First-principles study of deformation behavior and structural defects in $CuInSe_2$ and $Cu(In,Ga)Se_2$

N. I. Medvedeva,[1] E. V. Shalaeva,[1] M. V. Kuznetsov,[1] and M. V. Yakushev[2]
[1]*Institute of Solid State Chemistry, Ekaterinburg, Russia*
[2]*Department of Physics, Strathclyde University, Glasgow, United Kingdom*
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Electronic structure and total-energy calculations have been performed for $CuInSe_2$ and $Cu(In,Ga)Se_2$ using density-functional theory with generalized gradient corrections. To understand the fracture and deformation behavior in chalcopyrites, we calculated the cleavage and generalized stacking fault energies in $CuInSe_2$ and $Cu(In,Ga)Se_2$ and demonstrated a brittle character of crack propagation. Antiphase boundary and intrinsic stacking fault defects have low formation energies and are quite probable in these chalcopyrites. The main slip system and preferable cleavage plane should be $\langle\bar{1}10\rangle(112)$ and (112), respectively. For the $\langle 110\rangle(001)$ and $\langle\bar{1}10\rangle(112)$ dislocations in $CuInSe_2$, we predict a strong tendency for splitting in two partials.

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I. INTRODUCTION

Chalcopyrite $CuInSe_2$-based semiconductors are among the most successful materials used as an absorber layer in thin-film solar cells. The optical and electrical properties of these compounds strongly depend on alloying with other chalcopyrites ($CuGaSe_2$, $CuInSe_2$) as well as on the presence of intrinsic defects. The effect of point defects, especially vacancies, on the electronic properties has been extensively investigated (see Refs. 1 and 2 and references therein), however, very little attention has been paid to another type of crystal defects—dislocations, which are line defects and strongly affect the mechanical properties. Furthermore, dislocations may also affect the electrical properties due to the production of defect levels in the band gap. Currently the study on the mechanical properties of $CuInSe_2$ is limited to reports on microhardness[3,4] and analysis of the elastic characteristics;[5,6] very few studies are concerned with the dislocation structure and stacking faults either in single crystals or thin films.[7,8]

Theoretical atomistic simulation of the deformation behavior is very informative and important for understanding the mechanical properties of solids. The deformation models developed in Refs. 9–11 in combination with *ab initio* calculations have been successfully used for studying the ductile and brittle properties of metals and ordered intermetallics.[12,13] Using the Rice-Thompson criterion, the brittle-ductile behavior is analyzed by the comparison of two competitive processes: (1) crack opening (brittle fracture) and (2) emission of a dislocation near the crack tip (plastic deformation).[10,11] Two energy characteristics are calculated using first-principles methods to describe these processes quantitatively: (i) the cleavage energy, which models the fracture; and (ii) the unstable stacking fault (SF) energy, which represents the maximum energy for the sliding of atomic planes and simulates the lattice resistance to the dislocation emission.[9–11] A comparison of these energy parameters makes it possible to predict a brittle crack propagation or ductile behavior and to explain the microscopic fracture mechanism. Another important characteristic often used in theoretical and experimental studies is the energy of antiphase boundary (APB) defects, which determines the possibility of the dissociation of perfect dislocations. However, the formation energies of stacking fault defects in $CuInSe_2$ and the effect of gallium substitution were not investigated.

The aim of this paper is to present a theoretical study of structural defects and the deformation behavior in $CuInSe_2$ and $Cu(In,Ga)Se_2$. Here we calculated the generalized stacking fault (GSF) energies, which correspond to the total energy changes with a rigid shift of a crystal partly in the slip plane (the SF and APB energies are determined by GSF curve at some values of fault vector). The GSF energies are generally considered as key parameters, which determine the structure and mobility of dislocations.[9] Our approach is based on an *ab initio* description of the electronic structure, which allows an accurate calculation of the total energies.

The structure of this paper is as follows: both the theoretical method and crystal models used in our calculations are briefly described in Sec. II. The calculated results for the energy slip and cleavage characteristics for the main (001) and (112) planes in $CuInSe_2$ are presented in Sec. III. The formation of different stable stacking fault defects, such as the antiphase boundary on the (001) and (112) planes, and intrinsic defects on the (112) plane are modeled, and the possibility for the dissociation of a perfect dislocation into two superpartials is discussed. The comparison of the cleavage and unstable stacking fault energies allows us to analyze also the brittle-ductile behavior of $CuInSe_2$ in the framework of the Rice-Thompson criteria. Finally, the effect of the substitution of indium with gallium on the cleavage and GSF energies is investigated in order to model its influence on the mechanical properties of $CuInSe_2$. Concluding remarks and a summary are given in Sec. IV.

