

**Effect of Al³⁺ Co-Doping on the Dopant Local Structure, Optical Properties, and Exciton
Dynamics in Cu⁺-Doped ZnSe Nanocrystals**

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Table S1. Local structure parameters for Zn and Cu in nanocrystal samples determined after fitting the Fourier transformed data. ZnSe bulk parameters are also shown. Debye-Waller factor (σ^2) was used as a variable parameter whereas S_0^2 value was fixed to 0.81 for Zn and 0.83 for Cu data.

| Sample | Fit # | Path | R (Å) | N | σ^2 (Å ²) | ΔE_0 (eV) | R-factor | χ^2_{red} |
|------------|-------|--------|-----------|---------|-------------------------------|-------------------|----------|----------------|
| ZnSe bulk | | Zn-Se | 2.45 | 4 | 0.003 | -3.16±2.0 | 0.002 | |
| | | Zn-Zn | 4.01 | 12 | 0.005 | | | |
| | | Zn-Se | 4.70 | 12 | 0.006 | | | |
| ZnSe NCs | | Zn-Se | 2.45±0.01 | 4.0 | 0.004 | 3.56±2.0 | 0.007 | |
| | | Zn-Zn | 4.01±0.01 | 9.1±0.4 | 0.006 | | | |
| | | Zn-Se | 4.69±0.01 | 7.6±0.4 | 0.008 | | | |
| ZnSe:Cu | 1 | Cu-Se | 2.33±0.02 | 2.8±0.3 | 0.012 | -13.68±4.0 | 0.025 | 289 |
| | 2 | Cu-Se | 2.35±0.01 | 2.6±0.3 | 0.005 | -4.67±2.0 | 0.005 | 47 |
| | | Cu-O | 1.98±0.02 | 0.9±0.3 | 0.003 | | | |
| | 3 | Cu-Se | 2.34±0.01 | 2.7±0.3 | 0.006 | -5.06±2.0 | 0.006 | 61 |
| | | Cu-O | 1.97±0.02 | 0.9±0.3 | 0.007 | | | |
| | | Cu-Zn1 | 3.63±0.02 | 2.0±0.3 | 0.011 | | | |
| | | Cu-Zn2 | 4.00±0.02 | 4.0±0.3 | 0.013 | | | |
| | | Cu-Zn3 | 4.38±0.02 | 2.0±0.3 | 0.012 | | | |
| | | | | | | | | |
| ZnSe:Cu,Al | 1 | Cu-Se | 2.35±0.02 | 3.6±0.3 | 0.019 | -8.34±3.0 | 0.091 | 190 |
| | 2 | Cu-Se | 2.35±0.02 | 2.8±0.3 | 0.006 | -2.42±1.0 | 0.002 | 99 |
| | | Cu-Se | 2.67±0.02 | 0.9±0.3 | 0.008 | | | |

| | | | | | | | | |
|--|---|--------|-----------|---------|-------|-----------|-------|----|
| | 3 | Cu-Se | 2.35±0.02 | 2.8±0.3 | 0.006 | -3.92±2.0 | 0.002 | 52 |
| | | Cu-Se | 2.67±0.02 | 0.9±0.3 | 0.008 | | | |
| | | Cu-Zn1 | 3.62±0.02 | 2.2±0.3 | 0.009 | | | |
| | | Cu-Zn2 | 4.02±0.02 | 4.5±0.3 | 0.013 | | | |
| | | Cu-Zn3 | 4.39±0.02 | 2.2±0.3 | 0.014 | | | |

For Zn EXAFS, a fit region of $1.1 \leq R (\text{\AA}) \leq 4.7$ was used. In the case of Cu EXAFS for ZnSe:Cu and ZnSe:Cu,Al, fit # 1 and 2 were carried over the r-range $1.3 \leq R (\text{\AA}) \leq 2.7$ for each sample, whereas data were fit in the range $1.1 \leq R (\text{\AA}) \leq 4.4$ for fit # 3 in both the samples. Regarding k -space, a range of $3.5 \leq k (\text{\AA}^{-1}) \leq 14$ was used for Zn EXAFS, whereas a k -space window of $3.5 \leq k (\text{\AA}^{-1}) \leq 11$ was used for Cu EXAFS data.

