

Verwey transition in Fe_3O_4 thin films: Influence of oxygen stoichiometry and substrate-induced microstructure

Physical Review B 90, 125142 (2014)

Xiaozhe Zhang
20150403

Verwey transition

Charge ordering (CO) is a phase transition occurring mostly in strongly correlated materials such as transition metal oxides or organic conductors. Due to the strong interaction between electrons, charges are **localized on different sites** leading to a disproportionation and an ordered superlattice.

This long range order phenomena was first discovered in magnetite (Fe_3O_4) by Verwey in 1939. He observed an increase of the electrical resistivity by two orders of magnitude at $T_{\text{CO}}=120\text{K}$, suggesting a phase transition which is now well known as the **Verwey transition**.

Preparation of Fe_3O_4 thin film

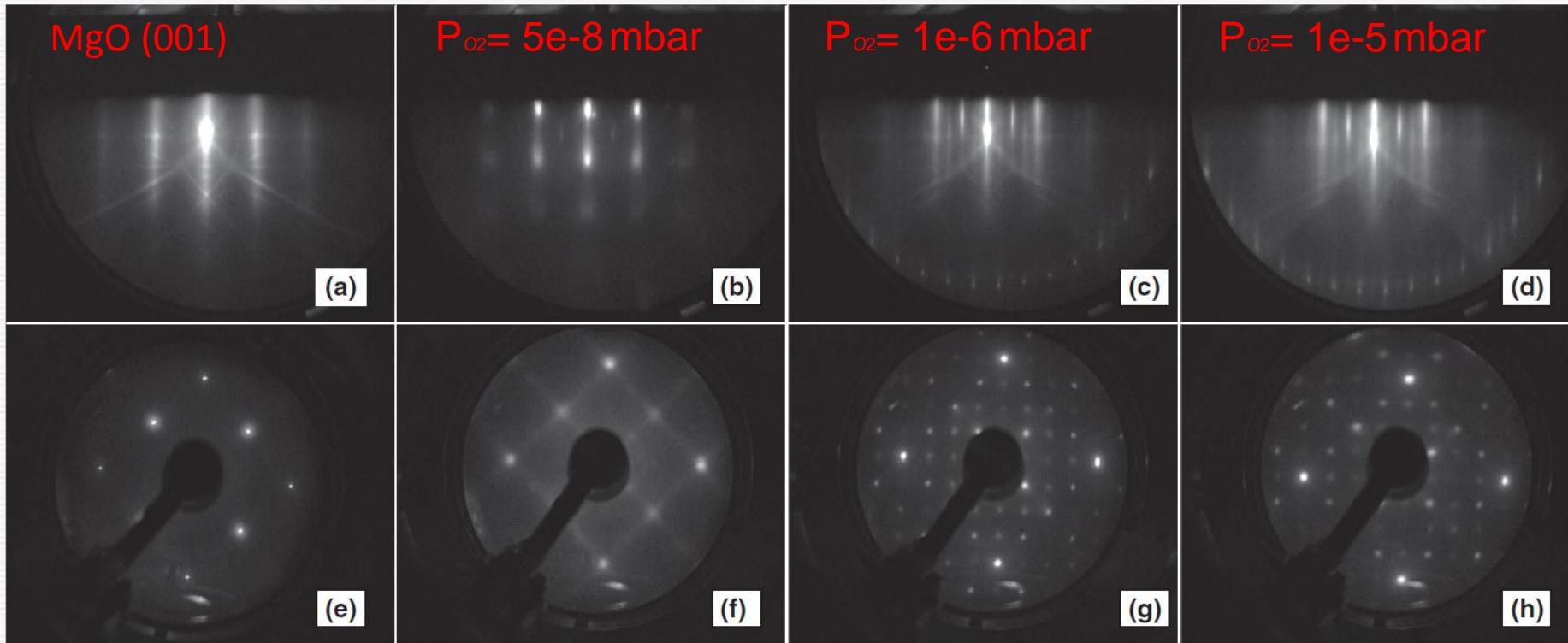
- ❖ A series of samples with a thickness of 40 nm
- ❖ The Fe flux is set at 1 Å/min
- ❖ Substrate temperature at 250 C
- ❖ Oxygen pressure varied from $5\text{e}-8$ to $1.0\text{e}-5$ mbar

Molecular beam epitaxy(MBE)

