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Paper

Mechanistic insights into the interaction between the energetic oxygen ions with nanosized ZnFe₂O₄: XAS-XMCD investigations

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1.1: About the structure of zinc ferrite

Bulk zinc ferrite has normal inverse spinel structure having *Fd3m* space group¹. In this structure oxygen ions form face centred cubic (FCC) structure. Metal ions are situated among tetrahedral (A-site) and octahedral (B-site) voids surrounded by 4 and six ions respectively. Ions are distributed among these sites, so that maximum occupancies of A-site and B-sites are 1 and 2 per ZnFe₂O₄ formula. Positions and occupancies of various ions in zinc ferrite are collated in following Table 1²⁻⁴. Position of oxygen ions in the lattice is termed as oxygen positional parameter (*u*)²⁻⁴. The detailed explanation of this parameter is described elsewhere⁵.

Table: Positions and occupancies of various ions in bulk ZnFe₂O₄

Ions	Positions			Occupancy	Site
	<i>x</i>	<i>y</i>	<i>z</i>		
Zn ²⁺	0.125	0.125	0.125	1	Tetrahedral
Fe ³⁺	0.500	0.500	0.500	2	Octahedral
O ²⁻	0.260	0.260	0.260	4	

Thus, all Zn²⁺ ions remains at A-site, however, all of Fe³⁺ remains at B-site, in case of bulk zinc ferrite. Hence, structure formula of bulk zinc ferrite is written as (Zn)_A[Fe₂]_BO₄.

When this material is synthesized in nano-regime, then it's structure transform to mixed spinel. It means that some amount of Fe³⁺ ions migrates to A-site. An inverse affect is observed for Zn²⁺ ions. In case of such redistribution of cations spinel structured material maintain it's characteristics behaviour that maximum occupancies of A-site and B-sites are 1 and 2 per ZnFe₂O₄ formula. If λ fraction of Fe³⁺ ions migrate to A-site from B-site, then structure formula is written as (Zn_{1- λ} Fe _{λ})_A[Zn _{λ} Fe_{2- λ}]_BO₄. Based on this structural formula cation inversion, *x*, is defined as

$$x = \left[\frac{\lambda}{2 - \lambda} \right]_{Fe^{3+}}$$

This concept was used for estimating cation inversion by using XRD and EXAFS techniques in these materials.

1.2: Synthesis, and phase of bulk zinc ferrite

Bulk zinc ferrite is synthesized using the method described in experimental section and by annealing precursor at 1200°C 1hr followed by sintering at 1200°C for 12 hr. Morphology and phase of bulk zinc ferrite is shown in Fig. S4. The material contains particles of size ~ 1µm having cubic spinel phase.

Table S1: Parameters estimated from Stopping and Range of Ions in Matter (SRIM) for O^{7+} ions and $ZnFe_2O_4$ interaction

Material	Ion Species	Energy (MeV)	Electronic stopping; $(dE/dx)_e$ (keV/nm)	Nuclear Stopping; $(dE/dx)_n$ (eV/nm)	S_e/S_n	R (μm)
$ZnFe_2O_4$	O^{7+}	100.00	1.09	0.618	1.7×10^3	65

Table S2: Position (x_c) and area (A) of XRD peak corresponding to impure phase and most intense peak of ZFP and ZFI nanoparticles. y_o is background intensity.

Material	Impure phase			Spinel phase		Ratio
	x_c ($^\circ$)	A (arb. unit)	y_o	x_c ($^\circ$)	A (arb. unit)	
ZFP	31.76 ± 0.05	2.6 ± 1.5	8.9 ± 0.8	35.16 ± 0.02	728 ± 3	0.003
ZFI	31.61 ± 0.05	4.2 ± 2.0	6.4 ± 0.9	35.16 ± 0.02	689 ± 3	0.006

Table S3: Bonds, co-ordination number and radial distance of A-site and B-site of bulk $ZnFe_2O_4$ estimated using ATOMs calculated from occupancies of metal ions given in section 1.1.

