Orbital-frustration-induced ordering in semiconductor alloys

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It is well known that ternary zinc-blende semiconductors are always more stable in the chalcopyrite (CH) structure than the Cu-Au (CA) structure because the CH structure has a large Coulomb interaction and a reduced strain energy. Surprisingly, an experimental study showed that the $ZnFeSe_2$ alloy takes the CA order as the ground-state structure, which is consistent with our density functional theory calculations showing that the CA order has lower energy than the CH order for $ZnFeSe_2$. We reveal that the orbital degree of freedom of a high-spin Fe^{2+} ion (d^6) in the tetrahedral crystal field plays a key role in stabilizing the CA order. First, the spin-minority d electron of the Fe^{2+} ion tends to occupy the $d_{x^2-y^2}$-like orbital instead of the $d_{3z^2-r^2}$-like orbital because of its large negative Coulomb energy. Second, for a nearest-neighboring Fe^{2+} pair, two spin-minority d electrons with occupied $d_{x^2-y^2}$-like orbitals on the plane containing the Fe-Fe bond have lower electronic kinetic energies. Both conditions can be satisfied in the CA ordered $ZnFeSe_2$ alloy, whereas there is an orbital frustration in the CH structure. Our results suggest that the orbital degree of freedom provides a new way to manipulate the structure and properties of alloys.

I. INTRODUCTION

Semiconducting alloys have attracted considerable interest because the material properties of the alloy can be tuned continuously by changing the alloy composition for specific electronic or optoelectronic applications [1–3]. For example, the band gap of GaInN alloys can change from 3.4 eV for pure GaN to 0.7 eV for pure InN, which has contributed to the great success of the nitrides-based semiconductor blue laser diode emitters for solid-state lighting [4]. Previous studies show that atomic ordering is another degree of freedom to tune the material properties of the alloys because the electronic properties of the alloys, such as the band gap, depend sensitively on the atomic ordering [5–10]. Therefore, by introducing ordering, one can change, for example, the energy band gap for specific applications without the need to change the alloy composition and, consequently, the lattice constants.

For zinc-blende ternary semiconducting alloys at a composition of $x = 0.5(ABX_2)$, the chalcopyrite (CH) or CuAu-like (CA) ordered structures are important because they have relatively low formation energy. Both CA and CH structures are derived from the zinc-blende structure. In the CH ordering, the A site and B site form a (2×2) superlattice along the $\langle 210 \rangle$ direction with the X site surrounded by two A and two B atoms. In the CA ordering, the X site is also surrounded by two A and two B atoms, but the A site and B site form the (1×1) superlattice along the $\langle 001 \rangle$ direction. Usually, for the ternary semiconducting alloys, the CH structure is more stable than the CA structure because the CH ordering results in not only a large negative Coulomb interaction energy,

but also a lower strain energy than the CA ordering [11–15]. Surprisingly, Park *et al.* found that for $Zn_{1-x}Fe_xSe(x \approx 0.5)$ it exists in the CA structure rather than the expected CH structure [16]. This experiment indicates that the CA phase might be more stable than the CH phase in $ZnFeSe_2$, thus violating the general consensus that the CH phase is more stable than the CA phase for ternary semiconductor alloys. From the physics point of view, it is interesting to understand the microscopic mechanism why the CA phase is more stable than the CH phase in $ZnFeSe_2$. Since ordering can change significantly the physical properties of an alloy, a deep understanding of this issue is important for paving a new way to design new functional semiconductors.

In this paper, using first-principles calculations and the constrained density-matrix technique we confirm that the CA phase is indeed more stable than the CH phase for $ZnFeSe_2$. We find that the orbital degree of freedom of a high-spin Fe^{2+} ion in the tetrahedral crystal field is responsible for this unusual trend. The single spin-minority d electron of the Fe^{2+} ion prefers to occupy the $d_{x^2-y^2}$-like orbital rather than the $d_{3z^2-r^2}$-like orbital because it has lower Coulomb energy. When two Fe^{2+} ions are next to each other, the spin-minority d electrons of the Fe atoms also prefer to occupy the $d_{x^2-y^2}$-like orbitals on the plane containing the Fe-Fe bond in order to lower the electronic kinetic energy. Both conditions can be satisfied in the CA ordered $ZnFeSe_2$ alloy, whereas there is an orbital frustration in the CH structure. Our results suggest that orbital degree of freedom can provide a new way to manipulate the structure and properties of alloys.

