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Atomic-scale structure, cation distribution, and bandgap bowing in $Cu(In,Ga)S_2$ and $Cu(In,Ga)Se_2$

S. Eckner,[1,a)] H. Kämmer,[1] T. Steinbach,[1] M. Gnauck,[1] A. Johannes,[1] C. Stephan,[2] S. Schorr,[2] and C. S. Schnohr[1,b)]
[1]*Institut für Festkörperphysik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany*
[2]*Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin, Germany*

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Mixed chalcopyrite semiconductors like $Cu(In,Ga)S_2$ and $Cu(In,Ga)Se_2$ are characterized by the coexistence of different local atomic arrangements around the S or Se anion. The resulting anion displacement strongly influences the material bandgap. We studied the atomic-scale structure of $Cu(In,Ga)S_2$ as a function of composition using x-ray absorption spectroscopy and valence force field simulations. Applying a specially developed model for not fully random cation distributions, we find that structural relaxation of the anion with respect to In and Ga contributes significantly more to the bandgap bowing observed for $Cu(In,Ga)S_2$ and $Cu(In,Ga)Se_2$ than relaxation with respect to Cu and group-III atoms. © *2013 AIP Publishing LLC*.
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Among the materials used for thin film solar cells, $Cu(In,Ga)Se_2$ has achieved the highest conversion efficiencies. Record values range from almost 19% to more than 20% on the laboratory scale not only for glass substrates[1] but also for flexible polymer foils[2] offering tantalizing new applications in the fields of architecture and product design. The use of the mixed $Cu(In,Ga)(Se,S)_2$ chalcopyrite system is particularly interesting from an industrial point of view as it offers an additional parameter for tuning the material properties by adjusting the composition. The nonlinear dependence of the bandgap energy on the chalcopyrite composition, known as bandgap bowing,[3] is thus of fundamental interest for any technological application.

The bandgap energy is inherently associated with the local structure and depends in a crucial way on the position of the S or Se anion within the unit cell. In defect-free chalcopyrite material, the anion is tetrahedrally coordinated by two Cu atoms and two group-III atoms (In or Ga). Due to the different properties of the neighboring cations, the S or Se anions are typically displaced from their ideal lattice site. This subtle structural variation turns out to have a remarkable influence on the material bandgap.[4–6] In the mixed cation system, the occupation of the two group-III lattice sites with either In or Ga atoms leads to three different first nearest neighbor (1NN) configurations of the anion.[7] For $Cu(In,Ga)Se_2$, it has already been demonstrated in a previous study that the anion position depends sensitively on the particular 1NN environment and that the material is thus characterized by an inhomogeneity of the structural parameters on the atomic scale.[7]

While diffraction measurements provide the long-range crystallographic structure, extended X-ray absorption fine structure spectroscopy (EXAFS) presents a powerful tool to study the element-specific structural parameters of the 1NN environment. Using EXAFS, we have studied the atomic-scale structure of $Cu(In,Ga)S_2$ as a function of composition. Based on these experiments and on previous studies of $Cu(In,Ga)Se_2$,[7] we have modeled all three 1NN configurations. Together with a specially developed model to describe the observed cation distribution, we estimate the contribution of the configuration dependent anion position on the bandgap bowing of $Cu(In,Ga)S_2$ and $Cu(In,Ga)Se_2$. Structural relaxation of the anions with respect to (i) Cu and group-III atoms and (ii) In and Ga atoms both give rise to a bandgap bowing, although we demonstrate that the latter is the dominant effect in these mixed chalcopyrite systems.

$Cu(In,Ga)S_2$ powder samples were synthesized by solid state reaction, using wavelength dispersive X-ray analysis to determine the elemental composition,[8] which is summarized in Table I. Low temperature (17 ± 1 K) EXAFS measurements of the Cu, Ga, and In *K*-edges were performed in transmission mode at Beamline C of HASYLAB, Hamburg, Germany. The data were processed and analyzed with standard parameters[7] using the IFEFFIT code[9] and the corresponding user interfaces ATHENA and ARTEMIS.[10] Phase shifts and scattering amplitudes were calculated using FEFF9.[11] The mean value d (element-specific bond length) and the width σ^2 of the 1NN distance distribution were fitted with all higher cumulants set to zero.[12] The coordination number was fixed to four, whereas the amplitude reduction factor S_0^2 and the threshold energy E_0 were set to average values determined from all samples. The element-specific bond lengths d_{Cu-S}, d_{Ga-S}, and d_{In-S} thus determined are summarized in Table I and plotted in Figure 1(a) as a function of the In/III ratio. The overall uncertainties amount to ± 0.003 Å.