II. METHOD AND MODELS

A. Calculation details

For the electronic structure and total energy calculations we used the first-principles full-potential linear muffin-tin

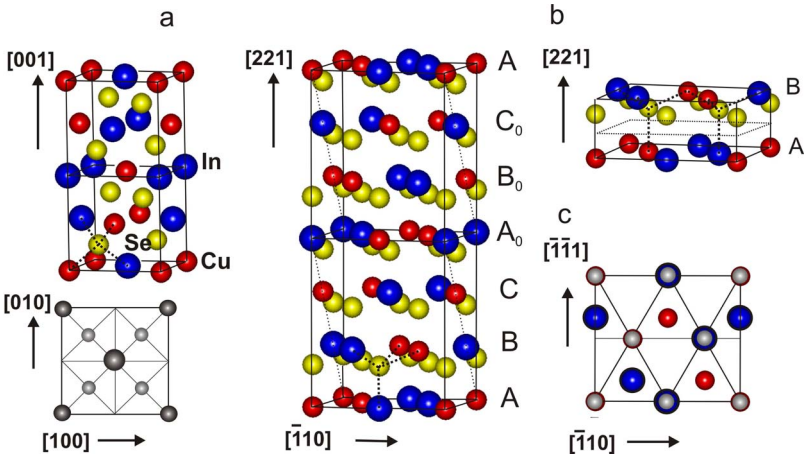

FIG. 1. (Color online) The structure of chalcopyrite $CuInSe_2$: (a) orientation along [001]; (b) orientation along [221], and (c) the structure projection on the (112) plane.

orbital (FLMTO) method without any shape approximation for the potential and charge density.[14] Taking into account the interstitial region and nonoverlapping muffin-tin spheres is important for the calculation of the total energy changes on atomic relocations, which model the cleavage and sliding processes. All calculations of the cleavage and GSF energies presented here have been performed using the generalized gradient approximation (GGA) with the Perdew-Burke-Wang function[15] for the exchange correlation. This approach is known to describe the ground state properties such as lattice parameters, cohesive energy, and elastic moduli more accurately. The standard triple-kappa basis (−0.01, −1.0, and −2.3 Ry) and the angular momentum cutoff for the interstitial fitting $l_{\max}=5$ and inside muffin-tin spheres $l_{\max}=6$ were taken. The muffin-tin radii were chosen to be 2.2 a.u. for Cu, In, and Se spheres.

Previous calculations of the band structure within the framework of local-density approximation (LDA) (VASP code) did not predict the semiconducting properties of $CuInSe_2$ ($E_g^{\mathrm{LDA}}=0$ eV) and gave a low value of the band gap for $CuGaSe_2$ ($E_g^{\mathrm{LDA}}=0.25$ eV).[16] For the interpretation of the results, a shift of the LDA conduction band has been introduced as $\Delta E_g=E_g^{\mathrm{exp}}-E_g^{\mathrm{LDA}}$, where the experimental values, E_g^{exp}, are equal to 1.04 and 1.71 eV for $CuInSe_2$ (Ref. 17) and $CuGaSe_2$,[18] respectively. Our FLMTO-GGA calculations for the experimental crystal parameters [$a=5.781$ Å, $c=11.609$ Å, $u=0.2281$ (Ref. 19) for $CuInSe_2$, and $a=5.596$ Å, $c=11.004$ Å, $u=0.2423$ for $CuGaSe_2$ (Ref. 20)] also gave a zero band gap for $CuInSe_2$ and $E_g=0.28$ eV for $CuGaSe_2$. The cohesive energies of 15.14 and 16.69 eV obtained for $CuInSe_2$ and $CuGaSe_2$, respectively, are slightly less than the theoretical LDA results of 16.49 and 17.06 eV, showing the usual LDA overestimation by 0.5–1.5 eV.[16] The experimental value for cohesive energy in $CuInSe_2$ is 13.5 eV.[21] For calculations of cleavage and generalized stacking fault energies we used the experimental values of crystal parameters. As an accuracy test we performed the total energy versus cell volume minimization for the experimental values of a/c and u, and found that the equilibrium volume $V_0=388.74$ Å^3 and bulk modulus $B_0=68.6$ GPa in $CuInSe_2$ are in a good agreement with other *ab initio* results [$V_0=386.87$ Å^3,[16] $B_0=70.9$ GPa,[22] $B_0=64.01$ GPa (Ref. 23)] and experimental data [$V_0=387.97$ Å^3,[19] $B_0=55.8$ GPa,[24] $B_0=53.6$ GPa (Ref. 25)].

