A model for electronic phase transitions of $CoFe_2O_4$ and $NiCo_2O_4$ thin film surfaces: Temperature dependent X-ray photoemission studies of $CoFe_2O_4$ and $NiCo_2O_4$ thin films

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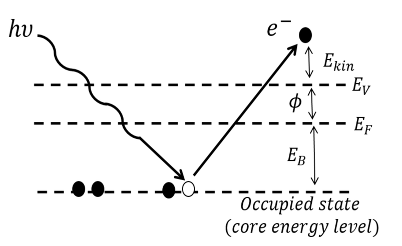
Abstract

We observed large binding energy shifts of the Co and Fe $2p_{3/2}$ core levels in X-ray photoemission spectroscopy (XPS) of $CoFe_2O_4$ thin films at room temperature due to large photovoltaic surface charging. This shows that the films can be dielectric. Temperature dependent XPS of the $CoFe_2O_4$ thin film showed that core level binding energies (BE) decreased with increasing temperature (T), but above 182 ^{0}C, during heating of the sample, shifts in the core level binding energies were not observed. This suggested an evolution of the film to more metallic condition after annealing to 182 ^{0}C. The dielectric nature of the film was restored only when the film was annealed in sufficient oxygen, indicating that the oxygen vacancies play a role in the transition of the film from dielectric (or insulating) to conducting. In contrast, similar studies on $NiCo_2O_4$ thin films showed that heating of $NiCo_2O_4$, a conductor, could make $NiCo_2O_4$ insulating, and the original more metallic character of the $NiCo_2O_4$ film could be restored only when the sample was annealed in sufficient oxygen. A model which could describe the phase transitions in both $CoFe_2O_4$ and $NiCo_2O_4$ thin films is thus proposed:

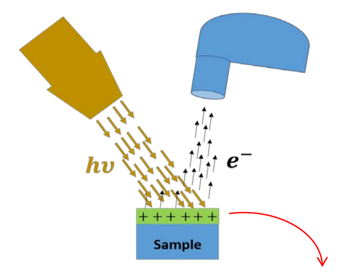
$|\Delta BE| = A\ exp\left[\frac{-E_a}{R\ |\Delta T|}\right]$

Introduction and motivation



$E_B = h\nu - E_{kin} - \phi$

Fig. 1. Binding energy in photoemission without surface charging. The sample is a conductor.



$E_B = h\nu - E_{kin} - \phi + eV$

Fig. 2. Binding energy in photoemission with (photovoltaic) surface charging . The sample is an insulator (or dielectric).

