Supporting Information: Atomic structure of CdS magic-size cluster by X-ray absorption spectroscopy

Ying Liu, Lei Tan, Martin T. Dove, and Andrei V. Sapelkin

School of Physics and Astronomy, Queen Mary University of London, Mile End Road, London, E1 4NS, UK

Giannantonio Cibin, Diego A. Gianolio

Diamond Light Source Ltd, Harwell Science and Innovation Campus, Didcot, OX11 0DE, UK

Shuo Han, Kui Yu

Institute of Atomic and Molecular Physics, Sichuan University, Chengdu, 610065, P. R. China

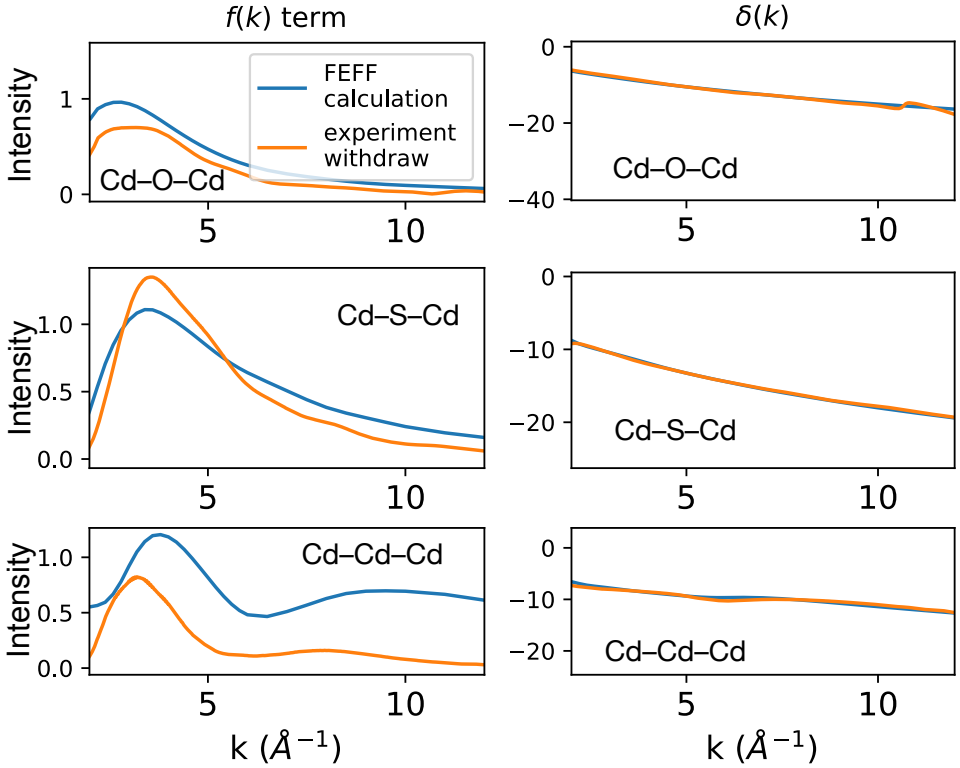

Fig. S1 Two parameters, the effective backscattering amplitude term (left) and the phase term (right) are plotted separately with the comparison between the calculated value from the FEFF package and extracted experimental value from the bulk reference.