High purity Fe target, evaporated from Radak cell at 1250 C

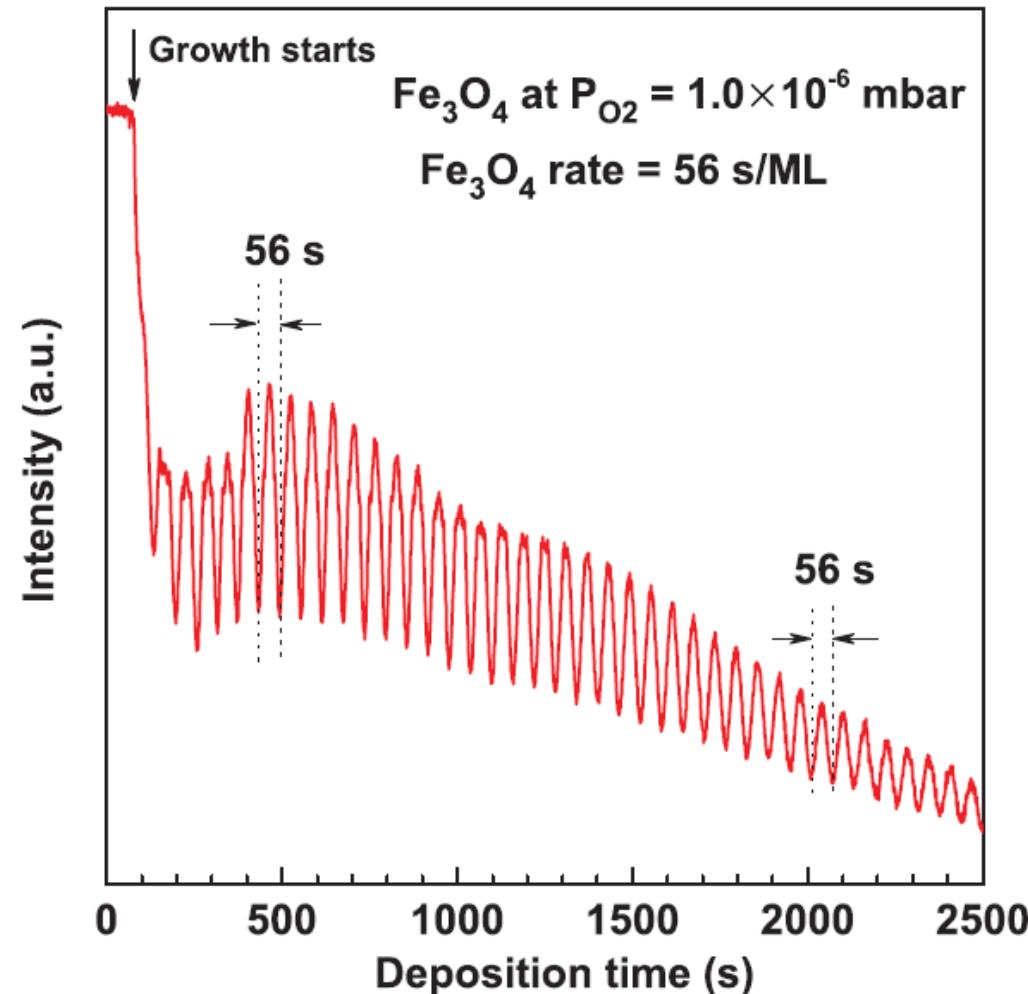
Substrates MgO (001), SrTiO₃ (001) (STO), and MgAl₂O₄ (001) (MAO)

