Supplemental Material for

Unusual ferrimagnetism in $CaFe_2O_4$

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Contents:

1. Electric quadrupole contribution to resonant x-ray diffraction

Resonant x-ray scattering is anisotropic, and the scattering length *f* is represented by a tensor,

$$f = \begin{pmatrix} f_{xx} & f_{xy} & f_{xz} \\ f_{xy} & f_{yy} & f_{yz} \\ f_{xz} & f_{yz} & f_{zz} \end{pmatrix}. \qquad \text{(S1)}$$

Here we take a Cartesian coordinate system where *x*, *y*, and *z* are along [100], [010], and [001], respectively. Two Fe^{3+} sites of $CaFe_2O_4$ locate at the Wyckoff position of 4*c*. Because of the mirror symmetry normal to [010] of the position, $f_{xy} = f_{yz} = 0$. Four Fe^{3+} of 4*c*, labelled as Fe(1), Fe(2), Fe(3), and Fe(4), are connected by (1) the identical operation 1, (2) two-fold screw operation along [001] 2_1, (3) inversion operation -1, and (4) the combination of -1 and 2_1. Therefore, the scattering lengths of Fe^{3+} at respective positions are

$$f_1 = f_3 = \begin{pmatrix} f_{xx} & 0 & f_{xz} \\ 0 & f_{yy} & 0 \\ f_{xz} & 0 & f_{zz} \end{pmatrix} \text{ and } f_2 = f_4 = \begin{pmatrix} f_{xx} & 0 & -f_{xz} \\ 0 & f_{yy} & 0 \\ -f_{xz} & 0 & f_{zz} \end{pmatrix}. \qquad \text{(S2)}$$

The scattering factor *F* of (001) is obtained by summing up *f* at each position with its phase,

$$F = f_1 e^{2\pi iz} + f_2 e^{2\pi i\left(z+\frac{1}{2}\right)} + f_3 e^{-2\pi iz} + f_4 e^{-2\pi i\left(z-\frac{1}{2}\right)}$$
$$= 4\cos(2\pi z) \begin{pmatrix} 0 & 0 & f_{xz} \\ 0 & 0 & 0 \\ f_{xz} & 0 & 0 \end{pmatrix}. \qquad \text{(S3)}$$

Hence, one quadrupole moment (the *xz* component) contributes to (001), resulting in finite (001) intensities even above T_{NB}.

2. Comparison between TEY and XEOL

A comparison of the XMCD spectra from the surface-sensitive total-electron yield (TEY) mode and from the bulk-sensitive x-ray excited optical luminescence (XEOL) mode is shown in Fig. S1. Here the XEOL signals including significant self-absorption distortion due to the film thickness were corrected with the method described in Ref. [1].

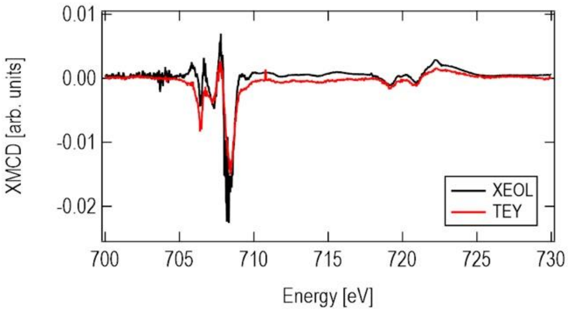

Fig. S1 Comparison of the XMCD spectra measured simultaneously with TEY and XEOL modes at 150 K and 6 T.

3. Comparison between L_3 and L_2 edges

Figure S2 shows experimental/simulated XMCD spectra, including both the Fe $L_{2,3}$ edges, measured at different conditions.

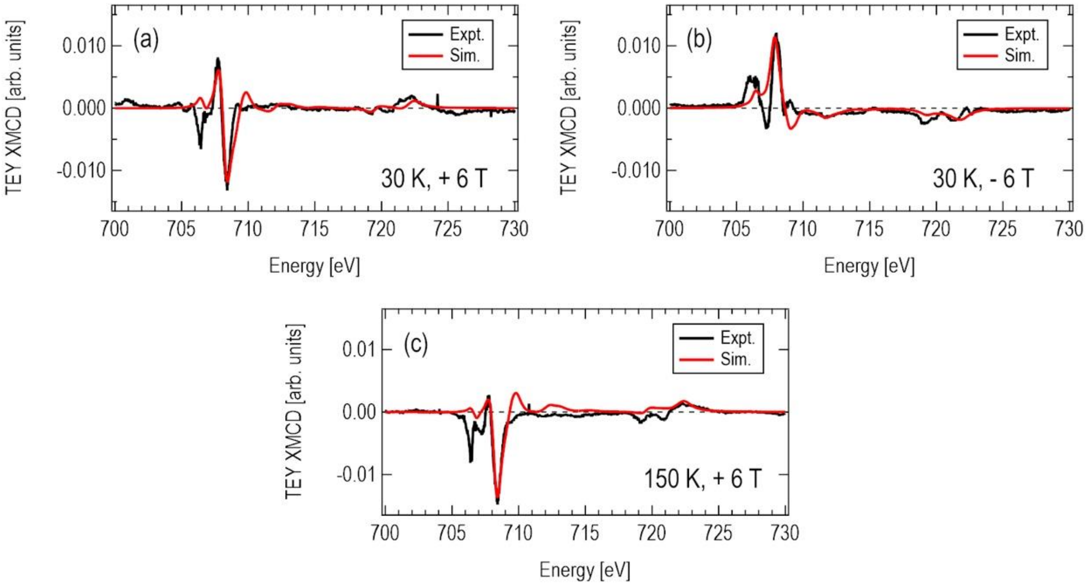

Fig. S2. Comparison of the experimental and simulated Fe $L_{2,3}$ edges XMCD spectra. (a) At 30 K and +6 T, (b) at 30 K and -6 T, and (c) at 150 K and +6 T.

References

1. C. Piamonteze, Y. W. Windsor, S. R. V. Avula, E. Kirk, and U. Staub, Soft x-ray absorption of thin films detected using substrate luminescence: a performance analysis. *J. Synchrotron Rad.* **27**, 1289-1296 (2020).