II. CALCULATION MODELS AND METHODS

Our first-principles spin-polarized density functional theory (DFT) calculations were performed on the basis of
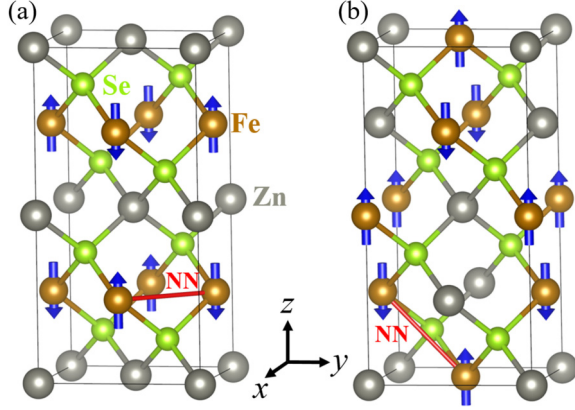
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FIG. 1. (a) CA structure ($P\bar{4}m2$). (b) CH structure ($I\bar{4}c2$). The blue arrows represent the spin directions of the AFM states. The red bonds connect the nearest-neighbor Fe ions.

FIG. 2. (a) Total density of states (DOS) of ZnFeSe$_2$ with the CA structure in the AFM state with the $d_{x^2-y^2}$ orbital order. (b) Partial DOS of a spin-up Fe^{2+} ion.

the projector augmented-wave method [17] encoded in the Vienna *ab initio* simulation package [18,19] (VASP) using the generalized-gradient approximation (GGA) of Perdew *et al.* [20]. The plane-wave cutoff energy was set to be 450 eV. To properly describe the strong electron correlation in the $3d$ transition-metal oxide, the GGA plus on-site repulsion U method (GGA $+ U$) was employed [21]. The effective U value ($U_{eff} = U - J$) of 3 eV are applied to the $3d$ electrons of the Fe atoms. Since our test calculations show that including spin-orbit coupling will not change the main results, we thereafter neglect the effect of spin-orbit coupling.

In the ZnFeSe$_2$ alloy, each Fe^{2+} ion is surrounded by four Se^{2-} ions, i.e., in a tetrahedral environment (see Fig. 1). In a tetrahedral crystal field, the five d orbitals split into a high-lying triply degeneracy $t(d_{xy}, d_{yz},$ and $d_{xz})$ manifold and a low-lying doubly degenerate e ($d_{x^2-y^2}$ and $d_{3z^2-r^2}$) manifold. Each Fe^{2+} ion has six d electrons with a high-spin configuration as confirmed by our DFT calculation. Five electrons occupy the five majority-spin orbitals, and a remaining electron occupies the minority-spin e orbitals. Since the e orbitals are twofold degenerate, there is an orbital degree of freedom which describes how the two minority-spin e orbitals ($d_{x^2-y^2}$ and $d_{3z^2-r^2}$) are occupied.

Since there may exist many locally stable electronic states in an orbital ordered system, a special treatment is required to take care of the orbital degree of freedom. We adopt a constrained density-matrix approach to compute the total energy of a give orbital ordered state. Two DFT static calculations are needed for each orbital ordered state: In the first DFT calculation, we fix the local-density matrices of the transition-metal ions to those in a given orbital ordered state. The wave function is saved when the calculation is converged. In the second step, we perform a conventional unconstrained DFT calculation in which the wave function is initialized to be that saved in the first step. We implement the constrained density-matrix approach in the VASP code. Note that the input density matrix is only used to generate an initial electron wave function, and the total energy is obtained from the second normal DFT calculation.
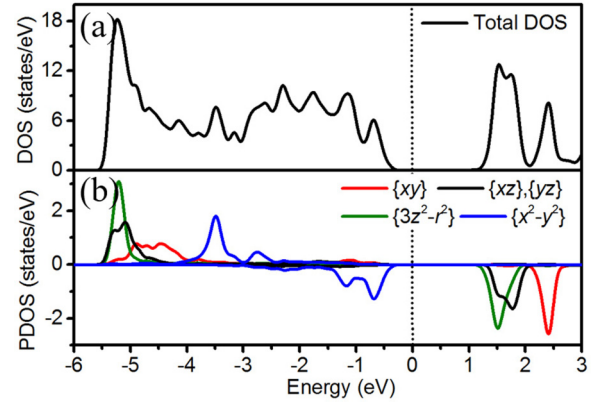
III. RESULTS AND DISCUSSION