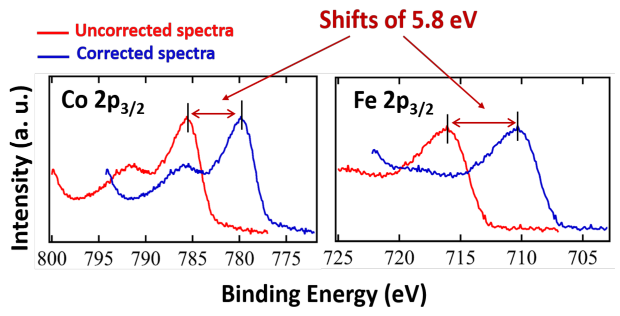


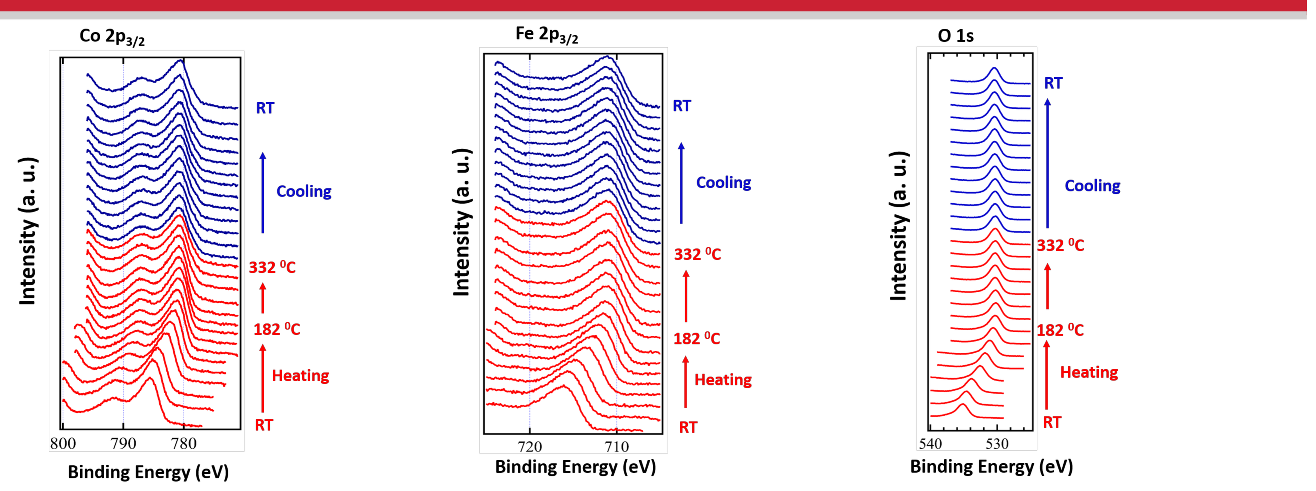
Fig. 3. Observation of binding energy shifts in core levels of Co and Fe in $CoFe_2O_4$ thin films in XPS measurement due to photovoltaic surface charging [1]. The prepared $CoFe_2O_4$ thin film is therefore an insulator.

Observation of photovoltaic surface charging in $CoFe_2O_4$ thin films leads to following questions:

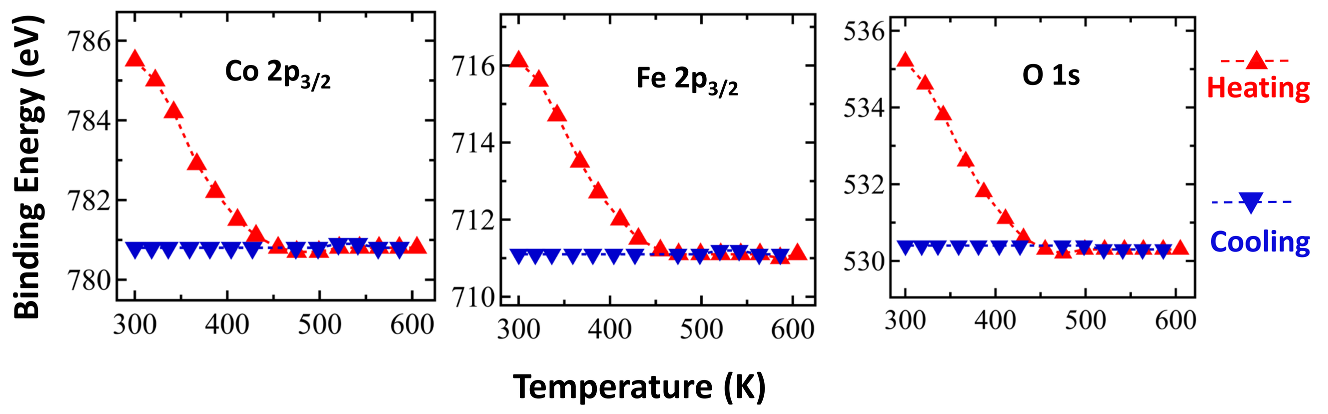
- What happens to surface charging (binding energy shifts) if temperature is changed?
- Do oxygen vacancies play any role in surface charging of complex oxides?
- What if similar studies are carried out for conducting oxide thin films?

From the device perspective, understanding of surface of the thin films is always important. Answers to above questions are therefore crucial for both fundamental science and device applications.

Temperature dependent X-ray photoemission of $CoFe_2O_4$ thin films



- The peak positions of the XPS spectra represent binding energies of the corresponding core energy levels of the elements.

