Supplementary materials for

Nanoscale heterogeneity in thermoelectrics: the occurrence of a phase separation in Fe-doped $Ca_3Co_4O_9$

Wei Xu,[*ab] Sajid Butt,[cd] Yingcai Zhu,[a] Jing Zhou,[e] Yong Liu,[f] Meijuan Yu,[a]
Augusto Marcelli,[bg] Jinle Lan,[h] Yuan-Hua Lin[c] and Ce-Wen Nan[*c]

(1) Theoretical XANES calculations of this layered structure at the Ca and Co *K*-edge and their derivative spectra

(2) Theoretical polarized XANES calculations of this layered structure at the Ca and Co *K*-edge and their derivative spectra

(3) Total energy calculations

(4) Electronic band structure of the pure and Fe doped $Ca_3Co_4O_9$

(1) Theoretical XANES calculations of this layered structure at the Ca and Co *K*-edge and their derivative spectra

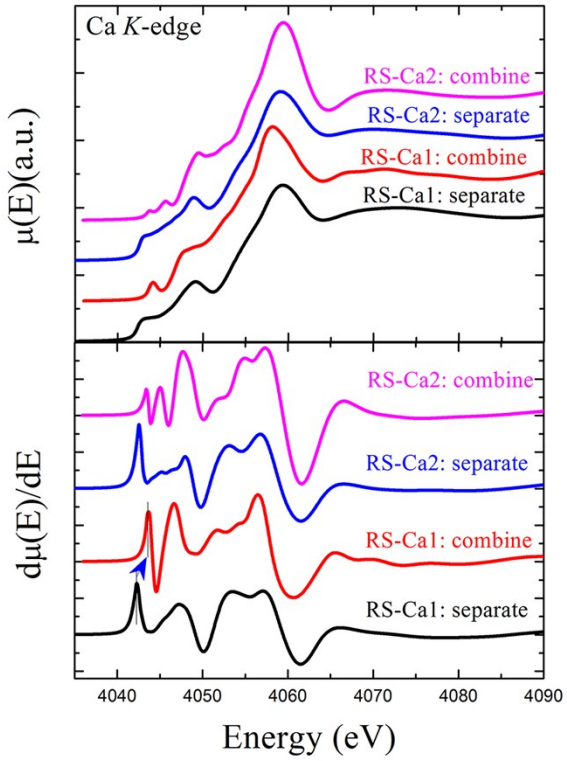

Figure S1 Theoretical XANES calculations at the Ca *K*-edge (upper panel) and its first derivative (lower panel) using either combined ($Ca_3Co_4O_9$) or separate (Ca_2CoO_3) structural models.

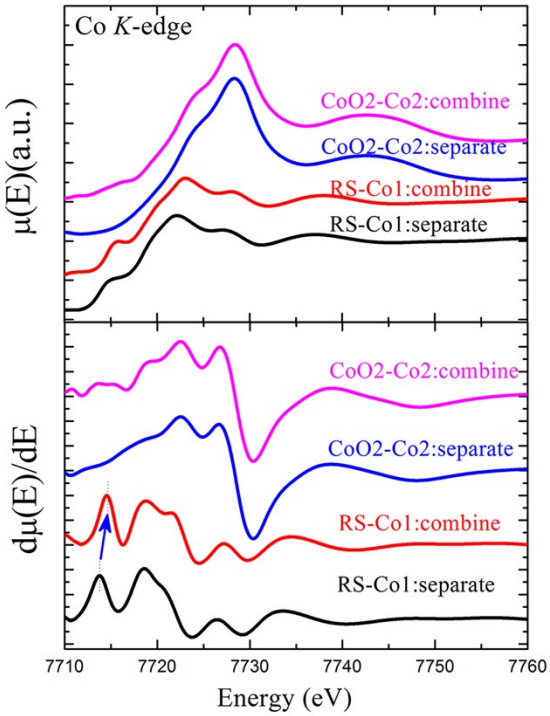

Figure S2 Theoretical XANES calculations at the Co *K*-edge (upper panel) and its first derivative (lower panel) using either combined ($Ca_3Co_4O_9$) or separate (Ca_2CoO_3 and CoO_2) structural models.

(2) Theoretical polarized XANES calculations of this layered structure at the Ca and Co

K-edge and their derivative spectra.

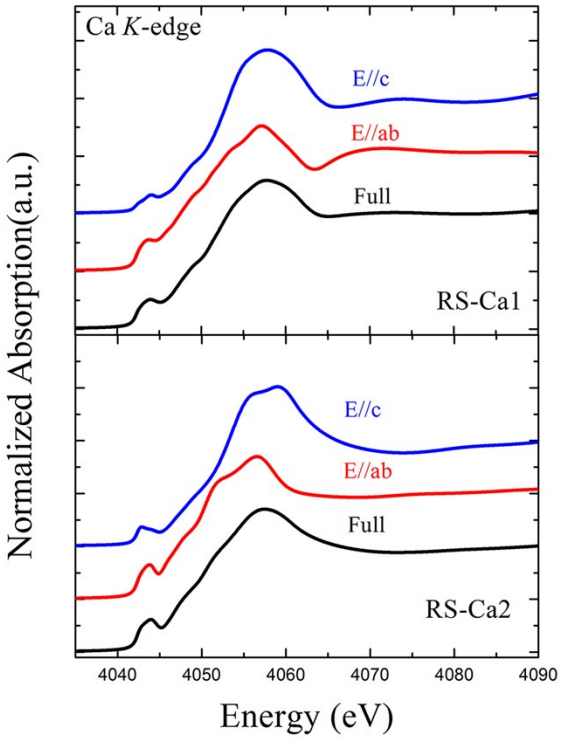

Figure S3 Comparison of polarized XANES spectra at the Ca *K*-edge for the two inequivalent calcium sites.