RHEED and LEED study of MgO substrate and Fe₃O₄ thin film



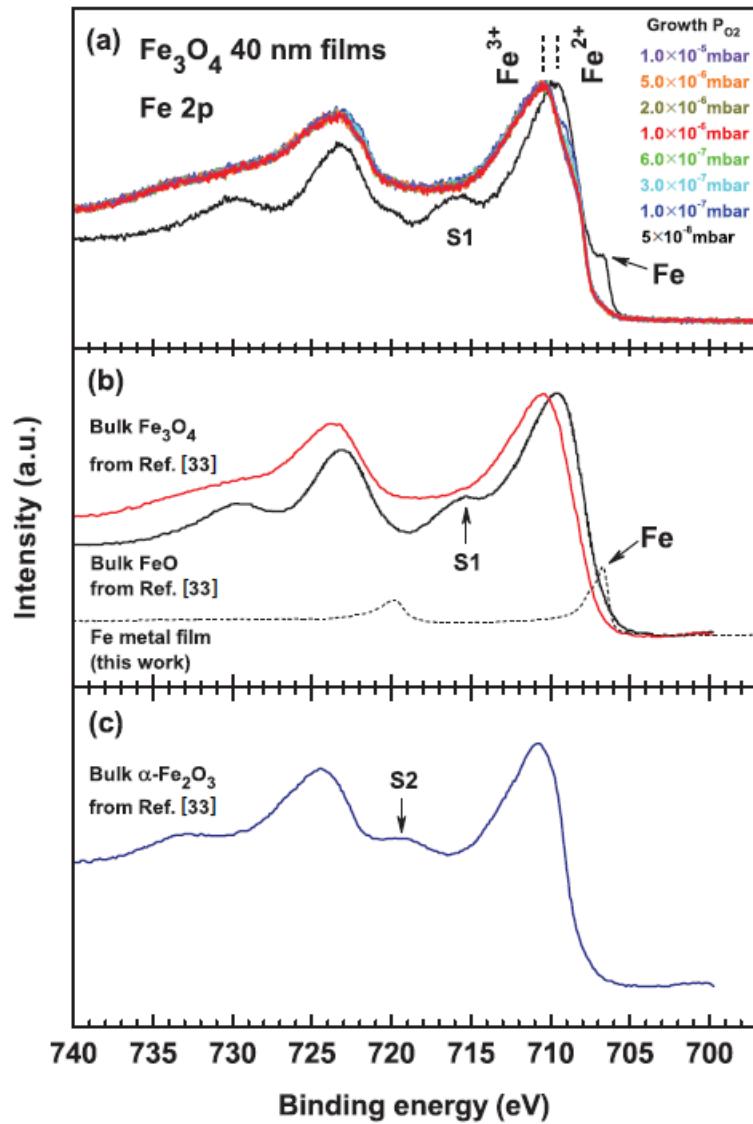
40 nm Fe₃O₄ films grown at Rate_{Fe} = 1 Å/min, T_{substrate} = 250 C

HEED Intensity Oscillations



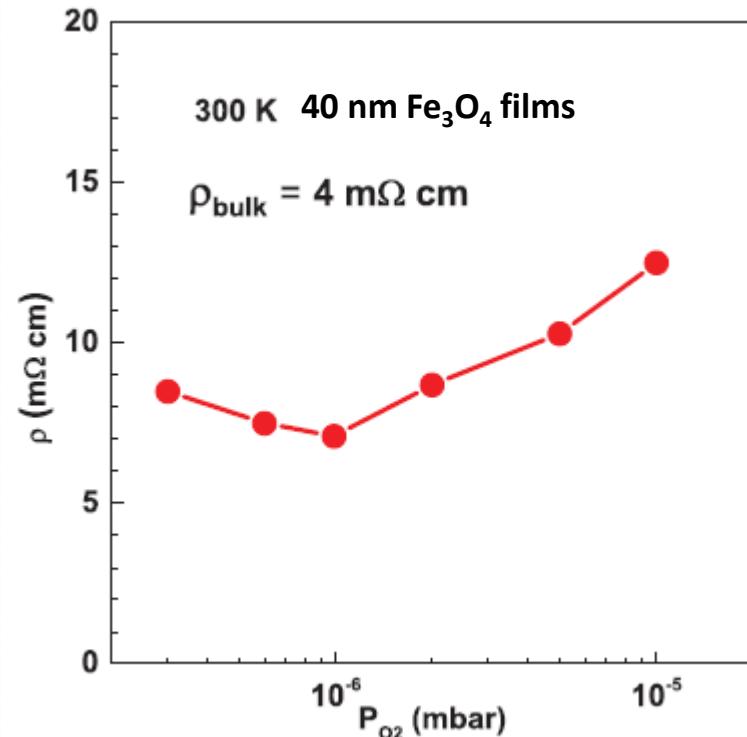
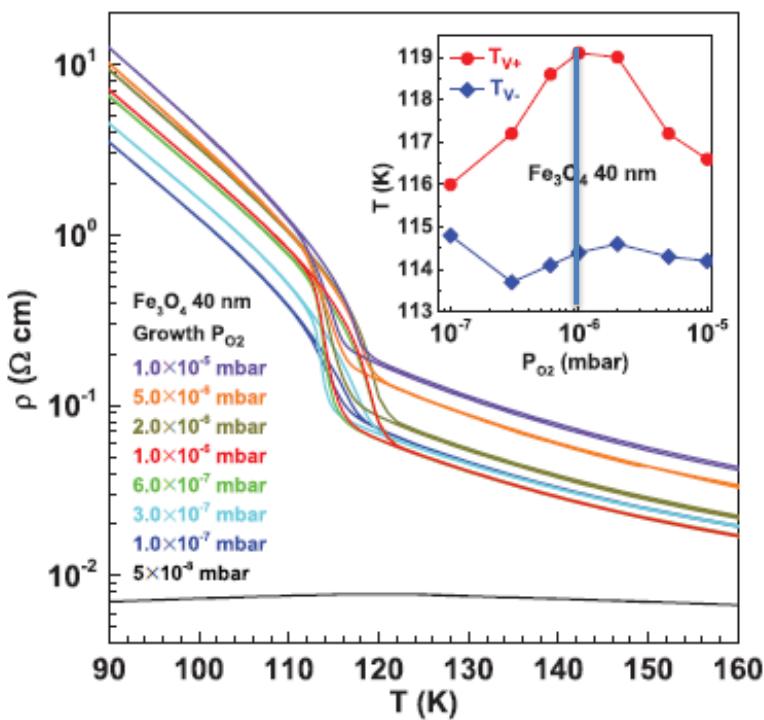
$\text{Fe}_3\text{O}_4/\text{MgO}$ 1 Å/min 1.0×10^{-6} mbar 250 C