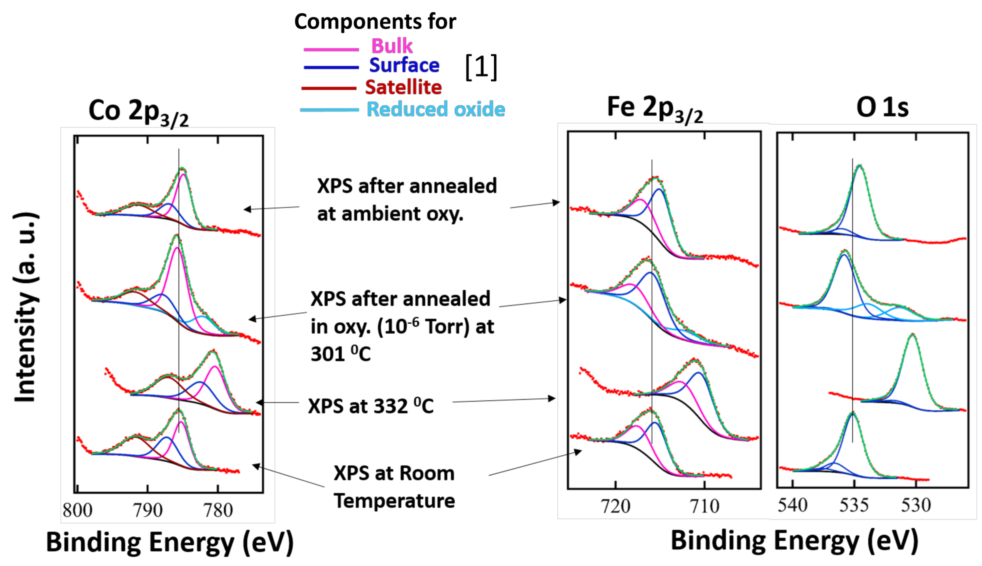


- $CoFe_2O_4$ thin film is an insulator [2, 3], the binding energies of the core levels therefore changed during heating of the sample.
- Core level binding energies ceased changing after reaching 182 ^{0}C, which means that the sample became conducting after 182 ^{0}C.

What's going on?

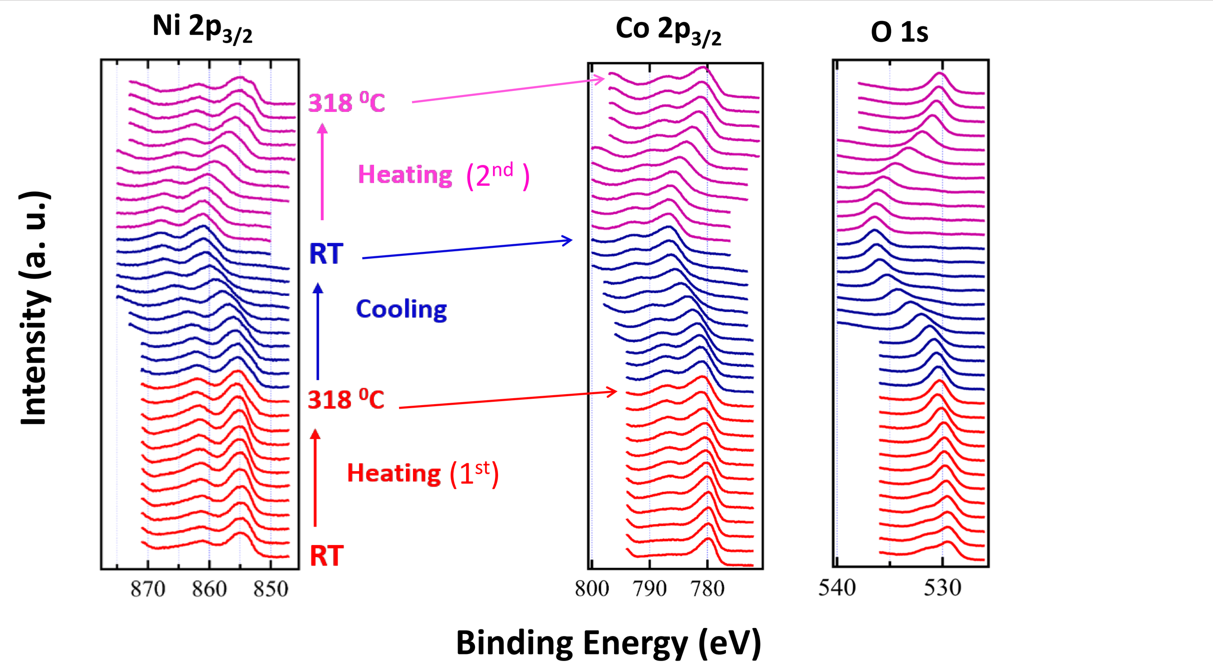
- Oxygen vacancies created at higher temperature might be playing a role.