A-site			B-site		
Bonds	Co-ordination number (N)	Radial Distance (\AA)	Bonds	Co-ordination number (N)	Radial Distance (\AA)
Zn-O	4	1.974	Fe-O	6	2.030

Table S4: Area of T, O_1 and O_2 spectral features of XMCD signals for ZFP and ZFI NPs

ZFP				ZFI			
T	O_1	O_2	$T/(O_1+O_2)$	T	O_1	O_2	$T/(O_1+O_2)$
0.02	0.01	0.05	0.33	0.009	0.004	0.004	1.1

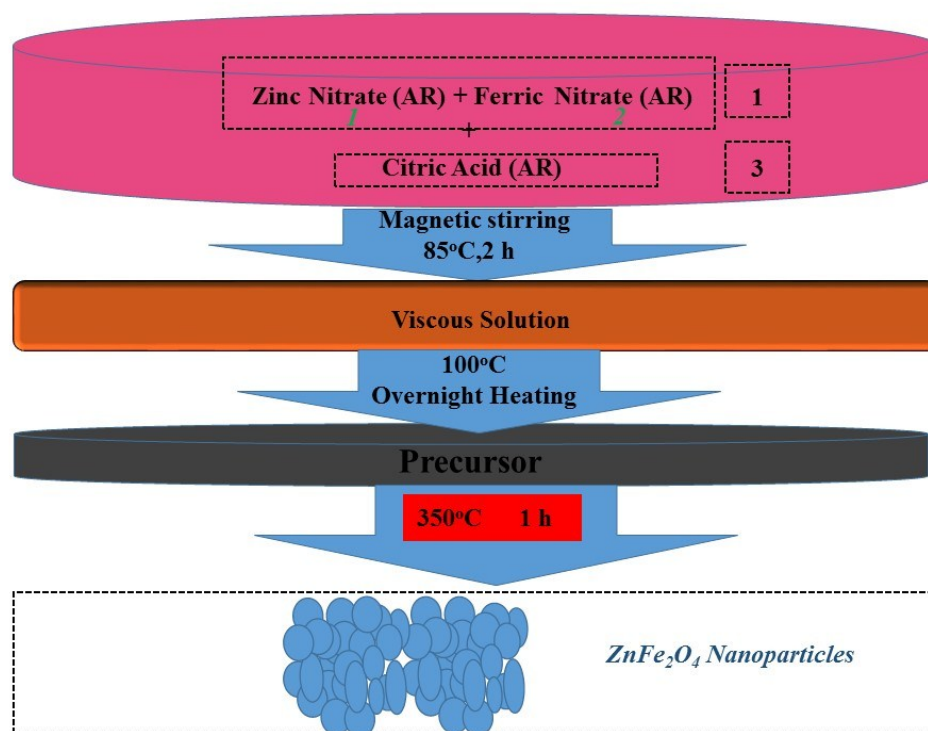


Fig. S1: Schematic of synthesis route adopted for ZnFe₂O₄ nanoparticles

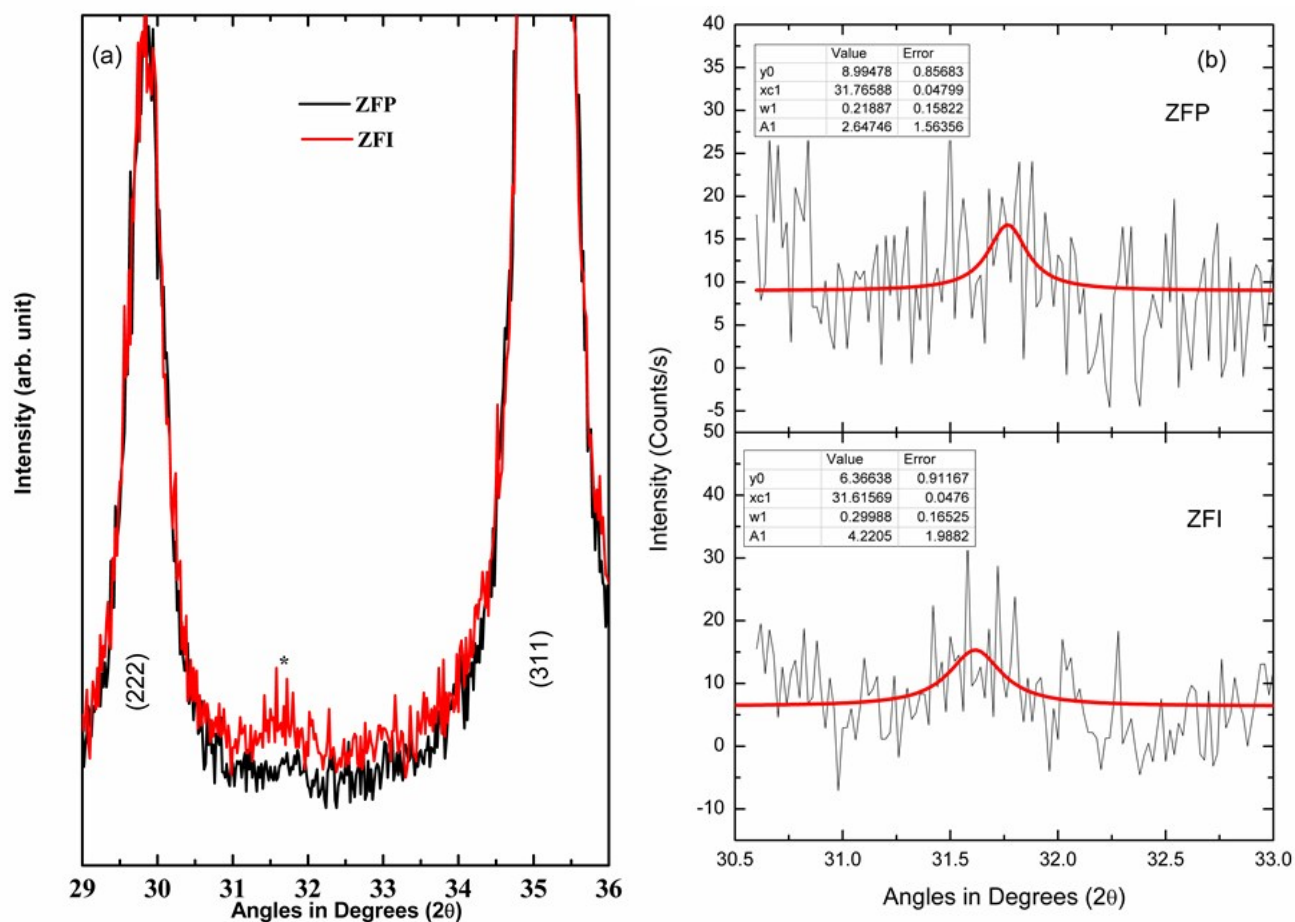


