Single-Element-Driven Crystalline Magnetic Anisotropy in the High-Entropy Oxide (Fe, Co, Ni, Cr, Mn)$_3$O$_4$

X-ray absorption spectroscopy, magnetic circular dichroism, and linear dichroism show that crystalline magnetic anisotropy in (Fe, Co, Ni, Cr, Mn)$_3$O$_4$ originates from the orbital anisotropy of Mn 3d states due to substrate-induced epitaxial strain.

The design of multicomponent materials or so-called high-entropy alloys and compounds has attracted enormous attention due to their extraordinary ability to tailor functional properties. However, it is not easy to identify the role of each element in terms of their impact on crystal structure and its relation to electronic and magnetic properties in such materials. In a recent study on high-entropy spinel oxide (Fe, Co, Ni, Cr, Mn)$_3$O$_4$ epitaxial films, Ying-Hao Chu's team (National Tsing Hua University) successfully grew high-quality films with varying strain states, and then carried out a detailed investigation on the crystal structure and magnetic properties, as well as used electron microscopy and synchrotron spectroscopy techniques to determine element-specific properties. The team discovered that the high-entropy oxide (HEO) thin film under compressive strain shows evidence of crystalline magnetic anisotropy that is derived from a single element.[1] Using a combination of X-ray absorption spectroscopy (XAS), X-ray magnetic circular dichroism (XMCD), and X-ray linear dichroism (XLD), the team showed that the observed crystalline magnetic anisotropy originates from orbital occupation changes in Mn 3d states induced by epitaxial strain in the films.

The team first fabricated high-entropy (Fe, Co, Ni, Cr, Mn)$_3$O$_4$ epitaxial films on single-crystal MgAl$_2$O$_4$ (MAO) and MgO substrates with a high-quality interface. This resulted in elimination of defects in the HEO film and imposed compressive and tensile strain on HEO films grown on MAO and MgO, respectively. The team then carried out extensive analyses for a detailed understanding of HEO films, including X-ray diffraction (XRD), reciprocal space mapping, Raman spectroscopy, macroscopic magnetic characterization, electron microscopy, and synchrotron spectroscopy. The XRD rocking curves of the HEO (004) peak on MAO and MgO substrates measured at **TLS 17A1** show full width at half maximum (FWHM) of 0.42° and 0.14°, respectively, demonstrating the superior crystallinity of HEO films on these substrates. Reciprocal space mapping (RSM) was then used to show that the HEO film is under an in-plane compressive strain of 0.52% on the MAO substrate, while the HEO film is under an in-plane tensile strain of 0.85% on the MgO substrate. Raman spectroscopy showed four peaks at 527 cm^{-1} (3F$_{2g}$), 588 cm^{-1} (3F$_{2g}$), 648 cm^{-1}, and 700 cm^{-1} (A$_{1g}$). The wavenumbers of 648 and 700 cm^{-1} indicate the octahedral and tetrahedral centers in HEO. Accordingly, the crystal structure of HEO was classified as a spinel based on results from XRD and Raman spectroscopy. Scanning transmission electron microscopy with electron energy loss spectroscopy further confirmed that the HEO films exhibited a spinel phase.