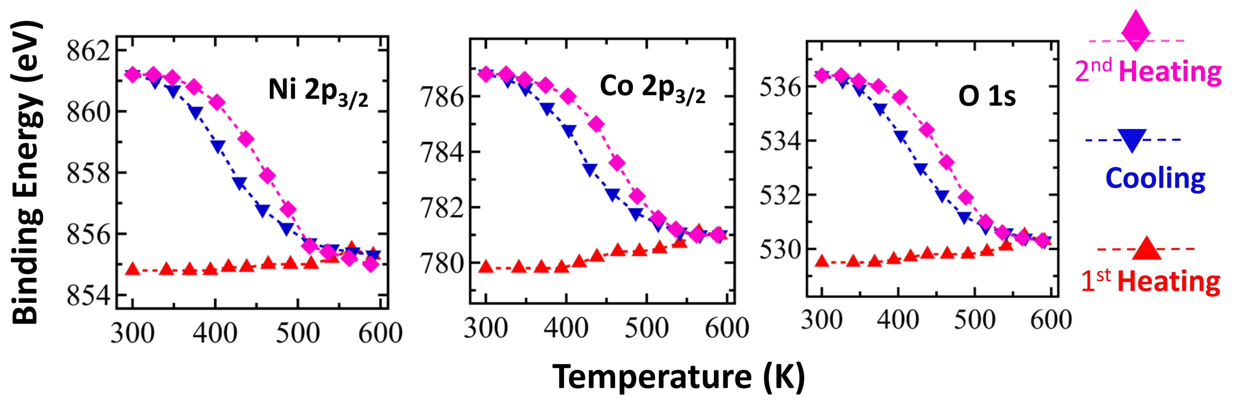
Oxygen vacancies check: XPS after annealing in oxygen



- XPS spectra after annealing of sample in sufficient oxygen showed increases in core level binding energies (insulating character again) indicating that number of oxygen vacancies can change electronic properties of $CoFe_2O_4$ thin films.