For $CuGaS_2$, d_{Cu-S} is somewhat larger than d_{Ga-S}, equivalent to a small displacement of the S anion towards the group-III lattice sites. In contrast, the anion in $CuInS_2$ is significantly displaced towards the Cu-atoms as seen from the much smaller d_{Cu-S} compared to d_{In-S}. This behavior is in good agreement with previous neutron powder diffraction studies.[8] As evident from Figure 1, the 1NN distances determined with EXAFS for the mixed $Cu(In,Ga)S_2$ compound

a)Email: stefanie.eckner@uni-jena.de
b)Email: c.schnohr@uni-jena.de

TABLE I. $Cu(In,Ga)S_2$ sample composition given by the In/III = In/(In+Ga) and Cu/III = Cu/(In+Ga) ratios determined from wavelength dispersive X-ray analysis (uncertainty ±0.01). The element-specific bond lengths measured at 17 K at the Cu, Ga, and In *K*-edges by EXAFS are also listed (uncertainty ± 0.003 Å).

Sample	In/III	Cu/III	d_{Cu-S} (Å)	d_{Ga-S} (Å)	d_{In-S} (Å)
A	1.00	0.99	2.325	…	2.463
B	1.00	0.99	2.325	…	2.463
C	0.80	0.93	2.324	2.299	2.458
D	0.75	0.90	2.325	2.298	2.461
E	0.64	1.05	2.323	2.297	2.456
F	0.43	1.07	2.320	2.294	2.451
G	0.40	0.97	2.320	2.293	2.452
H	0.30	1.10	2.318	2.292	2.446
I	0.29	0.99	2.318	2.291	2.449
K	0.22	1.07	2.318	2.291	2.442
L	0.00	0.99	2.312	2.286	…

remain close to their ternary values over the whole compositional range, very similar to the trend observed for $Cu(In,Ga)Se_2$ in Figure 1(b). The linear change of the lattice constants observed with diffraction studies[13] and known as Vegard's Law is thus achieved mainly by bond bending, which is known to be energetically favored over bond stretching in tetrahedrally coordinated systems.[7,14,15] The local atomic arrangements of $Cu(In,Ga)S_2$ therefore exhibit a striking deviation from the long-range crystallographic structure and the material is characterized by structural inhomogeneity on the atomic scale even if compositional fluctuations or secondary phases are absent. No effect of the Cu content on the mean 1NN distances is observed for this set of samples with $0.90 < Cu/III < 1.10$ (compare samples

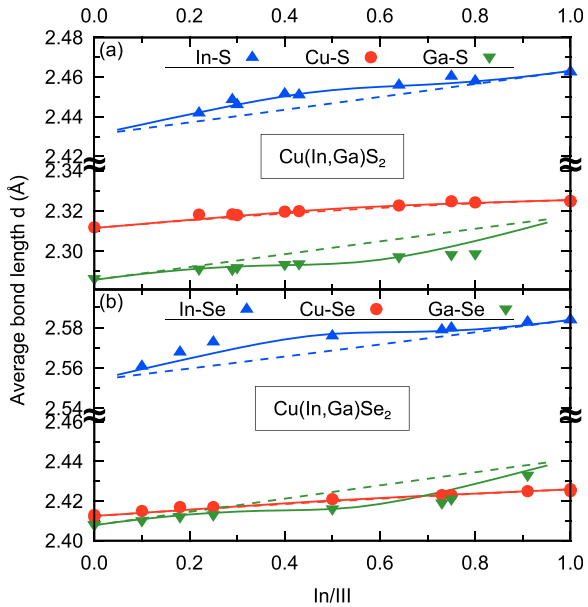

FIG. 1. Element-specific bond lengths measured at the Cu, Ga, and In *K*-edges (symbols) as a function of the In/III ratio for (a) $Cu(In,Ga)S_2$ and (b) $Cu(In,Ga)Se_2$ (see Ref. 7). The dashed lines represent the average element-specific bond lengths obtained from the valence force-field model based on a strictly random occupation of the group-III lattice sites. The solid lines show the results of this model assuming a non-random cation distribution based on the law of mass action. Note the break in scale for the bond length.