B. Crystal models

The cleavage energy γ_C is determined to be the energy required to split the crystal into two semi-infinite parts, i.e., γ_C is the energy required for creating two surfaces. A comparison of this energy for different planes allows one to determine the favorable plane for the fracture. The energy of a generalized stacking fault defect was modeled by the total energy change caused by a rigid shift of a half of the crystal along a direction in the chosen slip plane. Our goal is to give the qualitative predictions of brittle or ductile behavior, and so we did not take into account the reconstruction of the surface layers at the cleavage and the effect of atom relaxation on the GSF energies.

The cleavage and slip energetics were considered for two most important (112) and (001) planes in the chalcopyrite, which correspond to (111) and (001) planes, respectively, in the basic sphalerite structure (the sphalerite structure can be derived from chalcopyrite by disordering copper and indium atoms in the metallic sublattice[26,27]). For analysis of the fracture processes in the (001) plane, the chalcopyrite tetragonal structure [D_{2d} (Ref. 12)] is considered in the standard crystallographic coordinate system with orientation along a [001] axis as shown in Fig. 1(a). All positions of the cleavage (001) plane are equivalent. The initial unit cell for the simulation of these processes for the (001) plane was chosen similar to that used earlier for the calculations of the electronic structure of the ternary chalcopyrites ABX_2.[28] The translational vectors were: $\mathbf{a}_1=a(1,0,0)$, $\mathbf{a}_2=a(0,1,0)$, and $\mathbf{a}_3=a(0.5,0.5,\eta)$, where a is the cubic lattice parameter and η is the parameter of the tetragonal distortion, $\eta=c/2a$. To estimate the cleavage energy we calculated the dependence of the total energy of the tetragonal supercell with four unit cells of $CuInSe_2$ separated by a vacuum slab. We limited the thickness of the vacuum slab to two intralayers as this was shown[12,13,29] to be enough to reproduce γ_C correctly. The modeling of the crystal shift by the corresponding fault vector $\mathbf{u}(u_1,u_2,0)$ was performed using the triclinic supercell with two constant translation vectors and a variable vector: $\mathbf{a}_1=a(1,0,0)$, $\mathbf{a}_2=a(0,1,0)$, $\mathbf{a}_3=a(0.5+u_1,0.5+u_2,\eta)$. The substitution of one indium atom in the cleavage or slip planes by a gallium atom simulated the Ga doping effect.

For the cleavage and slip simulations on the (112) plane, the chalcopyrite structure is considered in a coordinate sys-

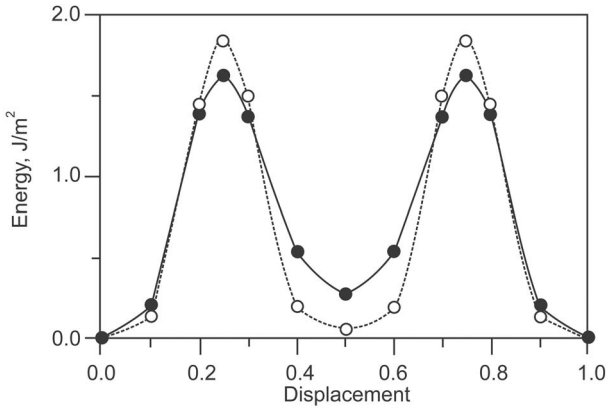

FIG. 2. The GSF energies for displacement u along the direction $\langle 110\rangle(001)$ for $CuInSe_2$ (black circle) and $Cu(InGa)Se_2$ (white circle).

tem with the z axis along the [221] direction. In the basis (112) plane the translation vectors have been taken along the directions $[\bar{1}\bar{1}1]$ and $[\bar{1}10]$ as shown in Figs. 1(b) and 1(c). The supercell includes six layers of the metal atoms (Cu, In, Ga) with the packing sequence—$ABCA_0B_0C_0$ [ordering of the metallic atoms Cu and In(Ga) in the $A_0B_0C_0$ layers is opposite to that in the A, B, C layers]. In the present calculations the supercell was limited to either two or three layers of the metallic atoms and the corresponding number of selenium layers. We considered the plane shear and cleavage to take place between two metallic and selenium layers with an interlayer distance of 2.51 Å.