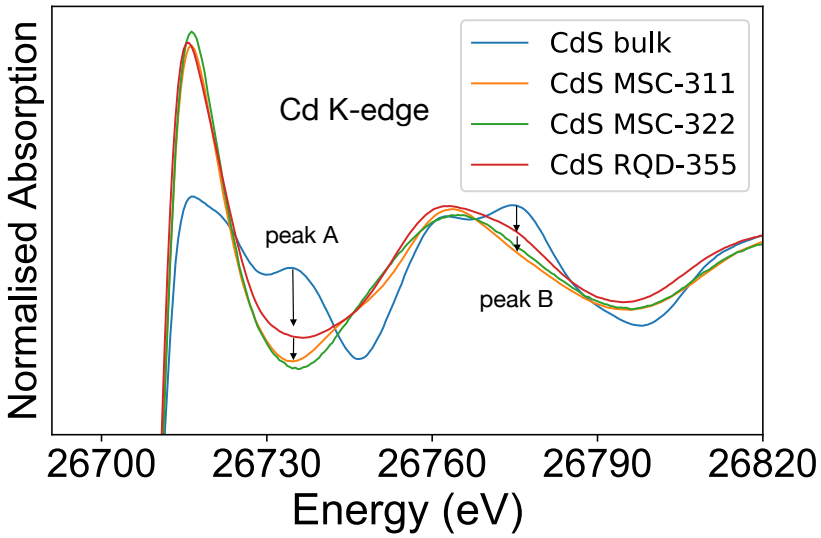

Fig. S2 The XANES evolution at Cd K-edge of samples from bulk CdS to RQD to MSC. Peak A and peak B has a reducing intensity when the sample goes from bulk to RQD to MSC.

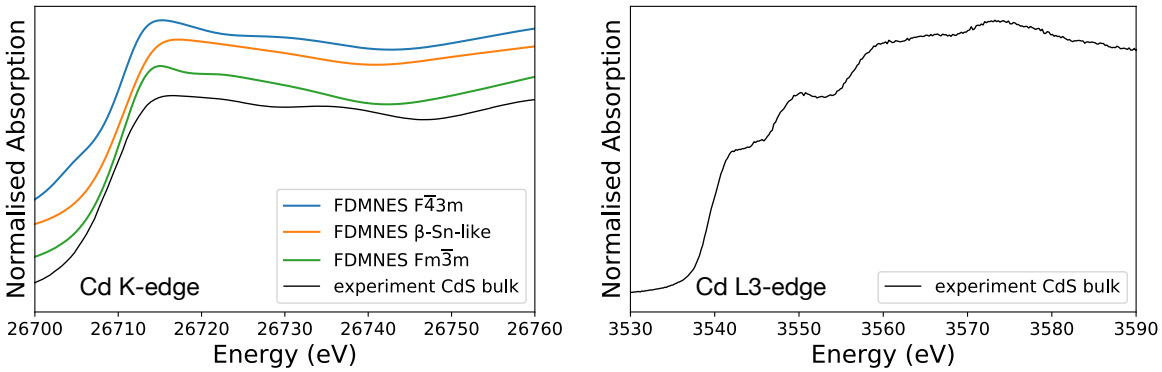

Fig. S3 (a). FDMNES simulation of CdS crystal at Cd K-edge with zinc-blende structure (space group: $F\bar{4}3m$), β-Sn-like structure and rock-salt structure (space group: $Fm\bar{3}m$) together with experimental XANES of CdS bulk sample. (b) The experimental XANES of CdS crystalline sample at Cd L3-edge. The Cd K-edge XANES shows less features compared with the L3-edge XANES. Hence, we used L3-edge data for the XAENS analysis of CdS MSC samples.