F and G or H and I), which is again very similar to the result found for $Cu(In,Ga)Se_2$.[7]

In order to estimate the influence of the atomic-scale structure on the bandgap bowing, the anion displacement has to be determined for each of the three 1NN configurations of the mixed system: (C1) two Cu and two Ga atoms; (C2) two Cu, one Ga, and one In atom; and (C3) two Cu and two In atoms.[7] Using a valence force field approach, we have obtained the minimum energy anion position for each of these configurations together with the corresponding *individual* bond lengths. *Average* element-specific bond lengths were then calculated from the simulated bond lengths for comparison with the EXAFS results which represent the element-specific average over all 1NN configurations.

We used the model by Balzarotti *et al.*[16] as previously described in the simulation of $Cu(In,Ga)Se_2$.[7] The cations are fixed to the ideal lattice sites while assuming a strictly random distribution of In and Ga atoms. Parameters needed to obtain the minimum energy anion position for a given configuration are the lattice constants according to Vegard's law together with the natural lengths and force constants of the individual bonds. Lattice constants were extrapolated to 17 K based on the work of Bodnar and Orlova,[17] yielding $a = 5.34$ Å, $c = 10.48$ Å and $a = 5.51$ Å, $c = 11.11$ Å for $CuGaS_2$ and $CuInS_2$, respectively. Force constants were taken from the literature[18,19] as 90 N/m, 175 N/m, and 150 N/m for the Cu-S, Ga-S, and In-S bonds, respectively, while the bond lengths determined with EXAFS for the ternary compounds were used as the natural lengths of the individual bonds. Parameters for modeling $Cu(In,Ga)Se_2$ were taken from a previous work[7] except for the force constants, which were taken here from literature that includes values for both sulfides and selenides[18,19] to ensure better comparability of the results obtained for both material systems. Thus, 80 N/m, 150 N/m, and 130 N/m were used for the Cu-Se, Ga-Se, and In-Se bonds, respectively.

The simulated average element-specific bond lengths are plotted in Figure 1 as dashed lines. The overall trend of the values determined with EXAFS is reproduced, but differences are visible especially for the Ga-S(e) and In-S(e) bond length, where the simulated curve does not follow the nonlinear increase of the experimental values. This qualitative difference could originate either from neglecting a possible charge redistribution and cation relaxation or from a not fully random cation distribution. Therefore, we considered in more detail the distribution of In and Ga atoms on group-III lattice sites. The frequency of occurrence of each 1NN configuration can be calculated from the simulated individual bond lengths and the measured average Ga-S(e) or In-S(e) bond lengths. The results for the mixed configuration C2 are plotted in Figure 2 (symbols) as a function of the In/III ratio. Values obtained from the Ga-S(e) or In-S(e) bond lengths are consistent with each other confirming the validity of this approach. Obviously, this mixed configuration occurs more often, than expected for a strictly random occupation of the group-III lattice sites, which would lead to the binomial distribution given by the dashed lines in Figure 2. Consequently, the pure Ga and pure In configurations, C1 and C3, respectively, occur less often than for a strictly random distribution of the group-III atoms (not shown). This is