XPS study of the prepared samples



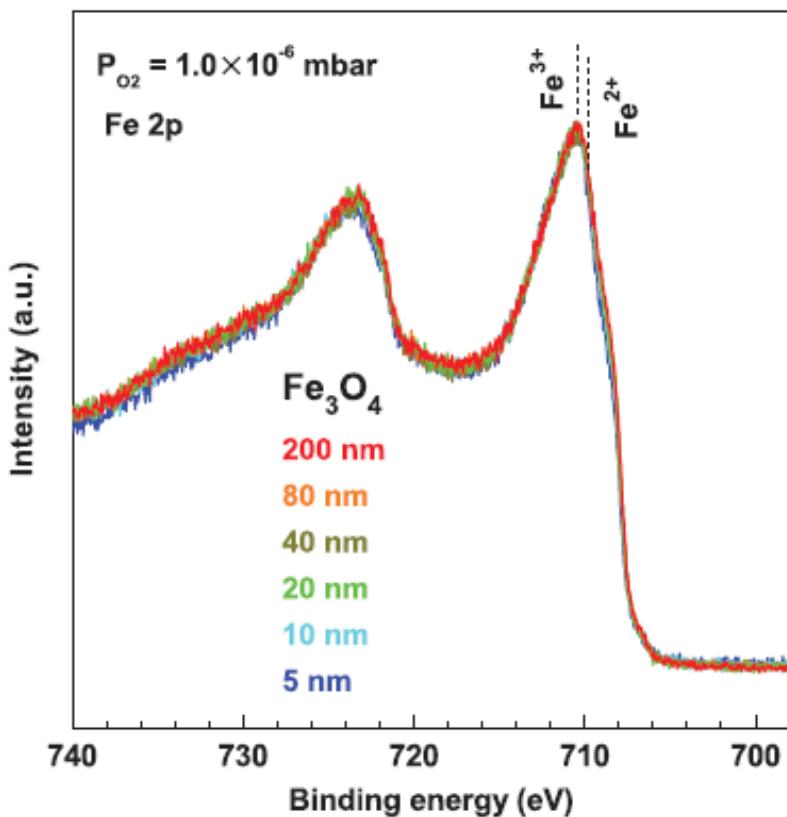
- XPS Fe 2p core-level spectra
- (a) 40 nm epitaxial Fe_3O_4 / MgO (001)
oxygen pressure: $5.0\text{e-}8$ to $1.0\text{e-}5$ mbar
 - (b) bulk Fe_3O_4 and bulk FeO from Ref. [33]
and Fe metal film
 - (c) bulk $\alpha\text{-Fe}_2\text{O}_3$ from [33]