A. Relative stability between the CA and the CH orderings

It has been shown theoretically that for almost all ternary zinc-blende-based alloys, the formation energy of the CA structure is higher than that of the CH structure. [12] Therefore, it is necessary to check whether this is also true for the highly correlated ZnFeSe$_2$ alloy. Our DFT calculations show that in contradiction to the conventional wisdom, the CA order in the ZnFeSe$_2$ alloy is more stable than the CH order. For both atomic orderings, we consider the ferromagnetic (FM) and antiferromagnetic (AFM) configurations (see Fig. 1). In the AFM configuration, the two spins of any nearest-neighbor (NN) Fe-Fe pair are antiferromagnetically aligned. For the orbital ordered states, we consider two cases: Either the minority-spin $d_{x^2-y^2}$ orbital or the $d_{3z^2-r^2}$ orbital is occupied for Fe^{2+} ions. Thus, in total we consider four states for both CA and CH orderings. For each state, the internal atomic positions and cell parameters are fully relaxed. We find all these states are insulating (see Fig. 2 for the electronic structure of CA ZnFeSe$_2$), in agreement with the experimental result [16]. The relative energies of the optimized CH structure and CA structure of ZnFeSe$_2$ with different electronic states are listed in Table I.

From Table I, three interesting trends about the stability can be observed. First, for a given atomic order and orbital order, the AFM state always has a lower energy than the FM state.

TABLE I. The GGA $+ U$ calculated relative total energies (in units of meV/4 atoms) of ZnFeSe$_2$ as function of atomic structure and orbital occupation of the minority spin of the Fe ion. "$x^2 - y^2$" ("$3z^2 - r^2$") refers to the case where every Fe ion occupies the minority-spin $d_{x^2-y^2}$ ($d_{3z^2-r^2}$) orbital. The numbers in parentheses are the results obtained without the structural relaxation.

Orbital occupation	AFM		FM	
	CA	CH	CA	CH
$x^2 - y^2$	0.0 (0.0)	33.7 (32.2)	92.4 (95.0)	87.2 (84.6)
$3z^2 - r^2$	84.7 (83.9)	42.2 (43.0)	134.1 (139.7)	116.5 (127.1)

TABLE II. The DFT calculated relative energies (in units of meV/4 atoms) of ZnFeSe$_2$ with a perfect zinc-blende structure whose lattice constants and atomic coordinates are unrelaxed. The energies outside and inside the parentheses are obtained with $U_{eff} = 2$ and $U_{eff} = 4$ eV, respectively. Therefore, our main results remain the same if a reasonable U value is adopted.

Orbital occupation	AFM		FM	
	CA	CH	CA	CH
$x^2 - y^2$	0.0 (0.0)	38.4 (27.1)	125.3 (71.0)	115.5 (74.7)
$3z^2 - r^2$	87.7 (80.9)	38.5 (45.6)	157.6 (124.2)	148.3 (109.4)

As a matter of fact, all the AFM states studied here are more stable than the FM states. This is because of the presence of strong AFM NN Fe-Fe superexchange interactions [22]. Second, for a given atomic order and spin order, the states with the $d_{x^2-y^2}$ orbital occupation are more stable than those with the $d_{3z^2-r^2}$ orbital occupation. Third, the state with CA atomic order, AFM spin order, and $d_{x^2-y^2}$ orbital occupation has the lowest energy among all the considered states, i.e., it is the ground state. This verifies that the CA phase is more stable than the CH phase in ZnFeSe$_2$. This is opposite to most of ternary semiconductors, such as CuGaSe$_2$ where the CH order is the ground state [11]. To see the effect of the strain relaxation, we also compute the corresponding total energies of ZnFeSe$_2$ without structural relaxation, i.e., all the atoms sit on a perfect site of a zinc-blende structure. It can be seen that the results are qualitatively the same as those obtained with the relaxed structures (Table I). Experimentally, it is only observed that using ZnSe as a buffer layer can improve the quality but not the ordering of the ZnFeSe$_2$ crystal grown on a GaAs substrate [16], possibly due to the reduction of the chemical mismatch. Therefore, the relaxation of the structure is not important for this system since the size of Zn and Fe are similar. We also checked the effect of the U_{eff} by computing the corresponding total energies of ZnFeSe$_2$ with U_{eff} values of 2 and 4 eV. The relative energies are listed in Table II. It can be seen that the results are qualitatively the same as those obtained with U_{eff} values of 3 eV. Therefore, in the following discussion, to isolate the orbital occupation effect, we will fix the atoms on the ideal zinc-blende site with U_{eff} values of 3 eV.