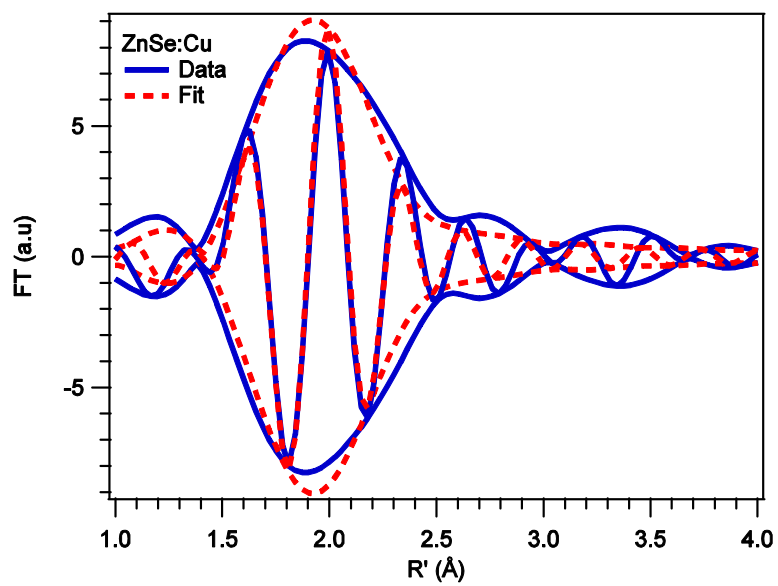


Figure S1. Cu EXAFS data (blue) for ZnSe:Cu along with the fit # 1 (red) without taking into account the surface Cu site but allowing Cu-Se distance to vary.

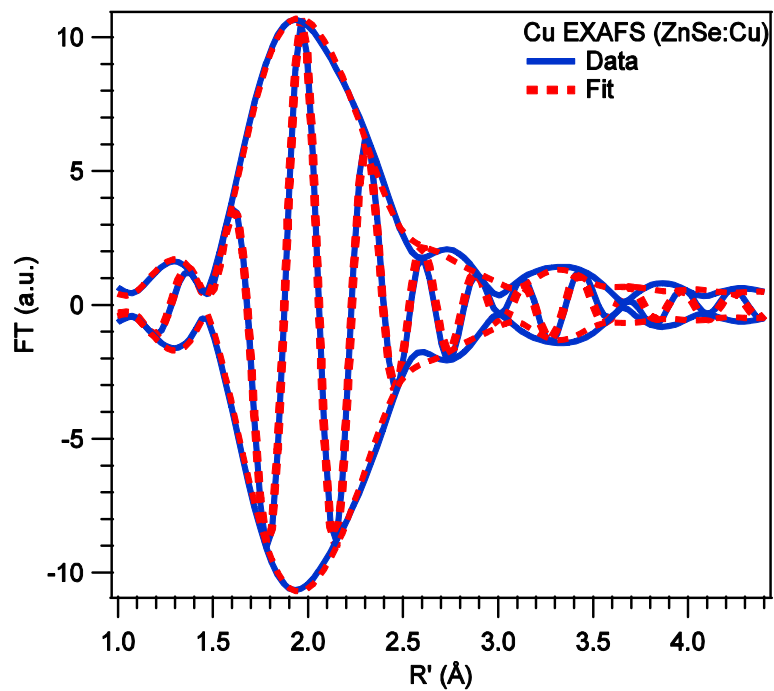


Figure S2. Cu EXAFS data (blue) for ZnSe:Cu along with the fit # 3 (red) carried over a range of 1.1 to 4.4 Å.

