Parameterization of $CuIn_{1-x}Ga_xSe_2$ ($x = 0$, 0.5, and 1) energy bands

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ABSTRACT

Parameterization of the electronic band structure of $CuIn_{1-x}Ga_xSe_2$ ($x = 0$, 0.5, and 1) demonstrates that the energy dispersions of the three uppermost valence bands [$E_j(\mathbf{k})$; $j = v1$, $v2$, and $v3$] are strongly anisotropic and non-parabolic even very close to the Γ-point valence-band maximum $E_{v1}(\mathbf{0})$. Also the lowest conduction band $E_{c1}(\mathbf{k})$ is anisotropic and non-parabolic for energies ~0.05 eV above the band-gap energy. Since the electrical conductivity depends directly on the energy dispersion, future electron and hole transport simulations of $CuIn_{1-x}Ga_xSe_2$ need to go beyond the parabolic approximation of the bands. We therefore present a parameterization of the energy bands, the **k**-dependency of the effective electron and hole masses $m_j(\mathbf{k})$, and also an average energy-dependent approximation of the masses $m_j(E)$.

1. Introduction

The effective electron and hole masses $m_j(\mathbf{k})$ are very often utilized to represent the shape of the energy bands, thus assuming parabolic energy dispersion. However, typically these effective masses describe the energy bands only near the considered **k**-point, whereas away from this point the bands can be strongly non-parabolic. If the non-parabolicity occurs within the energy region of temperature statistics (~0.03 eV), band-filling effects (~0.1 eV) or sunlight absorption and hot electron transport (~0.5 eV), the exact shape of the bands has to be considered when analyzing modeled and measured results involving for instance electron transport or band filling of the materials.

In this work, we have parameterized the lowest conduction band (CB) and the three uppermost valence bands (VBs) of $CuIn_{1-x}Ga_xSe_2$ ($x = 0$, 0.5, and 1; thus $CuInSe_2$, $CuIn_{0.5}Ga_{0.5}Se_2$, and $CuGaSe_2$) in order to better describe the non-parabolic and anisotropy of the energy bands $E_j(\mathbf{k})$. We report that the three topmost VBs ($E_j(\mathbf{k})$ with $j = v1$, $v2$, and $v3$) are very non-parabolic and anisotropic for energies $E_j(\mathbf{k}) < E_{v1}(\mathbf{0}) - 0.01$ eV. This non-parabolicity is mainly due to the split of degeneracy caused by the spin-orbit and crystal-field interactions. Also the lowest CB ($j = c1$) starts to become non-parabolic and anisotropic for energies above $E_{c1}(\mathbf{k}) > E_{c1}(\mathbf{0}) + 0.05$ eV. However, this non-parabolicity is a normal effect of the Bloch-periodic crystal potential. With the parameterized energy dispersion, the **k**-dependent electron and hole masses are analyzed, and especially the hole masses of the two topmost VBs show a strong **k**-dependency. We also present an energy-dependent approximation of the masses $m_j(E)$ that can be used in already existing analysis methods involving the parabolic approximation and/or strong band-filling effects.

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2. Parameterization of the energy bands

The employed electronic band structure originates from an all-electron and full-potential linearized augmented plane wave calculation [1,2] using the Engel–Vosko (EV) exchange-correlation potential within the generalized gradient approximation [3]. We have recently shown [4] that the regular local density approximation (LDA) underestimates the effective masses for materials with small direct energy gaps; this is due to a too strong coupling between the CB and VBs. For GaAs for instance (which is the group-III-V analogue to $CuGaSe_2$, having also similar band-gap energies), the measured Γ-point electron mass is $m_c = 0.067\ m_0$, the heavy-hole mass (averaged over **k**-direction) is $m_{hh} = 0.51\ m_0$, the light-hole mass is $m_{lh} = 0.08\ m_0$, and the spin-orbit split-off hole mass is $m_{hh} = 0.15\ m_0$ [5]. LDA underestimates the masses [6]: $m_c = 0.018\ m_0$, $m_{hh} = 0.55\ m_0$, $m_{lh} = 0.01\ m_0$, and $m_{so} = 0.08\ m_0$, whereas the EV potential generates much more accurate masses [6]: $m_c = 0.061\ m_0$, $m_{hh} = 0.55\ m_0$, $m_{lh} = 0.07\ m_0$, and $m_{so} = 0.16\ m_0$. The reason for the improved energy dispersion of the EV potential is that this exchange-correlation model generates better interaction potentials but less accurate total energies compared with LDA.

The employed calculation from Refs. [1] and [2] shows (solid lines in Fig. 1) that the VBs are anisotropic in an energy region about 0.0–1.0 eV below the VB maximum (VBM). In the (110) and (112) directions the two uppermost VBs are very flat, and they reach the Brillouin zone (BZ) edge at about −0.5 eV. A closer look at the VBM (Fig. 2; solid lines) reveals that the energy bands start to become very non-parabolic already in the 0.01–0.1 eV region below VBM. The parabolic approximation of ellipsoidal energy bands reads

$$E_j^{pb}(\mathbf{k}) = E_j(\mathbf{0}) \pm \left[\frac{\tilde{k}_x^2 + \tilde{k}_y^2}{m_j^{\perp}} + \frac{\tilde{k}_z^2}{m_j^{\parallel}}\right] \quad \text{with} \quad \tilde{k}_\alpha^2 = \frac{\hbar^2 k_\alpha^2}{2e}, (\alpha = x, y \text{ and } z), \tag{1}$$