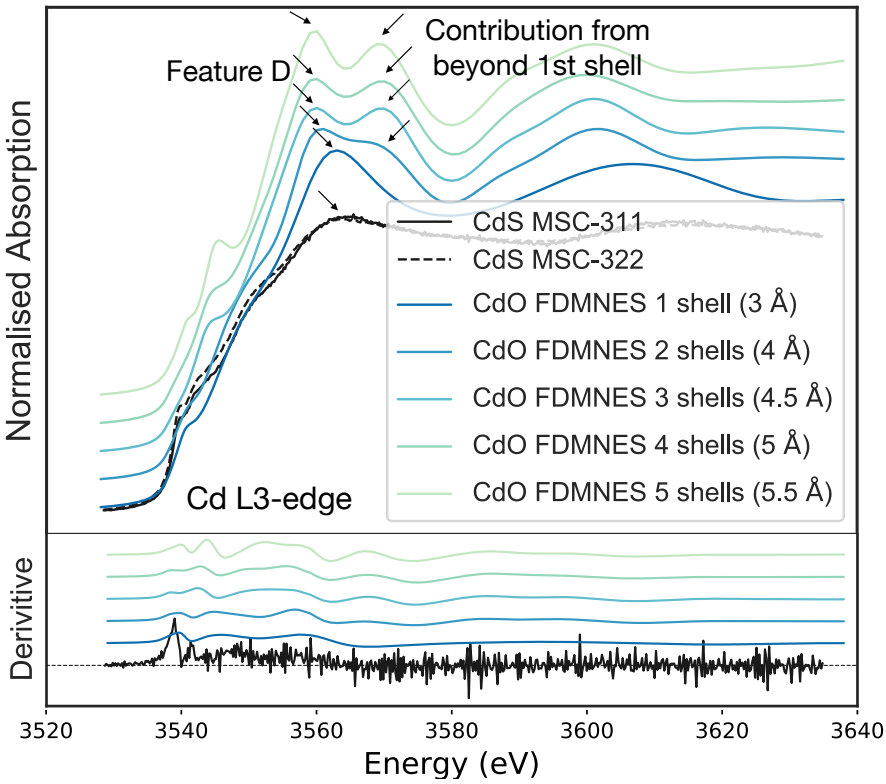

Fig. S4 FDMNES simulation of CdO with rock-salt structure (space group: $Fm\bar{3}m$) compared with CdS M311 and M322 experiment. The CdO FDMNES simulations are exhibited as a function of the calculated shells around absorbing atom. It ranges from 1 shell to 5 shells. As it evolves beyond the first shell around Cd, a peak which is at about 3570 eV shows up indicating that peak is not from the first shell signal. In the MSC experiment, no such peak observed at a similar location showing that CdO contribution doesn't extend beyond the first coordination shell.

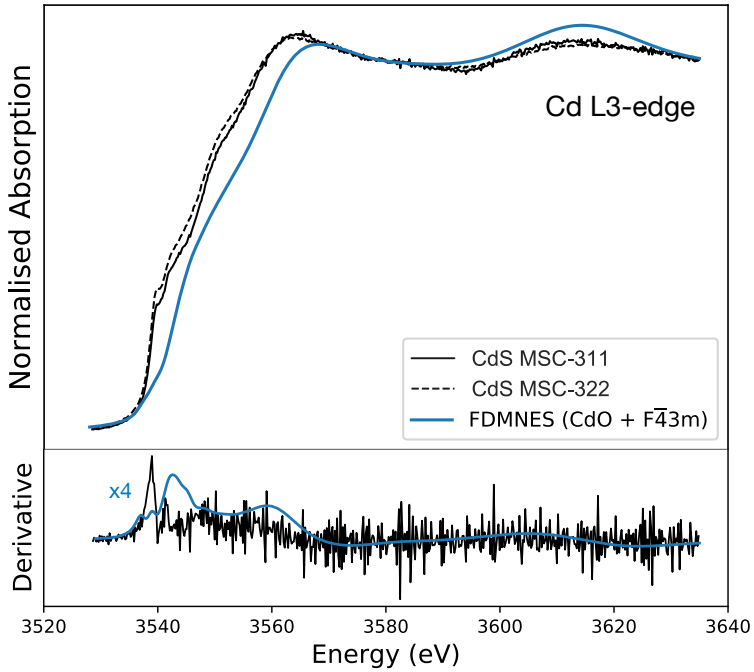

Fig. S5 Comparison of the CdS MSC experiment with the weighted sum of CdS zinc-blende structure (space group: $F\bar{4}3m$) and CdO bulk structure using their FDMNES simulation with calculated sphere of 3 Å. Its derivatives are plotted at the bottom.