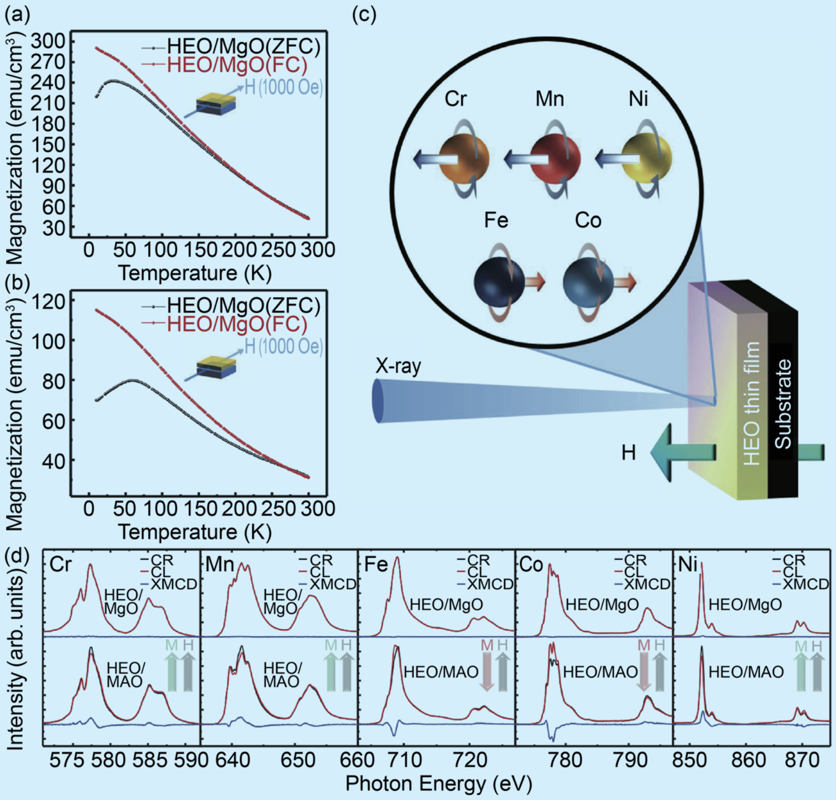

Fig. 1: M(T) and XMCD results. Temperature-dependent magnetization for (a) HEO/MgO and (b) HEO/MAO heterostructures under ZFC and FC processes with a DC magnetic field of 1000 Oe along the in-plane direction. (c) Schematic diagram illustrating the relationship between the applied magnetic field and the direction of the element's magnetic moment. (d) XMCD spectra of each element for the HEO/MgO and HEO/MAO structures. [Reproduced from Ref. 1]

Next, in order to understand the magnetic behavior of HEO films as a function of temperature, zero-field-cooled (ZFC) and field-cooled (FC) magnetization (M_{ZFC} and M_{FC}, respectively) measurements of the HEO/MgO and HEO/MAO heteroepitaxies were carried out as shown in **Figs. 1(a) and 1(b)**. It was found that both samples show a spin-glass-like behavior since considerable deviation was observed between M_{ZFC} and M_{FC} below ~280 K.

The team carried out XMCD measurements at **TPS 45A**, with the samples in a remanence state and the incident X-ray normal to the surface at 200 K, as shown schematically in **Fig. 1(c)**. The samples were magnetized with a field of 3 T normal to the sample surface before they were introduced into the chamber. **Figure 1(d)** shows clear XMCD signals for all five transition metals. For the HEO/MAO structure, a positive XMCD signal at the main absorption peak of the Cr, Mn, Ni L_3 edge spectra was observed. In contrast, Fe and Co spectra showed a negative XMCD signal at the L_3 edge. These results indicate that the spin direction of Cr, Mn, and Ni corresponds to the direction of the applied magnetic field (parallel), and that of Fe and Co is opposite to the applied magnetic field (antiparallel), as shown in **Fig. 1(c)**. In addition, a higher-intensity XMCD signal for the HEO/MAO structure and a lower-intensity XMCD signal for HEO/MgO were observed (**Fig. 1(d)**). The team concluded that because of the strong in-plane shape of its magnetic anisotropy, the magnetic moments of the HEO/MGO structure are aligned in-plane, while the magnetic moments of the HEO/MAO structure are aligned with the out-of-plane direction. This suggests that crystalline magnetic anisotropy dominates over the shape of magnetic anisotropy in the HEO/MAO structure. These results were further confirmed by superconducting quantum interference device (SQUID) magnetometry measurements. The authors also carried out SQUID measurements of HEO/MAO samples with film thicknesses from ~50 nm to over 1 μm and quantified the relationship between anisotropy energy density and film thickness. These results show that the thinner is the HEO film, the greater is the anisotropy energy density ($\sim 3 \times 10^6$ erg cm^{-3}), indicating that it is more affected by crystalline magnetic anisotropy. It is speculated that this magnetic anisotropy behavior comes from the epitaxial strain imposed by the substrate.

The team then carried out XAS measurements at T = 300 K as shown in **Fig. 2(a)** in order to check the valency and local geometry of the transition-metal ions. **Figure 2(b)** shows a schematic illustrating 3d orbital splitting when transition-metal elements occupy octahedral and tetrahedral sites. By comparing with standard reference samples, we concluded that Cr ions exhibit octahedral coordination with a valency of Cr^{3+}. On the other hand, Mn was found to adopt multiple valence states with Mn^{2+} in tetrahedral coordination and with Mn^{3+} and Mn^{4+} in octahedral coordination. The Mn^{2+} ion exhibits a half-filled 3d orbital, implying that it has a spherically symmetric