III. RESULTS AND DISCUSSION

A. GSF energies for (001) plane

The calculated GSF energies for the different fault vectors **u**, corresponding to the slip $u\langle 100\rangle(001)$, $\mathbf{u}\langle 110\rangle(001)$ systems in $CuInSe_2$, and $Cu(In,Ga)Se_2$, are shown in Figs. 2 and 3. The GSF energy curve for a crystal shift along the $\langle 110\rangle(001)$ direction (Fig. 2) exhibits a maximum at $u/b=0.25$ (where **b** is the Burgers vector); this value defines the energy of an unstable stacking fault, γ_{US}. The deep local minimum at $u/b=0.5$ [$1/2\langle 110\rangle(001)$ slip] corresponds to the formation of an antiphase boundary defect, when a change in the type of atom ordering takes place [copper sites are taken by In(Ga) and vice versa], while the selenium sublattice transforms into itself. The low value of the antiphase boundary energy $E_{APB}=0.26$ J/m^2 for $CuInSe_2$ indicates that the formation of stable antiphase defects is quite probable (for example, much higher APB energies of 1.0 and 0.7 J/m^2 were found in NiAl and FeAl, respectively[12]).

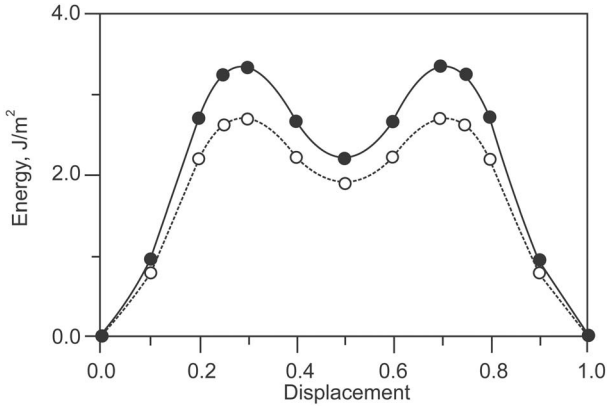

FIG. 3. The GSF energies for displacement u along the direction $\langle 010\rangle(001)$ for $CuInSe_2$ (black circle) and $Cu(InGa)Se_2$ (white circle).

The value of E_{APB} plays an important role in the dislocation mobility for ordered crystals, because it determines the trend for the perfect dislocation to split into two partials (with smaller Burgers vectors) joined by the APB stacking fault defect. The motion of such a pair of partial dislocations is energetically more favorable for ordered crystals than the motion of perfect dislocations with larger Burgers vectors. According to the elasticity theory, the width of the splitting, δ, is inversely proportional to the APB energy, $\delta \sim \mu b_i^2/E_{APB}$, where μ is the shear modulus. The perfect dislocation is not split and its motion is impeded in the case of high value of E_{APB}, when the distance between the partials is close to the core width.[12] The low APB energy obtained for $CuInSe_2$ and the large Burgers vector favor a large splitting width and one can suggest that the perfect dislocation $\langle 110\rangle(001)$ may be split into two $1/2\langle 110\rangle(001)$ partials.

For $\langle 100\rangle(001)$ slip (Fig. 3), the GSF maximum (γ_{US}) also corresponds to a shift by $u/b=0.25$ and the local minimum at $\mathbf{u}/b=0.5$ is significantly shallower. The energy of this structural defect, which is not APB in the chalcopyrite structure, is an order of magnitude higher than that for $1/2\langle 110\rangle(001)$ slip and this defect is unstable. The perfect $\langle 100\rangle(001)$ dislocation probably has a compact core and does not split into partials. The motion of this perfect dislocation is unlikely because of the high values of shear stress and γ_{US}.

