigation [10] showing that the out-of-plane orbital magnetic moment originates from the $d_{x^2-y^2}$ orbital in the T\textsubscript{d}-site Co, leading to the perpendicular magnetic anisotropy in NCO. Our results indicate the significance of the site-dependent cation valence states for the magnetic and transport properties of NiCo\textsubscript{2}O\textsubscript{4} films. The Co\textsubscript{Td} determines the magnetic anisotropy while it provides almost no density of states at the Fermi level and less influence the magnetization and electrical conduction of the NCO films. On the other hand, the Ni\textsubscript{Oh} has little contribution to the magnetic anisotropy, while it closely ties with the electronic structure around $E_F$, strongly influencing the magnetization and the electrical conduction. These correlations between the site-dependent cation states and the functional properties explain why NiCo\textsubscript{2}O\textsubscript{4} has the half-metallic band structure and the perpendicular magnetic anisotropy simultaneously.

IV. Summary

We evaluated the cation valence states and spin and orbital magnetic moments in the ferrimagnetic Ni\textsubscript{1-x}Co\textsubscript{2+y}O\textsubscript{4-z} (NCO) epitaxial films with the perpendicular magnetic anisotropy. We found that the oxygen pressure $P_{O2}$ during the film growth by pulsed laser deposition influences not only the cation stoichiometry but also the cation valence states. For the film having a cation site-occupation close to the stoichiometric one, the Oh-site Ni is in the intermediate valence state while the Td-site and Oh-site Co dominantly have the +2 and +3 valence states, respectively. On the other hand, for the films grown under the lower $P_{O2}$ the Oh-site-occupation of Ni is reduced, and its valence state is also lowered closer to +2. The Co additionally accommodated in the Oh-site is in the +2 valence state while the valence state of the Td-site Co remains unchanged. The spin magnetic moments in the NCO films dominantly originate from the Td-site Co (Co\textsubscript{Td}) and Oh-site Ni (Ni\textsubscript{Oh}). Both Co\textsubscript{Td} and
Ni$_{Oh}$ spin moments become larger when the cation site-occupation is closer to the stoichiometric one. These observations indicate that the intermediate valence state of the Ni$_{Oh}$ is responsible for the delocalization of conduction carriers and plays the key role in stabilizing the electrical conduction and the ferrimagnetic moment. We also show that the orbital magnetic moment originating from the Co$_{Td}$ is as large as 0.14 $\mu_B$/Co$_{Td}$ and is anisotropic, parallel to the out-of-plane direction. On the other hand, the Ni$_{Oh}$ orbital moment is as small as ~0.07 $\mu_B$/Ni$_{Oh}$ and is rather isotropic. The Co$_{Td}$ therefore plays the key role in the perpendicular magnetic anisotropy in the films. Our results demonstrate the significance of the site-dependent cation valence states for the magnetic and transport properties of NiCo$_2$O$_4$ films.

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