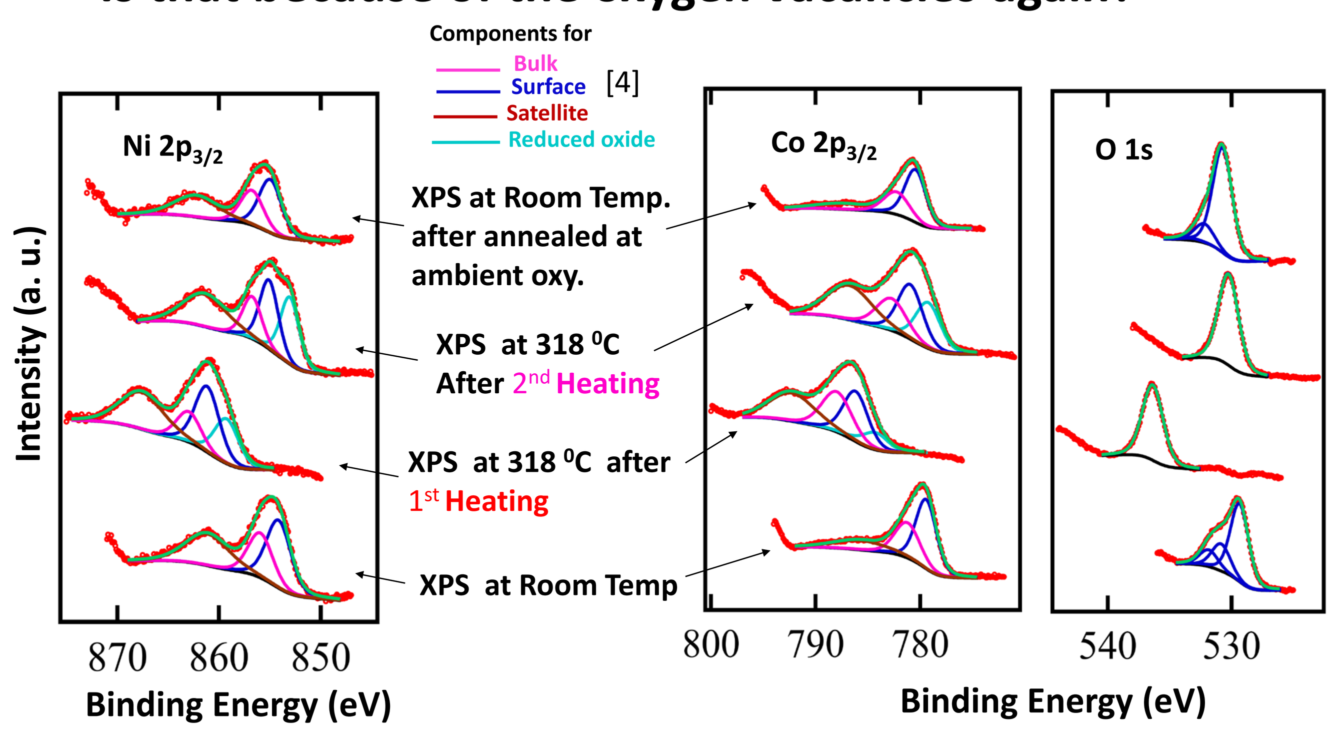
Temperature dependent X-ray photoemission of $NiCo_2O_4$ thin films





- Since $NiCo_2O_4$ thin film is conducting [3], it did not show appreciable binding energy change with temperature during the first annealing cycle.
- $NiCo_2O_4$ thin film showed reversible core level binding energy changes during cooling and the second heating cycle, indicating that the film became dielectric (or insulating) after reaching 318 ^{0}C during the first annealing treatment.

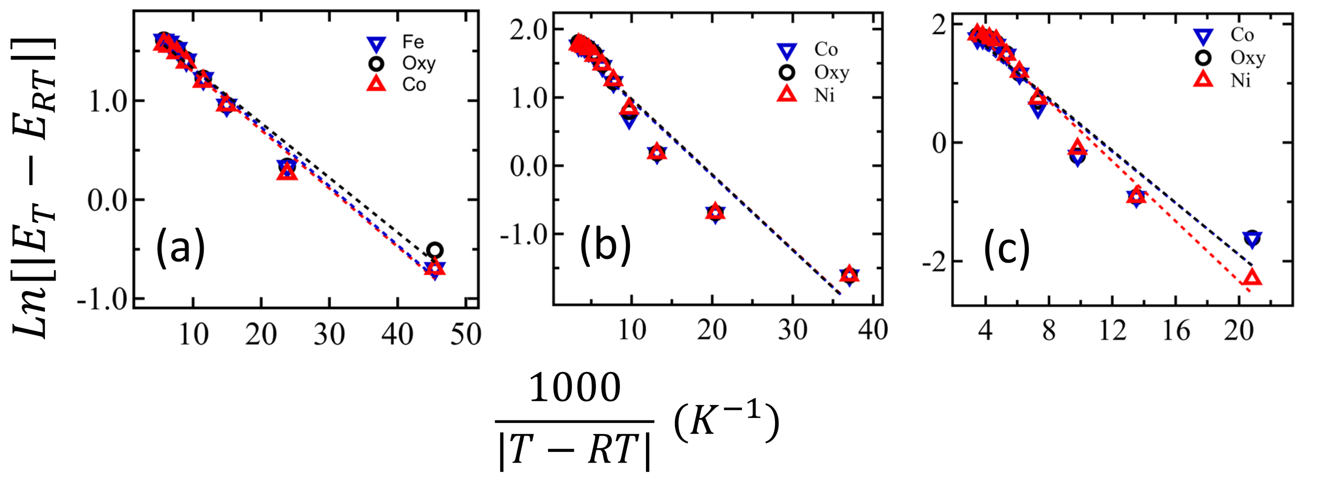
Is that because of the oxygen vacancies again?