Fig. S2: XRD patterns showing (a) evolution of ZnO phase for ZFI nanoparticles. (b) Impurity peak fitted for ZFP and ZFI nanoparticles. y_0 shows background level. xc_1 , w_1 and A_1 are position, width and area of peak. Intensity of impure phase is less than background of pattern in both materials.

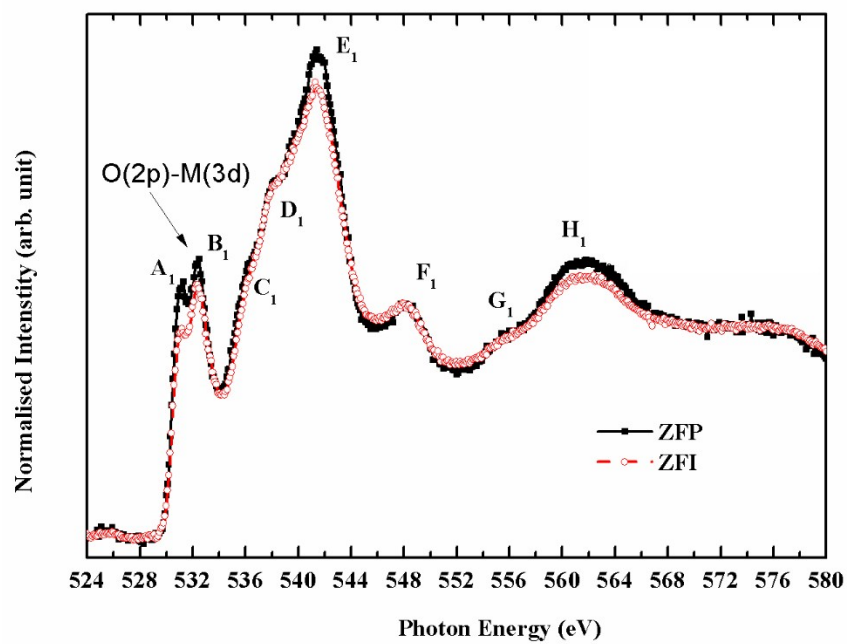


Fig. S3. O K-edge spectra of ZFP and ZFI. Arrow indicates that pre-edge spectral feature is related with O (2p)-Metal M (3d) hybridization