Thus, the $1/2\langle 110\rangle(001)$ slip forming the antiphase boundary is energetically favorable for the (001) plane in $CuInSe_2$. The low APB energy points to the possibility of a splitting of the perfect $\langle 110\rangle$ dislocation into the $1/2\langle 110\rangle$ partials. The available experimental data support these suggestions. Transmission electron microscopy has been used to study the dislocation structure in single crystals of $CuInSe_2$ grown by the vertical Bridgman technique.[7] The main type of the defect identified on the (001) plane is a superstructural dislocation, i.e., pairs of partial dislocations with Burgers vectors $a/2\langle 110\rangle$ joined by the antiphase boundary.[7]

A comparison of the results for the different slip directions on the (001) plane in $CuInSe_2$ and $Cu(In,Ga)Se_2$ shows that the partial In substitution with Ga does not result in significant changes of the GSF energetics for $\langle 100\rangle(001)$. However, gallium significantly reduces the APB energy corresponding to the $1/2\langle 110\rangle(001)$ slip (Table I). This effect may be due to the appearance of short covalent bonds in In(Ga)-Se tetrahedron near the antiphase boundary plane when In (Ga) replaces copper atom in the rigid shift model without taking into account the crystal relaxation. As known, the metal-selenium distances in the ideal lattice are different in $CuInSe_2$ ($d_{Cu\text{-}Se}=2.421$ Å, $d_{In\text{-}Se}=2.595$ Å) and equal in $CuGaSe_2$ ($d_{Cu\text{-}Se}=2.417$ Å, $d_{Ga\text{-}Se}=2.417$ Å) (Ref. 23) and

TABLE I. The cleavage γ_C, unstable stacking fault γ_{US}, and antiphase boundary E_{APB} energies (J/m^2) for $CuInSe_2$ and $Cu(In,Ga)Se_2$.

System	γ_C	γ_{US}	γ_C/γ_{US}	E_{APB}
$CuInSe_2$, $\langle 100\rangle(001)$	5.20 (001)	3.13 $\langle 100\rangle$	1.66	
$Cu(In,Ga)Se_2$, $\langle 100\rangle(001)$	5.31 (001)	2.74 $\langle 100\rangle$	1.94	
$CuInSe_2$, $\langle 110\rangle(001)$	5.20 (001)	1.63 $\langle 110\rangle$	3.19	0.26
$Cu(In,Ga)Se_2$, $\langle 110\rangle(001)$	5.31 (001)	1.83 $\langle 110\rangle$	2.90	0.05
$CuInSe_2$, $\langle \bar{1}10\rangle(112)$	3.44 (112)	0.74 $\langle \bar{1}10\rangle$	4.65	0.15
$Cu(In,Ga)Se_2$, $\langle \bar{1}10\rangle(112)$	3.52 (112)	0.80 $\langle \bar{1}10\rangle$	4.40	0.12

the formation of short bonds is more energy preferable for the Ga→Cu replacement than for In→Cu because of $d_{Cu\text{-}Se}(CuInSe_2) \approx d_{Cu\text{-}Se}(CuGaSe_2) \approx d_{Ga\text{-}Se}(CuGaSe_2)$.

The core of the $\langle 110\rangle$ dislocation should not be compact because its splitting width δ increases with a reduction of the APB energy. Therefore, the tendency of the dislocation to split into partials sharply increases. However, in this case one can expect a spread of the APB defect region on the (001) plane. The presence of extended antiphase boundaries in the crystal can affect its mechanical properties, initiating the effect of solid solution hardening.[30]

B. GSF energies for (112) plane

The $\langle \bar{1}10\rangle(112)$ slip in $CuInSe_2$ is characterized by lower values of γ_{US} and E_{APB} than slip in the (001) plane (Fig. 4, Table I). A very small stress, which is almost an order of magnitude smaller than that for slip calculated on the (001) plane, as well as the possibility of splitting the perfect dislocation into $1/2\langle \bar{1}10\rangle(112)$ partials (low value of E_{APB} testify

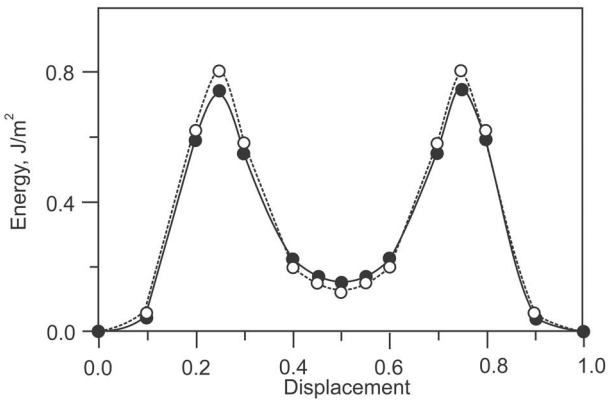

FIG. 4. The GSF energies for displacement along the direction $\langle \bar{1}10\rangle(112)$ for $CuInSe_2$ (black circle) and $Cu(InGa)Se_2$ (white circle); the shift was considered in the Cu-In layer, orientation $[\bar{2}\bar{2}\bar{1}]$.