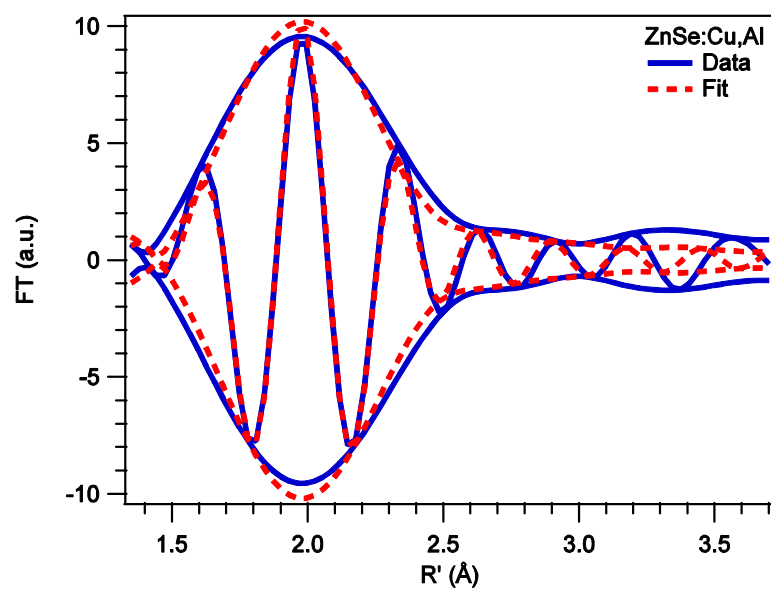


Figure S3. EXAFS data (blue) at Cu K -edge for ZnSe:Cu,Al including the fit # 1 (red) when allowing the Cu-Se distance to vary.

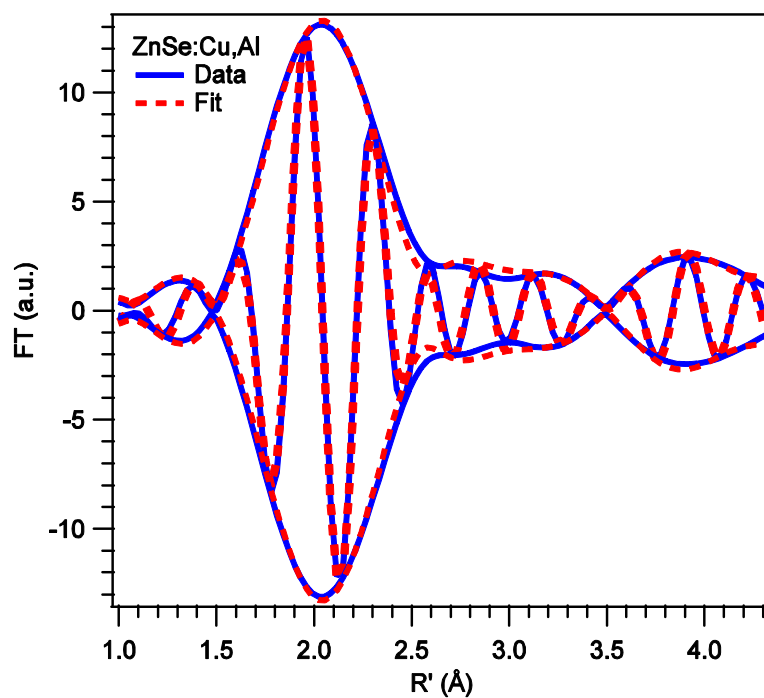


Figure S4. EXAFS data (blue) at Cu *K*-edge for ZnSe:Cu,Al including the fit # 3 (red) carried over the range 1.1 to 4.4 Å.