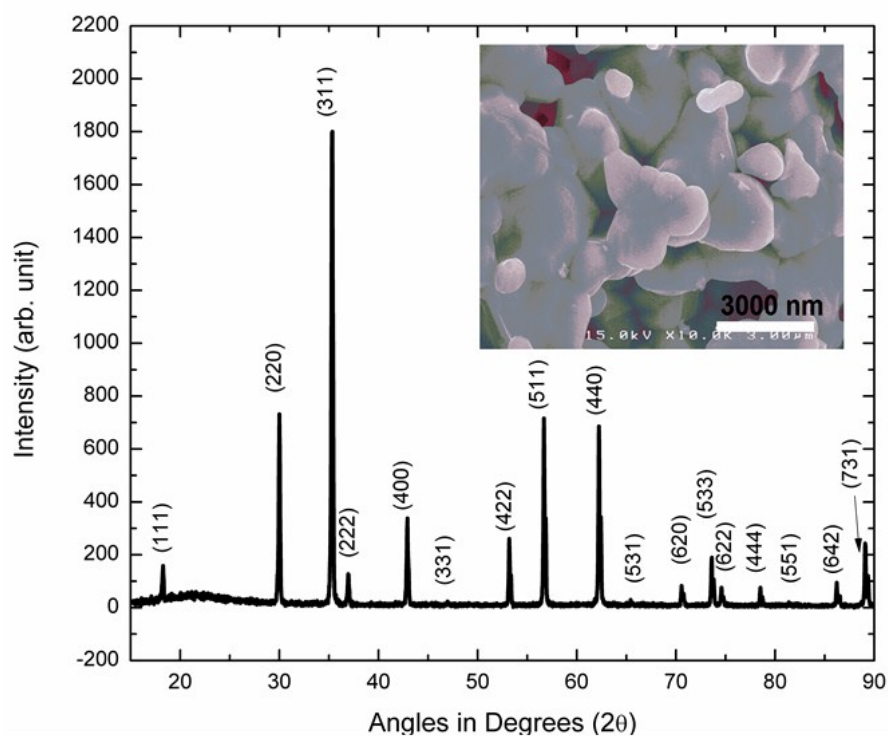


Fig. S4. X-ray diffraction pattern of bulk ZnFe₂O₄ synthesized using route adopted mention in section 1.2. Inset shows scanning electron micrograph of synthesized material.

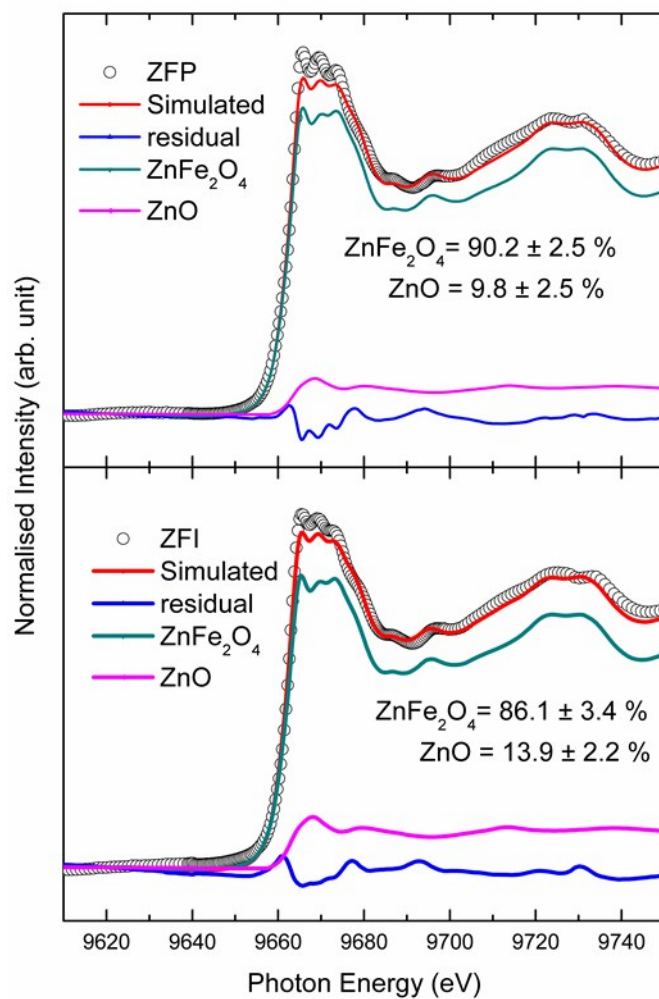


Fig. S5: Linear combination fitting of ZFP and ZFI using ZnFe_2O_4 bulk and ZnO standard