that this deformation mode is the most preferable among the slip systems considered here. For the sphalerite structure (disordered chalcopyrite), the corresponding $\langle \bar{1}10\rangle(111)$ slip was also found to be the most favorable.[26] Our calculations demonstrate a significant crystallographic anisotropy of the antiphase boundary energies in $CuInSe_2$: the APB energies for the (001) and (112) planes differ by a factor of 2. The APB energy anisotropy is apparently associated with the anisotropic character of the atomic interactions, which plays a decisive role in the order-disorder phase transition of the sphalerite-chalcopyrite type in the ternary selenides.[31]

For the (112) plane in $CuInSe_2$ the low energies of E_{APB} were obtained not only for the antiphase boundary stacking fault $1/2\langle \bar{1}10\rangle(112)$ defect, but also for the intrinsic stacking fault defects ($E_{ISF}=0.09$ and $0.11\ J/m^2$ for the structural models $ABC/B_0C_0A/CA_0B_0/\ldots$ and $AB/A_0B_0/AB/\ldots$, respectively). It convincingly shows that the $1/2\langle \bar{1}10\rangle(112)$ dislocation should split into superpartials with the Burgers vectors $1/12\langle \bar{2}4\bar{1}\rangle$ and $1/12\langle \bar{4}21\rangle$. Such dislocation reaction is similar to that found in both sphaleritelike and face-centered lattices: $1/2\langle \bar{1}10\rangle = 1/6\langle \bar{1}2\bar{1}\rangle + 1/6\langle \bar{2}11\rangle$.[26] The dislocation reaction, which corresponds to the formation of stacking faults on the (112) plane, is realized in both single crystals and thin films of the ternary selenides. As a rule, the concentration of these defects depends on the temperature and method of the crystal or film growth.[32]

Then, we consider the effect of gallium substitution on the $\langle \bar{1}10\rangle(112)$ slip characteristics. When Ga substitutes In, the APB energy for the (112) plane [$\mathbf{u}=1/2\langle \bar{1}10\rangle(112)$] decreases. This means that the anisotropy ratio of the APB energies for (001) and (112) planes is very sensitive to the presence of Ga: the APB energy for the (112) plane is changed only slightly, whereas for the (001) plane it becomes smaller by almost a factor of 5. Thus, the introduction of gallium atoms into the metallic sublattice leads to an APB energy decrease for both planes, but its influence is very anisotropic.

The larger change of the APB energy for (001) in comparison to that for the (112) plane following gallium substitution, correlates with the characteristics of order-disorder phase transitions observed in the ternary selenides, in particular in $CuInSe_2$ and $CuGaSe_2$ (Refs. 33 and 34). The formation of ordered $CuGaSe_2$ was found to be accompanied by larger atomic shifts along $\langle 001\rangle$ and a larger tetragonal distortion ($c/2a$) than in the case of ordered $CuInSe_2$. Furthermore, the ordering enthalpy for $CuGaSe_2$ includes a greater deformational contribution associated with the distortion along $\langle 001\rangle$ direction.

It is important that gallium substitution leads to a crucial change of the APB energy ratio and that E_{APB} for the (001) plane is much smaller ($0.05\ J/m^2$) than its value for the (112) plane ($0.12\ J/m^2$). Based on the model of dislocation structure in ordered phases,[35–37] we can suggest a possibility of the core transformation of the superstructure $\langle 110\rangle(112)$ dislocation. For example, one can expect that dissociated superdislocations may cross slip from the (112) plane to (001),

which will result in a reduction of the dislocation mobility with temperature increase and an anomalous flow stress.

C. Cleavage energies and brittle-ductile behavior

The calculated cleavage energies γ_C (Table I) demonstrate that for both $CuInSe_2$ and $Cu(In,Ga)Se_2$, the (112) plane is the preferable plane for fracture. This result correlates very well with both the experimental data on the cleavage planes in $CuInSe_2$ (Ref. 38) and the theoretical estimates of the surface energies.[39] The presence of gallium in the cleavage plane leads to a small increase in the cleavage energy (Table I). Strengthening of the chemical bonding by gallium is also demonstrated by a small increase in the calculated cohesive energy from 15.14 eV for $CuInSe_2$ to 15.39 eV for $CuIn_{0.75}Ga_{0.25}Se_2$.