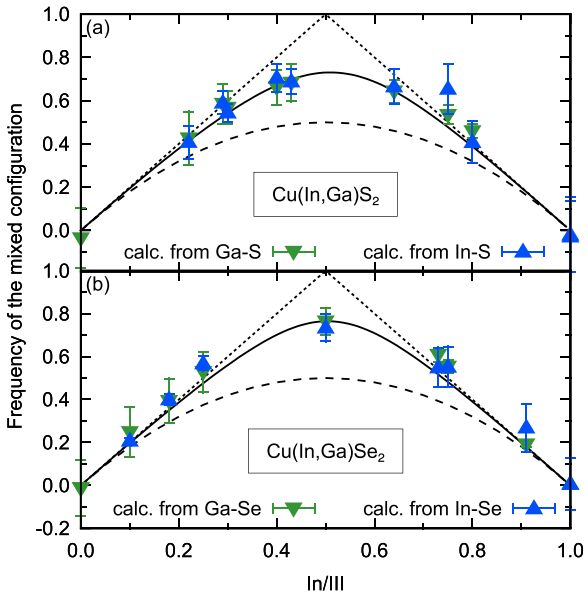

FIG. 2. Frequency of occurrence of the mixed 1NN configuration as a function of the In/III ratio for (a) $Cu(In,Ga)S_2$ and (b) $Cu(In,Ga)Se_2$ calculated from the measured Ga or In bond lengths (symbols). The solid lines represent the frequency of occurrence obtained from our model based on the law of mass action. Maximum entropy limit (binomial distribution, dashed lines) and minimum energy limit (dotted lines) are given for comparison.

in contrast to the demixing predicted by Ludwig *et al.* based on theoretical Monte Carlo calculations[20] but can be explained by the strain energy associated with the different configurations. For lattice constants given by Vegard's Law, the simulated strain energy is lower for two C2 configurations than for one C1 and one C3 configuration over the whole compositional range. Energy minimization would thus lead to the maximum number of C2 environments possible for a given In/III ratio, as shown by the dotted lines in Figure 2. In reality, the frequency of occurrence of the mixed configuration is determined by a competition between energy minimization (dotted lines) and entropy maximization corresponding to a strictly random distribution (dashed lines). This competition can be modeled by a law of mass action approach leading to a frequency of the mixed configuration of

$$\nu_{C2} = M\left[1 - \sqrt{1 - 4f(1-f)/M}\right],$$

where f denotes the In/III ratio. The factor

$$M(f,T) = \exp\left(-\frac{\Delta E(f)}{k_B T}\right) \Big/ \left(\exp\left(-\frac{\Delta E(f)}{k_B T}\right) - 1\right)$$

depends on the equilibrium temperature T, the Boltzmann constant k_B, and the difference in strain energy $\Delta E(f)$ between two mixed configurations ($2 \cdot C2$) or one pure Ga and one pure In configuration ($C1 + C3$). The only unknown parameter in this expression is the equilibrium temperature T, which can be used to fit the data. The resulting curves are shown as solid lines in Figure 2. They correspond to equilibrium temperatures of 360 K and 260 K for $Cu(In,Ga)S_2$ and $Cu(In,Ga)Se_2$, respectively, and represent the data very well. Consequently, these fitted distributions lead to average element-specific bond lengths (Fig. 1, solid lines) much closer to the EXAFS values than the simulation based on a strictly random cation distribution (Fig. 1, dashed lines). Most remarkably, the model captures some of the nonlinearity observed for both $d_{In-S(e)}$ and $d_{Ga-S(e)}$. The agreement between simulated and measured bond lengths is thus significantly improved just by assuming a not fully random In and Ga distribution.

The equilibrium temperature identified by fitting the frequency of the mixed configuration can be understood as the temperature at which the cation distribution is frozen in during the cooling of the material after the synthesis. At lower temperatures, the mobility of In and Ga atoms does not suffice for an effective redistribution. The influence of this theoretical temperature on the cation distribution is relatively small leading to a large uncertainty of approximately 100 K for the equilibrium temperature determined in the fit. Nevertheless, the higher value of 360 K for $Cu(In,Ga)S_2$ and the lower one of 260 K for $Cu(In,Ga)Se_2$ reflect the relation for melting and Debye temperatures observed for these two material systems.[21]

Based on the simulated minimum energy anion position, one can now calculate the displacement of the anion for each 1NN configuration and thus the influence of the atomic-scale structure on the bandgap bowing. As previously discussed,[7] two different relaxation effects have to be distinguished, namely a displacement of the anion with respect to Cu and group-III atoms, u, and a displacement of the anion with respect to In and Ga atoms, δ. While the displacement u is present in all three 1NN configurations, different group-III atoms and hence a nonzero δ are found only in the mixed configuration. In both cases, the *average* displacement shows a nonlinear change with increasing In/III ratio and therefore contributes to the bandgap bowing.