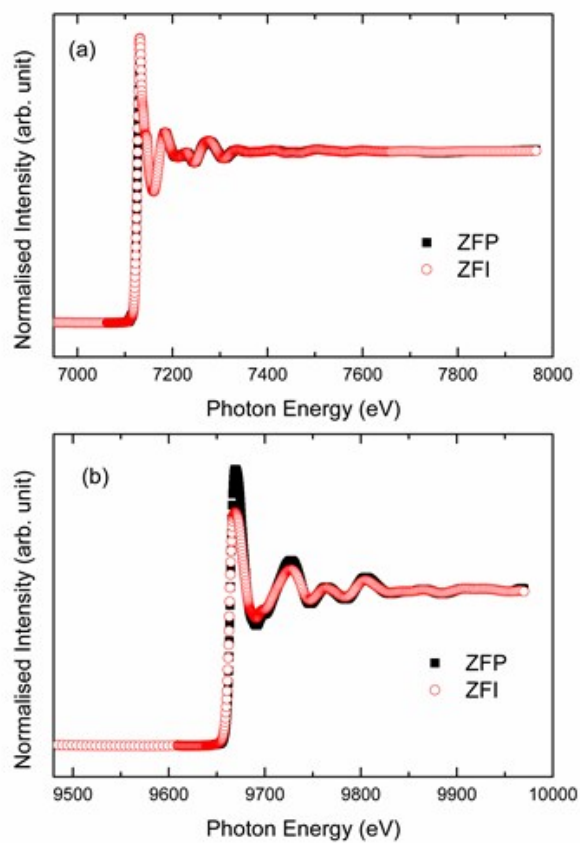


Fig. S6: Extended X-ray absorption fine structure (EXAFS) spectra of ZFP and ZFI at (a) Fe *K*-edge and (b) Zn *K*-edge

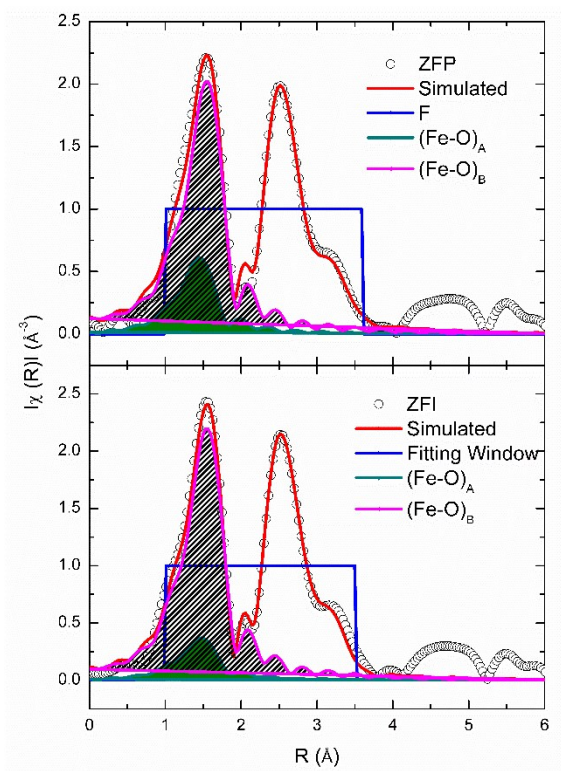


Fig. S7: Simulated non-phase corrected inverse Fourier Transform of EXAFS spectra at Fe K-edge for ZFP and ZFI nanoparticles. Spectra were simulated in R-range of 1-3.6Å.