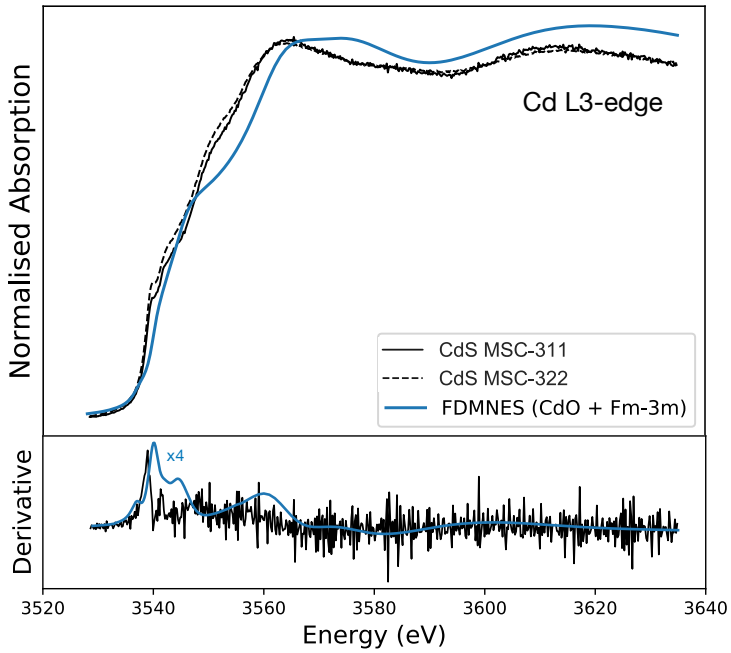

Fig. S6 Comparison of the CdS MSC experiment with the weighted sum of CdS rock-salt structure (space group: $Fm\bar{3}m$) and CdO bulk structure using their FDMNES simulation with calculated sphere of 3 Å. Its derivatives are plotted at the bottom. We can see that neither spectra or derivative fit the experiment very well.

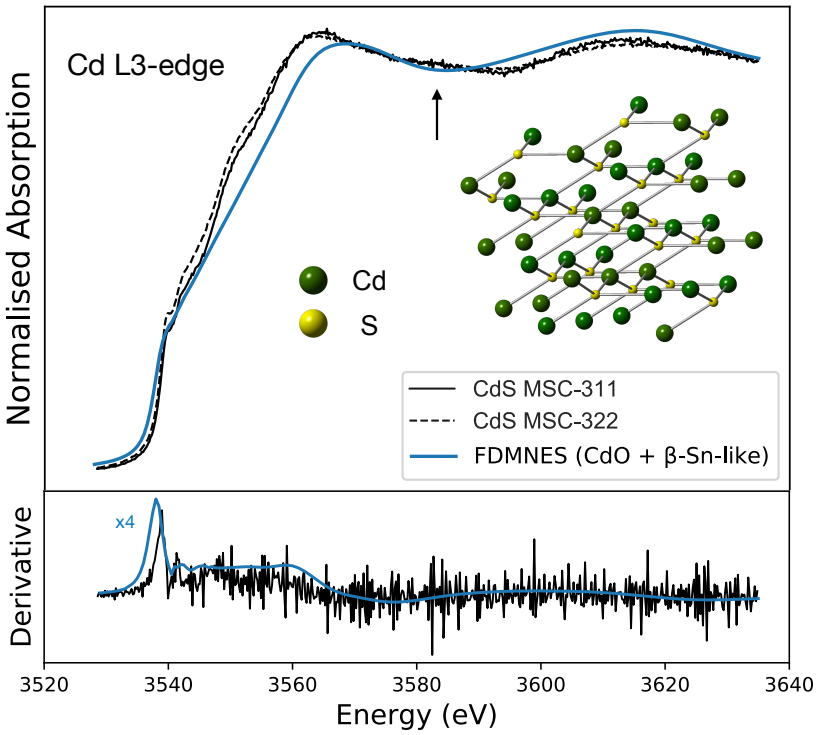

Fig. S7 Comparison of the CdS MSC experiment with the weighted sum of CdS ß-Sn-like structure (see inset) and CdO bulk structure using their FDMNES simulation with calculated sphere of 3 Å. Its derivatives are plotted at the bottom. We can see that neither spectra nor derivative fit the experiment very well. The peak at about 3585 eV cannot be reproduced in the fit result.