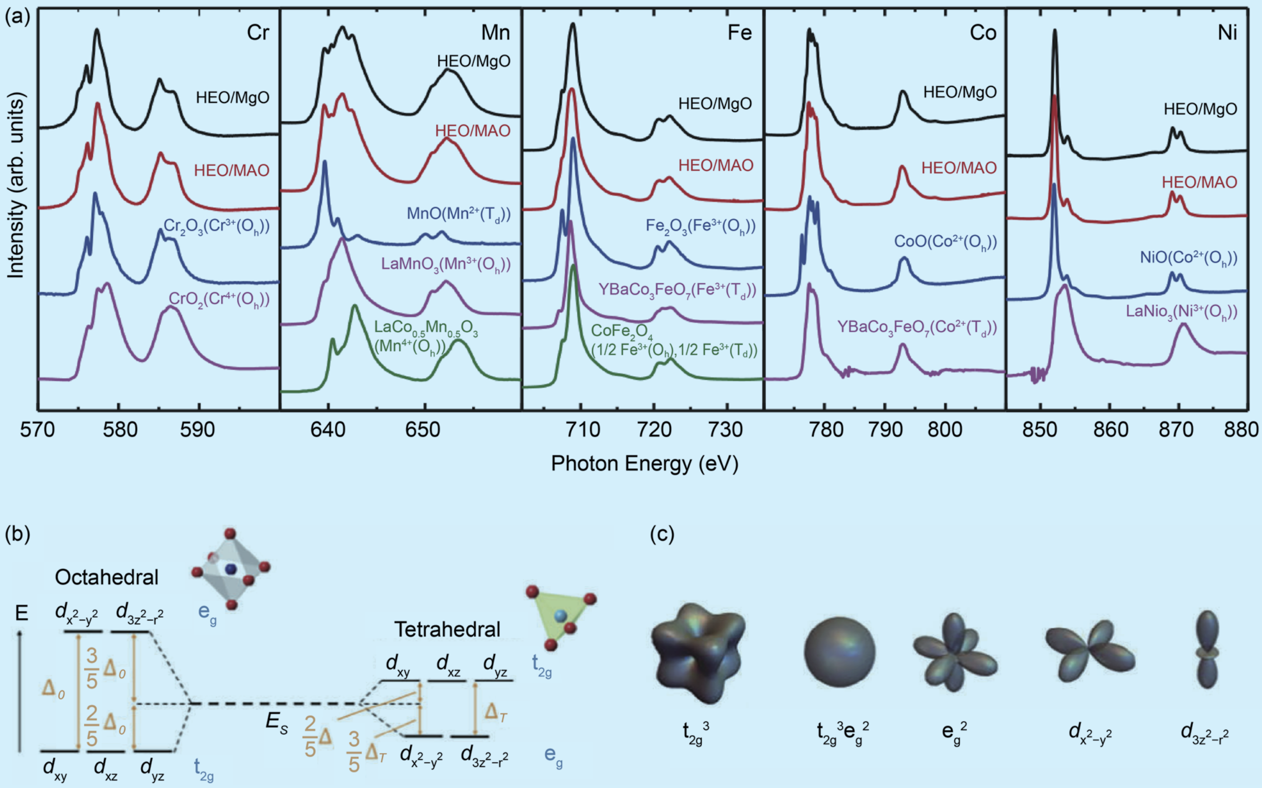

Fig. 2: XAS measurements. (a) XAS spectra of HEO/MgO and HEO/MAO structures. (b) 3D orbital splitting of a transition-metal ion at the octahedral and tetrahedral sites into e_g orbitals (d_{x2-y2}, d_{3z2-r2}) and t_{2g} orbitals (d_{xy}, d_{xz}, d_{yz}). (c) The electron clouds of different occupied orbitals. [Reproduced from Ref. 1]