B. An isolated Fe ion in the ZnSe matrix

To understand why the $d_{x^2-y^2}$ orbital order is more stable than the $d_{3z^2-r^2}$ orbital order and why the CA structure with the $d_{x^2-y^2}$ orbital order has a lower energy than the CH structure with the $d_{x^2-y^2}$ orbital order, we first study an isolated Fe ion in the ZnSe matrix. In our calculations, we adopt a 32-atom ZnSe supercell with one Zn ion replaced by a Fe ion. We have checked the convergence of the supercell and find that it is large enough so that the interaction between the periodic Fe^{2+} images can be neglected because the Fe 3d orbitals are relatively localized. It is convenient to describe the orbital degree of freedom of two minority-spin e orbitals ($d_{x^2-y^2}$ and $d_{3z^2-r^2}$) by means of the "pseudospin" operator $\hat{T}$, which is exactly analogous to the usual spin-1/2 operator $\hat{\sigma}$ [23,24]. We define $|T_z = 1/2\rangle = |3z^2 - r^2\rangle$ and
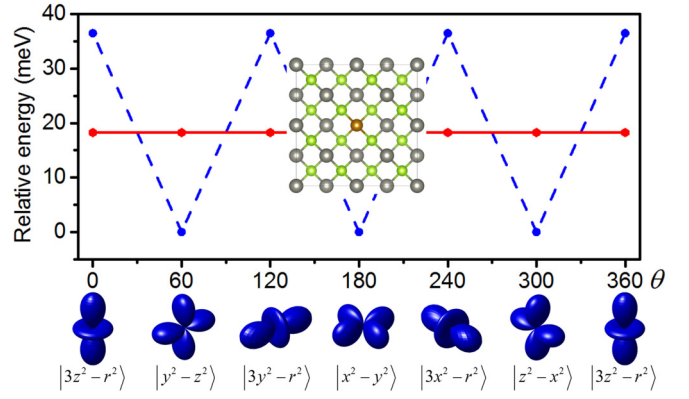

FIG. 3. The relative energies as a function of θ with the corresponding orbital picture and orbital designation. The blue dots are the DFT result, and the red dots are the result of the pseudospin model for a single Fe ion. The lines connecting the dots are guides for the eyes. The inset picture is a ZnSe supercell which we used to calculate the energy of a single Fe ion.

$|T_z = -1/2\rangle = |x^2 - y^2\rangle$. A composite state can then be characterized by angle θ as

$$|\theta\rangle = \cos\frac{\theta}{2}|3z^2 - r^2\rangle + \sin\frac{\theta}{2}|x^2 - y^2\rangle.$$

Angles $\theta = 0°, 60°, 120°, 180°, 240°, 300°$, and $360°$ correspond to $|3z^2 - r^2\rangle, |y^2 - z^2\rangle, |3y^2 - r^2\rangle, |x^2 - y^2\rangle, |3x^2 - r^2\rangle, |z^2 - x^2\rangle$, and $|3z^2 - r^2\rangle$, respectively. The total energies of these states computed with the constrained density-matrix approach are plotted as a function of θ in Fig. 3. We can see that it displays the 120° periodicity and the energy of the state with $\theta = 180°$ ($|x^2 - y^2\rangle$) is 36.5 meV lower than that with $\theta = 0°(|3z^2 - r^2\rangle)$. This result is consistent with the trend that the state with $d_{x^2-y^2}$ orbital occupation is more stable than that with $d_{3z^2-r^2}$ orbital occupation. The 120° periodicity can be understood from the symmetry point of view. For example, the state $|\theta = 0°\rangle = |3z^2 - r^2\rangle$ is symmetrically equivalent to the state $|\theta = 120°\rangle = |3y^2 - r^2\rangle$ due to the cubic T_d symmetry of the zinc-blende structure. The physical origin why the $|x^2 - y^2\rangle$ occupation has a lower energy than $|3z^2 - r^2\rangle$ can be understood by noticing that, although the two states are degenerate under cubic symmetry, when only a single state is occupied, the local symmetry is reduced because the electron density distribution of the $|x^2 - y^2\rangle$ state is different from that of the $|3z^2 - r^2\rangle$ state. We calculate the Coulomb interaction of the electron density and find that the Coulomb interaction of the $|3z^2 - r^2\rangle$ state is 33.4 meV lower than that of the $|3z^2 - r^2\rangle$ state. This energy difference is very close to the DFT total energy difference (36.5 meV). However, we note that our DFT result cannot be described by the widely adopted Kugel-Khomskii-like pseudospin model [23,24].