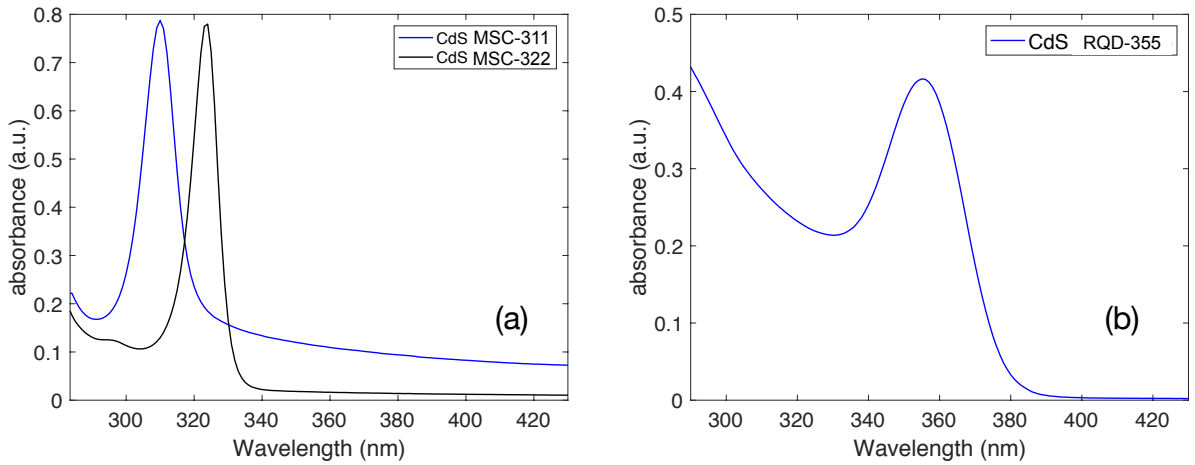

Fig. S8 (a) The absorption spectra of two CdS MSC samples discussed in the paper. (b) The absorption spectrum of the CdS RQD sample[1].

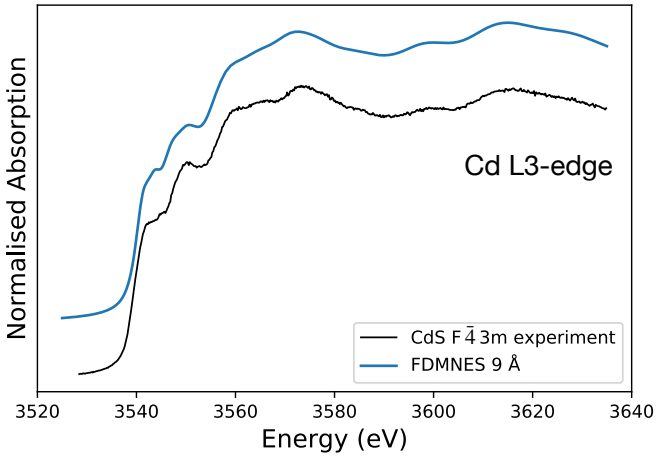

Fig. S9 FDMNES calculation of CdS zinc-blende crystal (space group: $F\bar{4}3m$) with calculating sphere radius of 9 Å around absorbing atom Cd. The result is very close to experiment.

Table S1. The lattice parameters in crystalline CdO (published in the American Mineralogist Crystal Structure Database) and CdS (measured in XRD).

scattering path	N_j	R_j (Å)
Cd-O	6	2.3475
Cd-S	4	2.5118
Cd-Cd from CdS bulk	12	4.1016

Reference

1 L. Tan, A. J. Misquitta, A. Sapelkin, L. Fang, R. M. Wilson, D. S. Keeble, B. Zhang, T. Zhu, F. S. Riehle, S. Han, K. Yu and M. T. Dove, *Nanoscale*, 2019, **11**, 21900–21908.