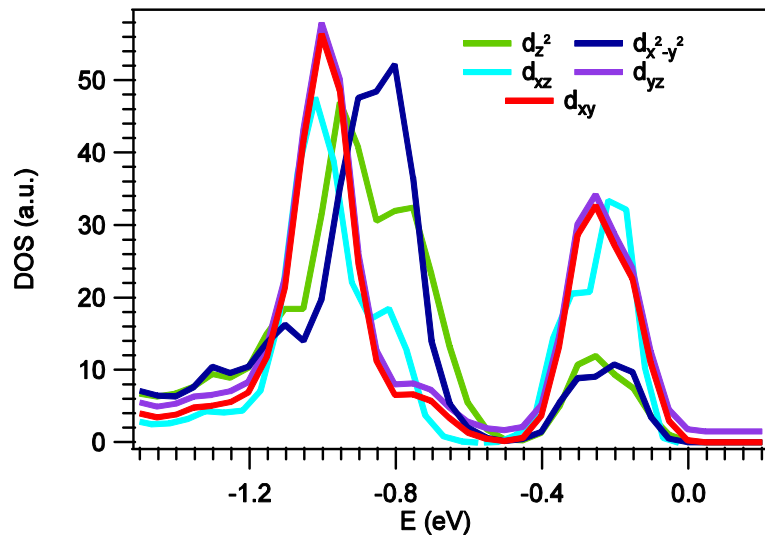


Figure S5. *d* orbital DOS for Cu in ZnSe:Cu 64 atom unit cell in a distorted tetrahedral site adjacent to a Se vacancy.

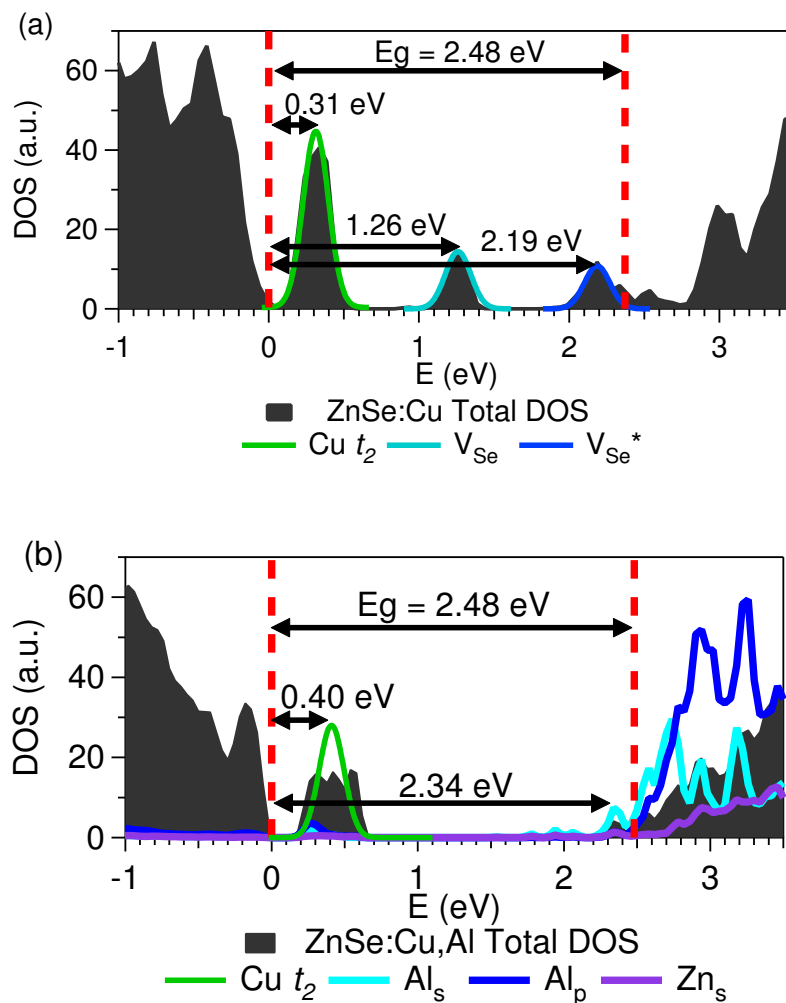


Figure S6. (a) DOS of ZnSe:Cu showing VB and CB edge (red), along with the Gaussian fits for $\text{Cu } t_2$ (green), V_{Se} (light blue), and V_{Se}^* (dark blue). (b) DOS for ZnSe:Cu,Al including the Al sp^3 (light and dark blue), Zn(s), and the Gaussian fit for $\text{Cu } t_2$ (green),