According to that theory, the Hamiltonian of the isolated Fe^{2+} ion with an orbital degree of freedom can be written as $\hat{H}_{single} = B_x\hat{T}_x + B_y\hat{T}_y + B_z\hat{T}_z + C$ where B and C are constants. By mapping the DFT total energies of the different states to the expectation values of the model Hamiltonian, the parameters of the Hamiltonian from the least-squares fitting process turns out to be $B_x = B_y = B_z = 0$ and $C = 18.3$ meV.

This means that the energy is independent of angle θ. Obviously, the Hamiltonian described by the pseudospin operator fails to reproduce the first-principles result. The failure of the model Hamiltonian roots in the fact that the full electronic Hamiltonian is approximated by a two-level Hamiltonian. This approximation may make the orbital ordering problem more tractable in many cases, but it is not enough for the system we are considering.

C. An isolated NN Fe-Fe pair in the ZnSe matrix

We now address the question why the CA structure with the $d_{x^2-y^2}$ orbital order has a lower energy than the CH structure with the $d_{x^2-y^2}$ orbital order. We find that the nearest-neighbor interaction between Fe^{2+} ions is responsible for this phenomenon. A 64-atom ZnSe supercell with two Zn ions replaced by two Fe ions is adopted in the calculation as shown in Fig. 4(a). Note that the relative positions of the NN Fe pairs in the CA structure are different from those in the CH structure. As shown in Fig. 1, the Fe-Fe pairs are on the xy plane in the CA structure, whereas the Fe-Fe pairs are out of plane in the CH structure. Nevertheless, the out-of-plane NN Fe-Fe pairs in the CH structure can be obtained by rotating the in-plane Fe-Fe pair [see Fig. 4(a)]. Therefore, it is sufficient to consider only the in-plane Fe-Fe pair. For the in-plane Fe-Fe pair, we calculate the total energies of 36 different orbital order states with the AFM spin order (see Table III). These states are characterized by θ_1 and θ_2, where $\theta_1(\theta_2)$ describes the orbital occupation of the first (second) Fe ion ($\theta_1, \theta_2 = 0°, 60°, 120°, 180°, 240°, 300°$).

For an isolated in-plane NN Fe-Fe pair, our calculation shows that the AFM state with $d_{x^2-y^2}$ orbital order ($\theta_1 = \theta_2 = 180°$) has the lowest energy (see Table III). By symmetry, the $d_{x^2-y^2}$ orbital order of the out-of-plane NN Fe-Fe pair is equivalent to the $d_{x^2-z^2}$ orbital order ($\theta_1 = \theta_2 = 300°$) of the in-plane NN Fe-Fe pair. We find that the energy for the $d_{x^2-z^2}$ orbital ordered state ($\theta_1 = \theta_2 = 300°$) is higher by 15.9 meV than that for the $d_{x^2-y^2}$ orbital ordered state ($\theta_1 = \theta_2 = 180°$). To understand this result, we perform a tight-binding analysis.
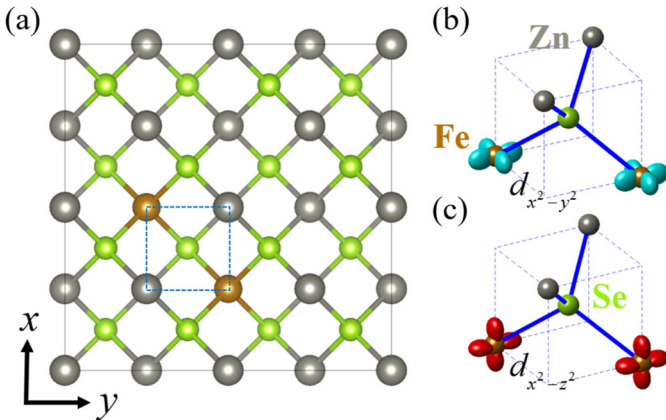