Relationship of resistivity and oxygen partial pressures

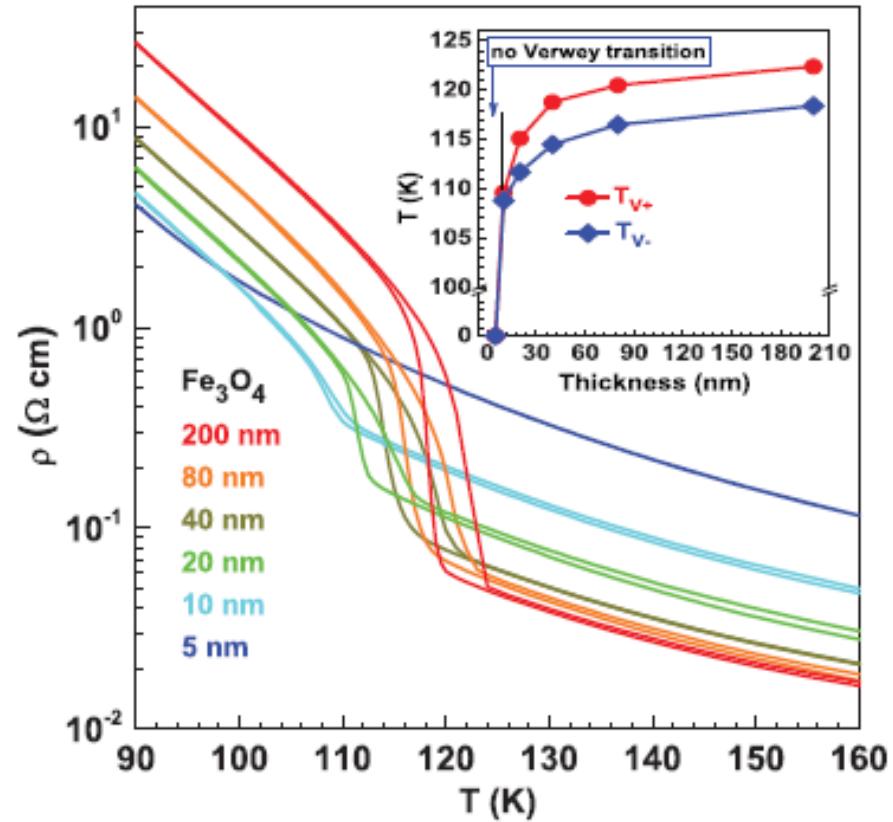


Verwey transition temperature T_{V-} and T_{V+} as the temperature of the maximum slope of ρ (T) curve for the cooling down and warming up temperature branch