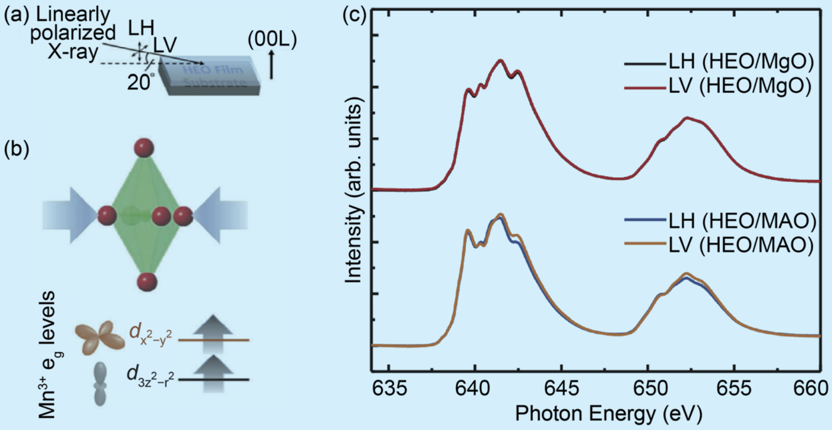

Fig. 3: XLD measurements. (a) Schematic of an XLD measurement. (b) A representation of MnO_6 under compressive strain and the subsequent effect on e_g splitting. (c) Mn $L_{2,3}$ XLD spectrum of the HEO/MgO and HEO/MAO structures. [Reproduced from Ref. 1]

electron cloud shape of $t_{2g}^3e_g^2$, as shown in **Fig. 2(c)**. For Mn^{4+} octahedral coordination, three electrons occupy the d_{xy}, d_{xz}, and d_{yz} orbitals, forming an electron cloud with cubic symmetry in t_{2g}^3, similar to that of Cr^{3+}. Similarly, it was found that Fe atoms show Fe^{3+} valency and adopt a half-filled 3d orbital for octahedral and tetrahedral sites, both corresponding to a spherically symmetric electron cloud shape $t_{2g}^3e_g^2$, while Co atoms show Co^{2+} valency in tetrahedral coordination with a fully occupied e_g but half-filled t_{2g} shell. Therefore, it exhibits an electron cloud with cubic symmetry in $t_{2g}^3e_g^4$. Lastly, Ni atoms exhibit an octahedral Ni^{2+} configuration with a fully occupied t_{2g} shell and half-filled e_g shell, resulting in a $t_{2g}^6e_g^2$ configuration and an electron cloud with cubic symmetry .

Finally, the team employed XLD to probe the asymmetric orbital occupation of Cr, Mn, Fe, Co, and Ni to verify the correlation between strain states and magnetic behavior. In the XLD measurements, linearly polarized X-rays were used with a grazing angle of 20° as depicted in **Fig. 3(a)**. The out-of-plane polarization (LH) absorption of Cr, Fe, Co, and Ni L edge spectra was very similar to the in-plane polarization (LV) absorption of the HEO/MAO structure. It was concluded that because of their symmetrical electron cloud shapes, these four elements should not contribute to orbital anisotropy. On the other hand, **Fig. 3(c)** indicates a discernible difference in the XLD spectrum of the Mn L edge absorption between the HEO/MgO (tensile) and HEO/MAO (compressive) structures. The LH absorption of the Mn L edge spectrum is weaker than that of LV in the HEO/MAO, suggesting a larger number of in-plane empty states in the e_g band. This indicates a higher occupancy of out-of-plane ($3z^2$-r^2) orbitals. This occupancy is primarily influenced by the strain state, which in turn determines the magnetic behavior of the HEO thin film. Since only the Mn^{3+} cation contains four electrons in the 3d orbitals, the crystalline magnetic anisotropy in HEO/MAO is primarily attributed to the higher electron occupancy of ($3z^2$-r^2) orbitals. **Figure 3(b)** depicts a schematic diagram illustrating the splitting of 3d orbitals in octahedral Mn under in-plane compressive strain. Thus, the authors could show that the difference in magnetic anisotropy originates from distortion in Mn^{3+} coordination, which is attributed to the strain applied from the substrate.

In conclusion, this study revealed that Mn^{3+} is the primary driver of crystalline magnetic anisotropy in the spinel HEO $(Fe, Co, Ni, Cr, Mn)_3O_4$ due to strain-modified orbital occupation.[1] This study shows that advanced synchrotron techniques can be fruitfully used to investigate the role of individual elements in influencing the electronic and magnetic properties of HEOs and to provide valuable insights for understanding the fundamental physics of HEOs. (Reported by Ashish Chainani)

This report features the work of Ying-Hao Chu, Chang-Yang Kuo, Yi-Cheng Chen and their collaborators published in Adv. Funct. Mater. ***34****, 2312856 (2024).*

TPS 45A Submicron Soft X-ray Spectroscopy
TLS 17A1 X-ray Powder Diffraction

- XRD, XAS, XMCD, XLD
- Materials Science, Condensed-matter Physics

Reference

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