Let us analyze the Rice-Thompson (R-T) criterion using the γ_C and γ_{US} values obtained from our *ab initio* calculations. The γ_C/γ_{US} ratios, obtained for different slip systems (Table I) have small values, which are typical for brittle materials. For example, for iridium, the fracture of which occurs with a cleavage, γ_C/γ_{US} is equal to 3.6, whereas for ductile materials such as Cu and Au this ratio is 11.8 and 13, respectively.[13] Thus, the brittle propagation of crack in $CuInSe_2$ has an intrinsic mechanism and such brittle behavior can be explained by a relatively small value of the cleavage energy in comparison with γ_{US}. This conclusion correlates well with traditional concepts about the brittle character of fracture, typical for materials with covalent bonding, such as $CuInSe_2$. We estimated the cleavage and stacking fault energies within the rigid crystal model when the cleavage and shear (slip) processes are considered without relaxation. However, one can expect that the neglecting of surface reconstruction under cleavage and atom relaxation near the plane slip will not significantly alter our qualitative conclusion.

Gallium substitution slightly increases γ_C for both (112) and (001) planes as well as γ_{US} for the $\langle 110\rangle(001)$ and $\langle \bar{1}10\rangle(112)$ slip systems. The ratio γ_C/γ_{US} decreases and one can expect a more brittle fracture for these planes (Table I). However, gallium only slightly affects γ_C/γ_{US} and the relaxation effects because of Ga substitution may obscure this tendency. Unfortunately, information on the shear and Young moduli is present in the literature only for $CuInSe_2$ (Refs. 5 and 6) and it is not possible to compare our findings with experimental data and other theoretical estimates.

IV. CONCLUSIONS

Using the full-potential linear muffin-tin orbital method (FLMTO), the cleavage energy and the energies of unstable and stable stacking faults have been obtained for (001) and (112) planes, and $\langle 100\rangle(001)$, $\langle 110\rangle(001)$, and $\langle \bar{1}10\rangle(112)$ slips in $CuInSe_2$ and $Cu(In,Ga)Se_2$. We established that the main slip system should be associated with the $\langle \bar{1}10\rangle(112)$ direction. Based on the low values of APB energies, we believe that the perfect $\langle 110\rangle(001)$ and $\langle \bar{1}10\rangle(112)$ dislocations are split into partials with Burgers vectors $1/2\langle 110\rangle(001)$ and $1/2\langle \bar{1}10\rangle(112)$, respectively. We also demonstrated the possibility of the formation of intrinsic stacking fault defects with the corresponding dislocation reaction

$$1/2\langle \bar{1}10\rangle = 1/12\langle \bar{2}4\bar{1}\rangle + 1/12\langle \bar{4}21\rangle.$$

Thus, one can suggest that APB defects are formed on both (001) and (112) planes due to the quite low APB energy and affect the plastic deformation in $CuInSe_2$. The anisotropy of APB energies was obtained for the (001) and (112) planes, where $E_{APB(112)} < E_{APB(001)}$. We found that the ratio of the cleavage and unstable stacking fault energies, γ_C/γ_{US}, has a small value for all the slip systems considered and that $CuInSe_2$ should be characterized by brittle crack propagation. The probable fracture plane is (112), as having the minimum value of cleavage energy.

Gallium additions in $CuInSe_2$ reduce the energy of the antiphase boundary on the (001) and (112) planes, favoring the splitting of perfect dislocations into two partials. This Ga effect is maximum for the (001) plane and $E_{APB(112)} > E_{APB(001)}$ in Ga-doped selenide. The sharp decrease of the APB energy following the partial substitution of In with Ga may lead to an increase in the width of the core dislocation and cause solid solution hardening. An additional strengthening with temperature is possible due to the core transformation, when the APB energy for the basic plane is much smaller than its value for the main slip plane. The dissociated superdislocations may cross slip from the (112) plane to the (001) and decrease the dislocation mobility. Gallium makes a small contribution to brittleness, but the fracture limit in $Cu(In,Ga)Se_2$ is somewhat higher than in $CuInSe_2$ $[\gamma_C(Cu(In,Ga)Se_2) > \gamma_C(CuInSe_2)]$.

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