Thickness dependence property of Fe_3O_4 thin film

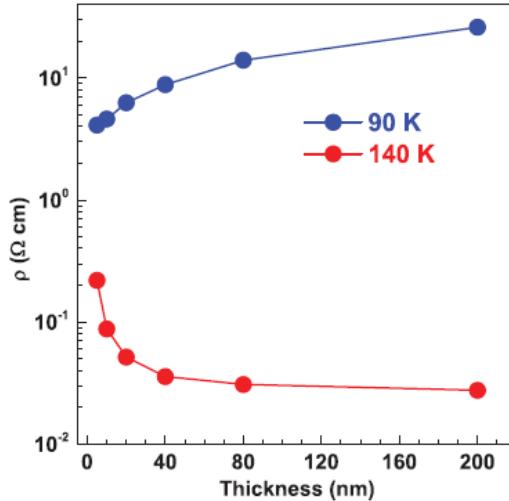


No indications for the presence of other iron oxide phases

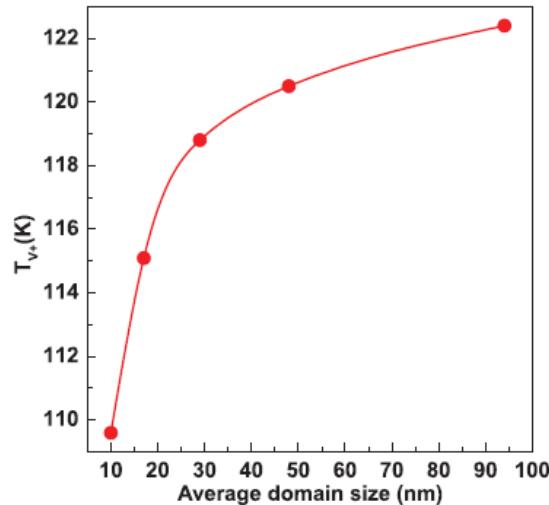
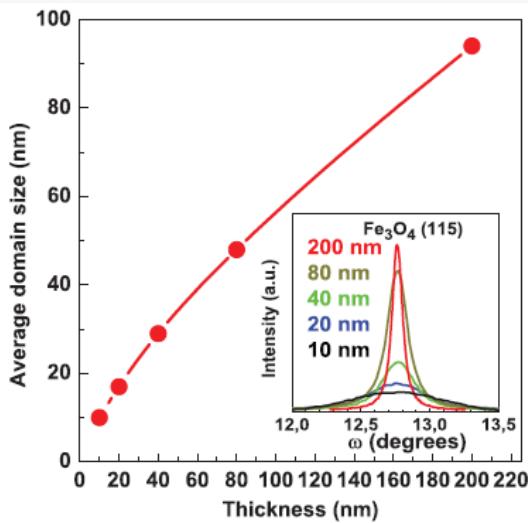


Resistivity as a function of temperature for Fe_3O_4 films with different thicknesses

Thickness dependence property of Fe_3O_4 thin film

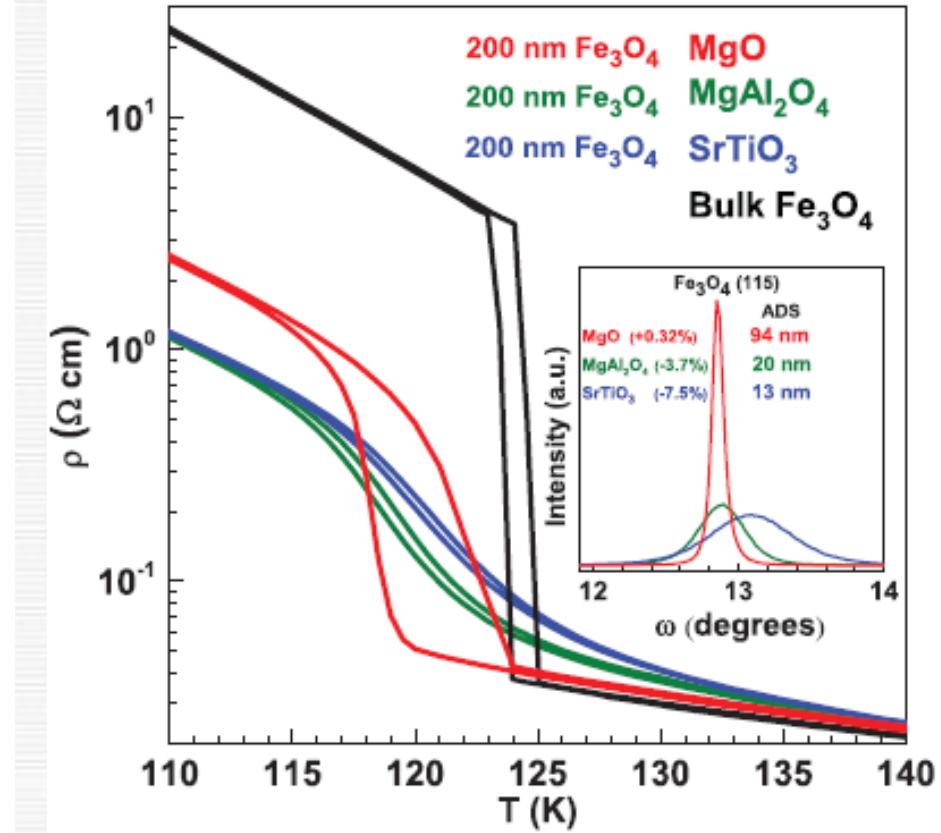
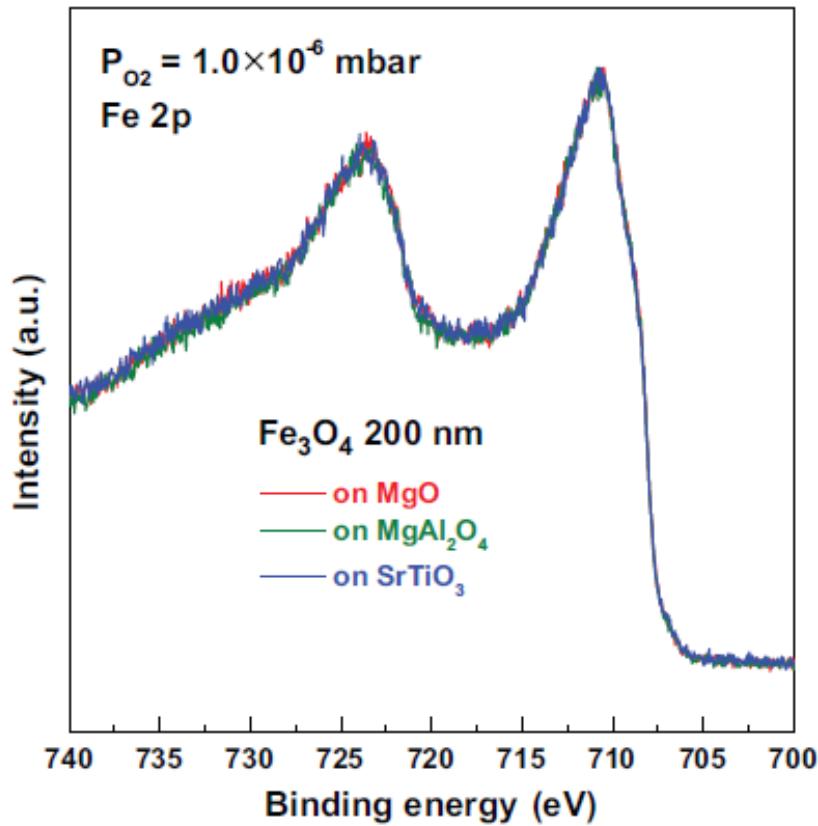