FIG. 4. (a) A ZnSe supercell adopted to calculate the nearest-neighboring interaction of the in-plane NN Fe pair. (b) A Fe pair with $d_{x^2-y^2}$ orbital order ($\theta = 180°$). (c) A Fe pair with $d_{x^2-z^2}$ orbital order ($\theta = 300°$). The energy of the $d_{x^2-y^2}$ orbital order state is 15.9 meV lower than that of the $d_{x^2-z^2}$ orbital order state.

TABLE III. The relative energies of the AFM states of the in-plane NN Fe-Fe pair with different orbital orders. Note that the occupied minority orbital of the two Fe ions is always $d_{x^2-y^2}$-like. It can be seen that two spin-minority d electrons with occupied $d_{x^2-y^2}$-like orbitals on the plane containing the Fe-Fe bond ($\theta_1 = \theta_2 = 180°$) have the lowest energies.

θ_1	θ_2	ΔE	θ_1	θ_2	ΔE
0	0	96.6	180	0	46.7
0	60	56.6	180	60	7.7
0	120	86.0	180	120	38.5
0	180	46.7	180	180	0.0
0	240	86.0	180	240	38.5
0	300	56.6	180	300	7.7
60	0	56.6	240	0	86.0
60	60	15.9	240	60	47.5
60	120	45.7	240	120	78.0
60	180	7.7	240	180	38.5
60	240	47.5	240	240	76.2
60	300	17.7	240	300	45.7
120	0	86.0	300	0	56.6
120	60	45.7	300	60	17.7
120	120	76.2	300	120	47.5
120	180	38.5	300	180	7.7
120	240	78.0	300	240	45.7
120	300	47.5	300	300	15.9

We find that there is a larger kinetic-energy gain due to a stronger effective hopping between the $d_{x^2-y^2}$ orbital and the five d orbitals of the NN Fe^{2+} ion in the former case. This scenario is similar to Anderson's superexchange mechanism.

In this paper, we assume the effective hopping parameters are orbital dependent but spin independent. Superexchange interaction between the NN Fe-Fe pair is via linked the Se ion. According to Slater-Koster's tight-binding method [25], the hopping between the i th d orbital of the Fe ion and the k th p orbital of the Se ion can be regarded as the linear combination between the σ-type interaction ($t_{pd\sigma}$) and that of the π-type interaction ($t_{pd\pi}$), namely, $t^{ik}_{\text{Fe-Se}} = a_{ik}t_{p\,d\sigma} + b_{ik}t_{p\,d\pi}$, where a_{ik} and b_{ik} are constants. We use $t_{pd\sigma} = -1.05$ eV and $t_{pd\pi} = 0.47$ eV as was adopted to calculate the electronic structure of FeO [26]. Because both O and Se are VI main group elements, using the ratio of the parameters of the FeO compound as the basis of our model parameters is qualitatively reasonable. The effective hopping between the i th d orbital of the Fe1 ion and the j th d orbital of the Fe2 ion can be written as

$$t^{ij}_{\text{Fe1-Fe2}} = \sum_k t^{ik}_{\text{Fe1-Se}}t^{jk}_{\text{Fe2-Se}} = At^2_{p\,d\sigma}+Bt^2_{p\,d\pi}+Ct_{p\,d\sigma}t_{p\,d\pi},$$

where A, B, and C are constants.