The nonlinear change of the bandgap with composition in mixed semiconductor systems originates from three different effects: (i) volume deformation, (ii) charge redistribution, and (iii) anion relaxation.[22,23] Regarding only the latter, the correlation between the anion displacement, u and δ, and the associated contribution to the bandgap bowing is by a simple coefficient each. Average values of $d\Delta E/du = 20\,eV$ and $d\Delta E/d\delta = 1.5\,eV$ were taken from literature as discussed previously for $Cu(In,Ga)Se_2$.[7] The resulting contributions of the average anion displacement to the bandgap bowing, ΔE^{Cu-III} and ΔE^{In-Ga}, are shown in Figure 3 for the fitted cation distribution (solid line) and a strictly random cation distribution (dashed line).

In both $Cu(In,Ga)S_2$ and $Cu(In,Ga)Se_2$, the cation distribution has a considerable influence on the values of ΔE^{In-Ga} but does not change the fact that the anion displacement δ contributes significantly to the experimentally observed bandgap bowing. Interestingly, the small nonlinear part of u is very sensitive to variation of the simulation parameters and its contribution to the bandgap bowing remains small despite the large coefficient $d\Delta E/du$, i.e., despite the remarkable influence of this displacement type on the bandgap energy.

In conclusion, the composition dependent atomic-scale structure of $Cu(In,Ga)S_2$ was studied using low temperature X-ray absorption spectroscopy and valence force field simulations. We find that the element-specific bond lengths are

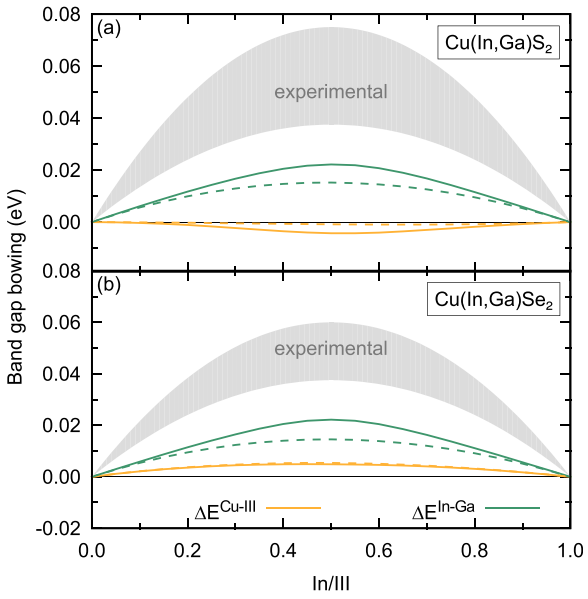

FIG. 3. Bandgap bowing, i.e., the energy difference ΔE between the weighted average of the ternary bandgaps and the bandgap of the mixed compound, versus the In/III ratio. Plotted are the contributions originating from structural relaxation of the anions with respect to Cu and group-III atoms, $\Delta E^{\mathrm{Cu-III}}$, and with respect to In and Ga atoms, $\Delta E^{\mathrm{In-Ga}}$, modeled using the binomial cation distribution (dashed lines) or the distribution according to the law of mass action (solid lines). The range of experimentally determined ΔE values (shaded area) is also shown (see Ref. 3).

very different from each other and remain nearly constant over the whole compositional range. As already observed for $Cu(In,Ga)Se_2$, the anion position of $Cu(In,Ga)S_2$ thus depends sensitively on the neighboring cation configuration and the mixed system is characterized by the coexistence of different structural parameters on the atomic scale. Applying a specially developed model of a not fully random cation distribution, we find that structural relaxation of the anion with respect to In and Ga contributes significantly more to the experimentally observed bandgap bowing of $Cu(In,Ga)S_2$ and $Cu(In,Ga)Se_2$ than structural relaxation of the anion with respect to Cu and group-III atoms.

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