- XPS after annealing of sample in sufficient oxygen showed that spectra shapes and original binding energies could be restored at room temperature, showing that original electronic properties could be restored if annealed in sufficient oxygen.
- Number of oxygen vacancies thus is playing a role in electronic phase transition of $CoFe_2O_4$ and $NiCo_2O_4$ thin films.
- The temperature dependent XPS showed that insulating $CoFe_2O_4$ thin films can become conducting and conducting $NiCo_2O_4$ thin film can become insulating if the films are annealed at certain higher temperature. Such phase transition can be reversed if the number of oxygen vacancies at the surface is changed.

A model for phase transitions of $CoFe_2O_4$ and $NiCo_2O_4$ thin films

- The figures below show plots for logarithmic of $|E_T - E_{RT}|$ vs $\frac{1}{|T-RT|}$ during the electronic phase transition of (a) $CoFe_2O_4$ thin film during heating, (b) $NiCo_2O_4$ thin film during cooling from 318 ^{0}C, and (c) $NiCo_2O_4$ thin film during heating again. E_T (E_{RT}) is the core level binding energy at certain T (RT, room temperature).



- Coefficients for the fitted lines as shown in above figures have values higher than 0.9 (see table 1), and some of the values are closer to one, suggesting that binding energies of core levels during the electronic phase transition of both thin films should follow a new Arrhenius type functional model:

$|\Delta BE| = A\ exp\left[\frac{-E_a}{R\ |\Delta T|}\right]$

Where $\Delta BE = E_T - E_{RT}$ and $\Delta T = T - RT$

Table 1. Activation energies (E_a) and coefficients of determination (r^2 values) using the best fitted lines. A perfect functional model has r^2 value of 1.

Core energy level of	Activation energy E_a (J/mol)	Coefficient of determination (r^2 value) for the fitted lines
For $CoFe_2O_4$ (During heating)		
Co	489.2	0.98
Fe	494.5	0.99
Oxygen	458.7	0.98
For $NiCo_2O_4$ (During cooling)		
Ni	913.5	0.94
Co	909.3	0.94
Oxygen	919.7	0.94
For $NiCo_2O_4$ (During 2nd heating)		
Ni	2103.0	0.98
Co	1807.7	0.93
Oxygen	1830.2	0.94

Conclusions and outlooks

- Oxygen vacancies play a role in temperature dependent photovoltaic surface changing and electronic phase transitions of $CoFe_2O_4$ and $NiCo_2O_4$ thin films.
- Annealing in vacuum can make a dielectric $CoFe_2O_4$ thin films a conducting and a conducting $NiCo_2O_4$ thin film a dielectric. During the phase transition, the core level binding energies measured by XPS technique follow a model as a function of temperature: $|\Delta BE| = A\ exp\left[\frac{-E_a}{R\ |\Delta T|}\right]$.
- Some of the directions for the future studies are to carry out similar studies on $NiFe_2O_4$ (structurally similar to $CoFe_2O_4$ and $NiCo_2O_4$) or/and some iridates (oxides containing iridium which are structurally different from $CoFe_2O_4$ and $NiCo_2O_4$) to see if the studies can give us similar results and justify the proposed model.

Acknowledgements

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