The energy levels of the AFM state with the $d_{x^2-y^2}$ orbital order and that with the $d_{x^2-z^2}$ orbital order are shown in Fig. 5. For clarity, we only show the spin-up levels since the diagram for the spin-down case is similar. In the case of the AFM state with the $d_{x^2-y^2}$ order, all five spin-up d orbitals of the Fe1 ion are occupied, whereas only the spin-up $d_{x^2-y^2}$ orbital of the Fe2 ion is occupied. Due to the effective hopping between the d orbitals of the two Fe ions, the interaction between the occupied d orbitals of the Fe1 ion and the unoccupied d
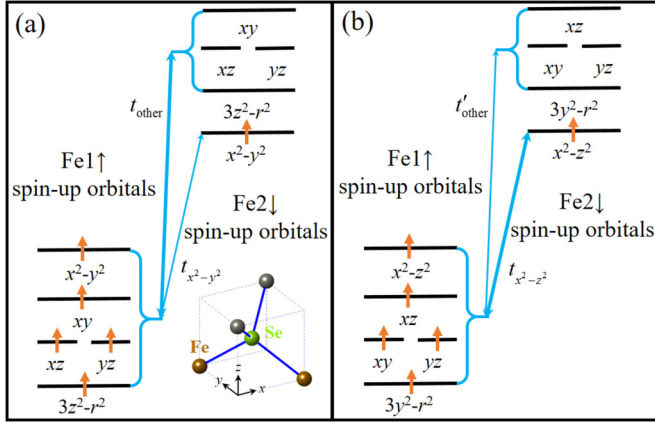
FIG. 5. Orbital interaction between the spin-up Fe1 ion and the spin-down Fe2 ion for the cases of (a) the $d_{x^2-y^2}$ orbital order and (b) the $d_{x^2-z^2}$ orbital order, respectively. The inset indicates the environment of the in-plane NN Fe1-Fe2 pair.

orbitals of the Fe2 ion will lead to a lowering of the electronic kinetic energy: $\Delta E \propto \frac{t^2}{U}$, where t is the effective hopping and U is the energy difference between the spin-minority and the spin-majority orbitals. This is similar to Anderson's superexchange mechanism. In the case of the AFM state with the $d_{x^2-z^2}$ order, only the spin-up $d_{x^2-z^2}$ orbital of the Fe2 ion is occupied. Because of the different orbital orders, the kinetic-energy gain differs between the two states. Since the total interaction between all the five d orbitals of the Fe1 ion and all the five d orbitals of the Fe2 ion remains the same for different orbital orders, we can focus instead on the interaction between the occupied five spin-up d orbitals of the Fe1 ion and the one occupied spin-up d orbital of the Fe2 ion. If the effective hopping ($t_{x_2-y_2}$) between the occupied $d_{x^2-y^2}$ of the Fe2 ion and the five d orbitals of the Fe1 ion are weaker than that ($t_{x_2-z_2}$) between the occupied $d_{x^2-z^2}$ of the Fe2 ion and the five d orbitals of the Fe1 ion, the effective hopping between the four spin-up empty d orbitals of the Fe2 ion and the five d orbitals of the Fe1 ion are stronger in the case of $d_{x^2-y^2}$ orbital order, and this will subsequently result in a lower energy of the AFM state with the $d_{x^2-y^2}$ orbital order. Hence, it is only necessary to investigate the hopping between the occupied $d_{x^2-y^2}$ ($d_{x^2-z^2}$) of the Fe2 ion and the five d orbitals of the Fe1 ion. Using the effective hopping parameters listed in Table IV, we find that $t_{x_2-y_2}^2 = 0.07 < t_{x_2-z_2}^2 = 0.10$ as illustrated in Fig. 5. Therefore, the kinetic-energy gain in the AFM state with the $d_{x^2-y^2}$ order is larger than that with the

TABLE IV. The constants A, B, and C for describing the hopping between the $d_{x^2-y^2}$ ($d_{x^2-z^2}$) of the Fe2 ion and the five d orbitals of the Fe1 ion.