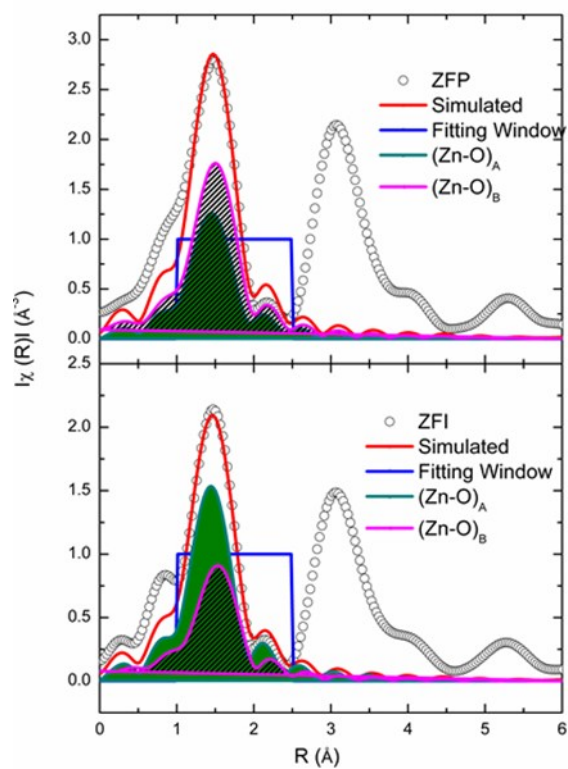


Fig. S8: Simulated non-phase corrected inverse Fourier Transform of EXAFS spectra at Zn K-edge for ZFP and ZFI nanoparticles. Spectra were simulated in R-range of 1-2.5 \AA

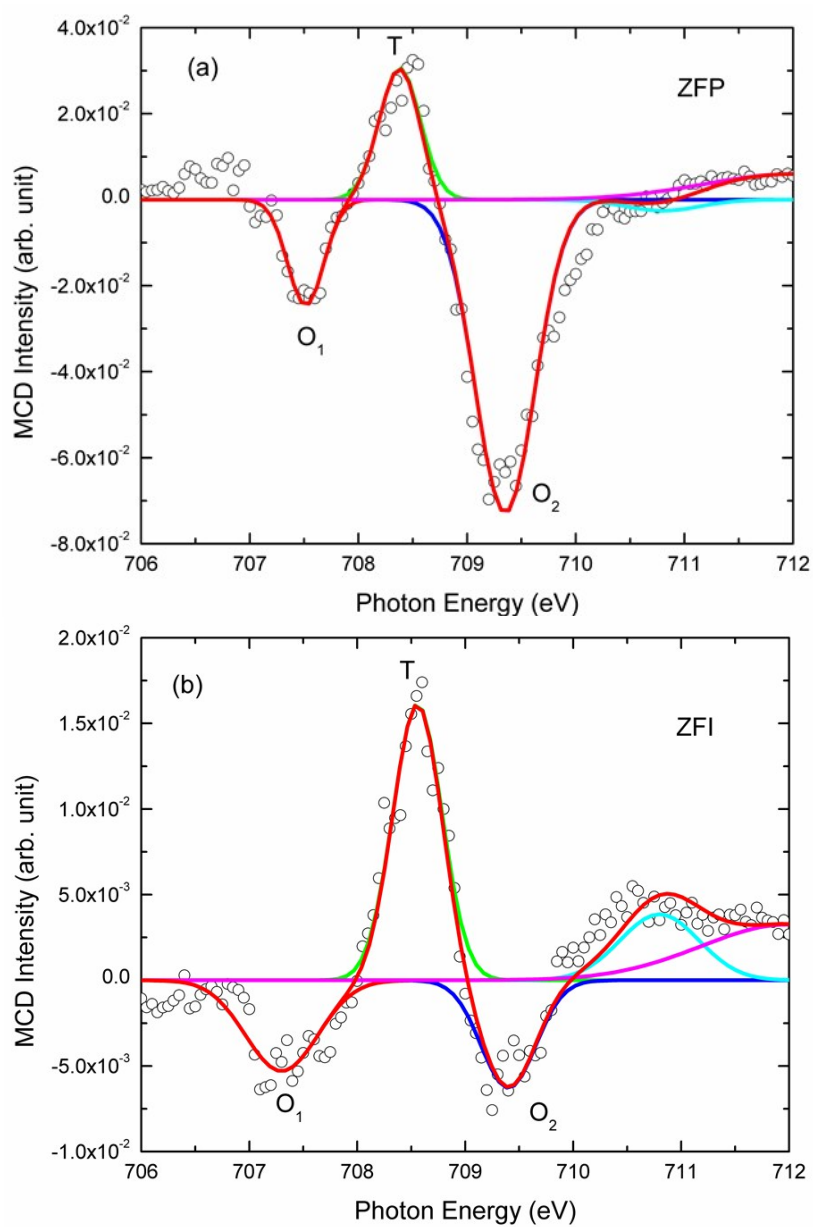


Fig. S9: de-convoluted T, O₁ and O₂ spectral features of XMCD signal for (a) ZFP and (b) ZFI NPs

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