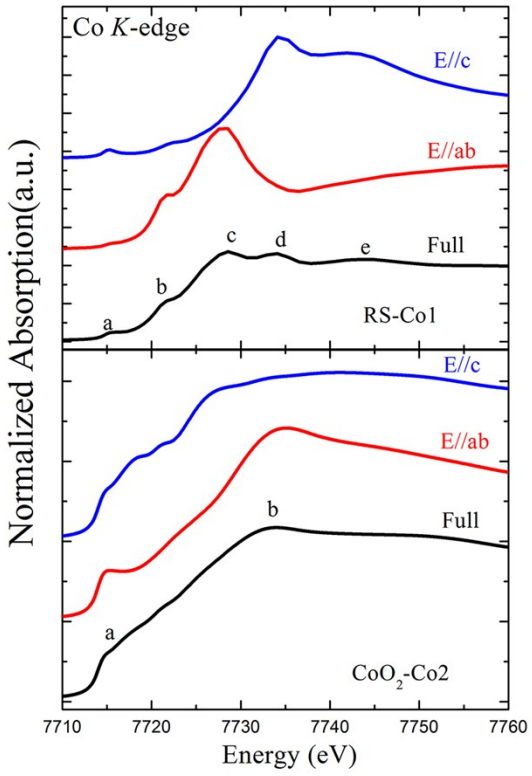

Figure S4 Comparison of polarized XANES spectra at the Ca *K*-edge for the two inequivalent cobalt sites.

(3) Total energy calculations

Table S1 Total energy and optimized lattice parameters for different models of pure and doped $Ca_8Co_{10}O_{24}$ by DFT

Super cells	Content	Total energy (eV)	a	b	c	$\delta a/a_0$	$\delta b/b_0$	$\delta c/c_0$	δE/at.
$Ca_8Co_{10}O_{24}$	0	-569.298905	4.858	17.595	10.837	0	0	0	0
Fe@Co1 in RS slab	10%	-571.190840	4.866	17.600	10.802	0.00165	2.84172E-4	-0.00323	-18.91935
Fe@Co2 in CoO_2 slab	10%	-570.523142	4.870	17.586	10.822	0.00247	-5.11509E-4	-0.00138	-12.24237
Fe@Ca1 in RS slab	12.5%	-572.220307	4.869	17.477	10.780	0.00226	-0.00671	-0.00526	-23.37122
Fe@Ca2 in RS slab	12.5%	-571.450338	4.893	17.448	10.775	0.0072	-0.00835	-0.00572	-17.21146

(4) Band structure

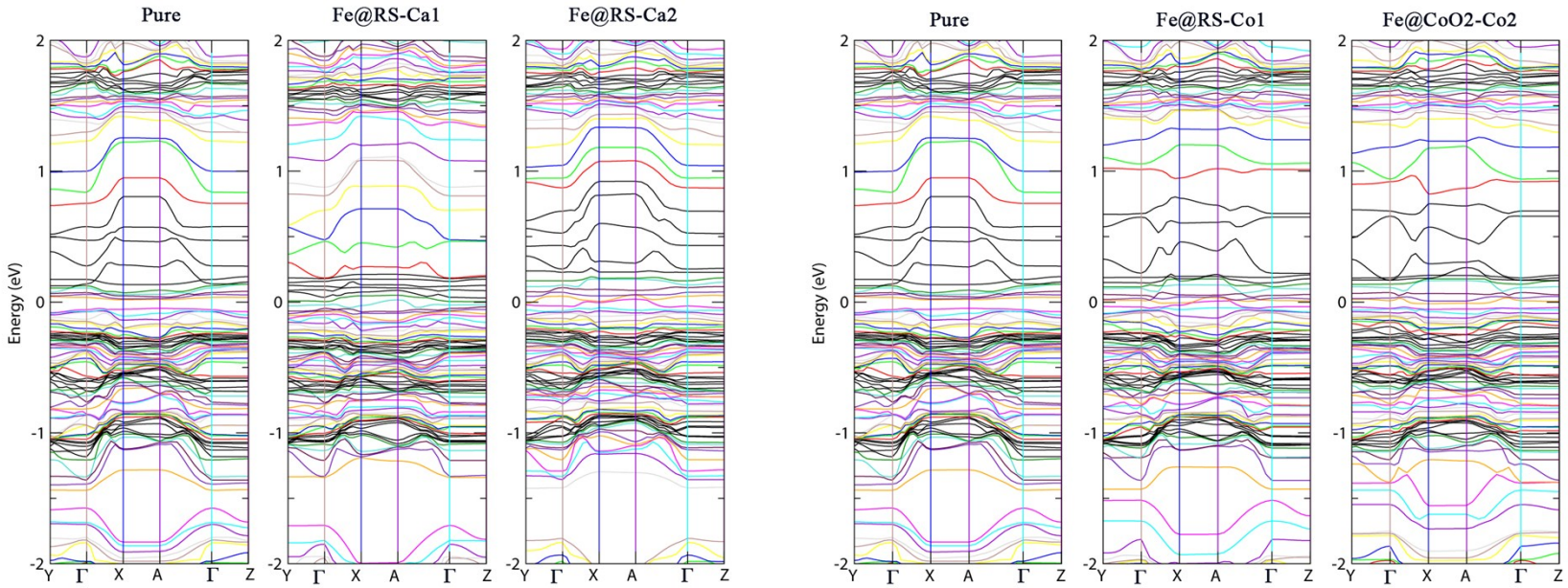

Figure S5 Comparison of band structure calculations for pristine and Fe doped $Ca_3Co_4O_9$