Resistivity of the Fe_3O_4 films at 90 K (blue) and 140 K (red) as a function of thickness.



The larger the ADS of Fe_3O_4 films the higher the transition temperature T_{v^*} and the larger the conductivity gap that can be opened in the low temperature phase.

Strain and microstructure effects



Substrate has no influence on the chemical composition of the film

Summary

- Substrate-induced microstructure plays a crucial role.
- In Fully stoichiometric films, the transition temperature, the resistivity jump, and the conductivity gap of greatly depend on the domain size, which increases gradually with increasing film thickness.
- The broadness of the transition correlates strongly with the width of the domain size distribution.

This is the end.

A photograph of a modern university building. The left side features a glass and steel structure with large windows. The right side is a red brick building with many windows. A row of small trees lines the sidewalk in front. Several people are walking or standing near the entrance, and a group of bicycles is parked. The sky is clear and blue.

Thank you for your time!

Metal–insulator transition

The classical band structure of solid state physics predicts the Fermi level to lie in a band gap for insulators and in the conduction band for metals, which means metallic behavior is seen for compounds with partially filled bands. However, some compounds have been found which show insulating behavior even for partially filled bands. This is due to the electron-electron correlation, since electrons cannot be seen as noninteracting. Mott considers a lattice model with just one electron per site. Without taking the interaction into account, each site could be occupied by two electrons, one with spin up and one with spin down. Due to the interaction the electrons would then feel a strong Coulomb repulsion, which Mott argued splits the band in two: The lower band is then occupied by the first electron per site, the upper by the second. If each site is only occupied by a single electron the lower band is completely filled and the upper band completely empty, the system thus a so-called Mott insulator.

Charge ordering

Charge ordering (CO) is a (first- or second-order) phase transition occurring mostly in strongly correlated materials such as transition metal oxides or organic conductors. Due to the strong interaction between electrons, charges are localized on different sites leading to a disproportionation and an ordered superlattice. It appears in different patterns ranging from vertical to horizontal stripes to a checkerboard-like pattern, and it is not limited to the two-dimensional case. The charge order transition is accompanied by symmetry breaking and may lead to ferroelectricity. It is often found in close proximity to superconductivity and colossal magnetoresistance.

This long range order phenomena was first discovered in magnetite (Fe_3O_4) by Verwey in 1939. He observed an increase of the electrical resistivity by two orders of magnitude at $T_{\text{CO}}=120\text{K}$, suggesting a phase transition which is now well known as the **Verwey transition**. He was the first to propose the idea of an ordering process in this context.

Antiphase boundary

An antiphase domain (APD) is a region of a crystal where the atoms are configured in the opposite order to those in the perfect lattice system and therefore is a Crystallographic defect. In other words, an APD is a region formed from antisite defects of a parent lattice.