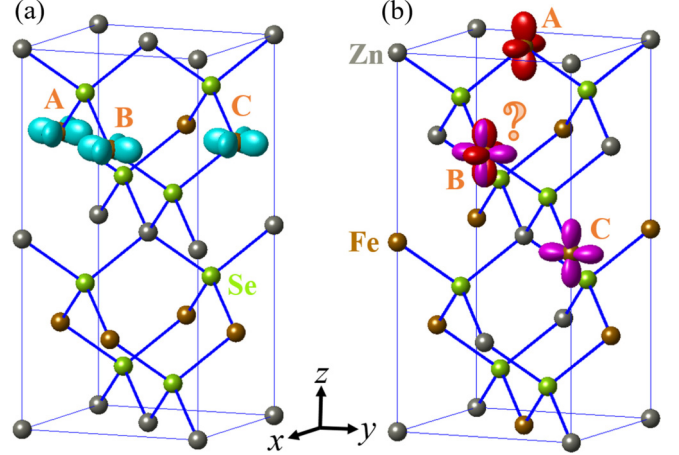|	A	B	C
$3z^2-r^2(3y^2-r^2)$	0.00 (0.00)	0.00 (0.39)	0.00 (0.00)
$x^2-y^2(x^2-z^2)$	−0.24 (0.00)	−0.24 (0.00)	−0.20(0.00)
$yz(yz)$	0.12 (0.00)	0.12 (−0.11)	0.10 (−0.38)
$xz(xy)$	0.12 (0.00)	0.12 (−0.11)	0.10 (0.38)
$xy(xz)$	0.00 (0.00)	0.00 (−0.22)	0.00 (−0.38)

FIG. 6. Orbital arrangement in (a) the CA structure and (b) the CH structure. The cyan, red, and magenta petal shapes represent minority-spin $d_{x^2-y^2}$, $d_{x^2-z^2}$, and $d_{y^2-z^2}$ orbitals, respectively, of the Fe ion. "?" in (b) illustrates the presence of orbital frustration in the CH structure.

$d_{x^2-z^2}$ order. This results in a lower energy of the AFM state with the $d_{x^2-y^2}$ order, in agreement with the DFT result.

D. Orbital frustration

The orbital preference in the in-plane NN Fe-Fe pair can account for the energy difference between the CA structure with the $d_{x^2-y^2}$ orbital order and the CH structure with the $d_{x^2-y^2}$ orbital order. In the CA structure with the $d_{x^2-y^2}$ orbital order, the orbital order for each NN Fe-Fe pair is the same as the $d_{x^2-y^2}$ orbital order of the in-plane NN Fe-Fe pair [Fig. 4(b)]. Whereas for the CH structure with the $d_{x^2-y^2}$ orbital order, the orbital order for each NN out-of-plane Fe-Fe pair is the same as the $d_{x^2-z^2}$ orbital order of the in-plane NN Fe-Fe pair [Fig. 4(c)]. Since there are two NN Fe-Fe pairs per ZnFeSe$_2$ formula unit in both CA and CH structures, the energy difference between the CA and the CH structures with the $d_{x^2-y^2}$ orbital order is estimated to be $2 \times 15.9 = 31.8$ meV/f.u., which is very close to the DFT total energy difference (32.2 meV/f.u.). Note that this energy difference has nothing to do with the energy difference between the $d_{x^2-y^2}$ orbital order and the $d_{3z^2-r^2}$ orbital order of an isolated Fe^{2+} ion since all the minority-spin electrons occupy the $d_{x^2-y^2}$ and equivalent orbitals. Our results indicate that the NN Fe-Fe pair interaction is responsible for the stability of the CA structure. Our test calculations indeed show that the longer-range interaction is less than 0.1 meV.

As shown above, the lowest-energy NN Fe-Fe pair should have the minority-spin electrons occupying the $d_{x^2-y^2}$-like orbitals, and the Fe-Fe bond should be on the orbital plane of the two $d_{x^2-y^2}$-like orbitals [see Fig. 4(b)]. In the CA structure, all the NN Fe-Fe bonds are along the [110] [AB in Fig. 6(a)] or [1$\bar{1}$0] [BC in Fig. 6(a)] directions. In this case, the orbital could order in the most favorable way for every NN Fe-Fe pair. Namely, all the Fe ions take the $d_{x^2-y^2}$ orbital order [see Fig. 6(a)]. However, this is not possible in the CH structure. In the CH structure, the NN Fe-Fe bonds can be along [101], [10$\bar{1}$], [011], or [01$\bar{1}$] directions [(see Fig. 6(b)]. It can easily

be seen that the orbitals of the NN Fe-Fe pairs could not order in the most favorable way simultaneously. For the AB Fe-Fe pair of the CH structure along the $[10\bar{1}]$ direction, the minority-spin electrons of both A and B Fe ions occupy the $d_{x^2-z^2}$ orbitals in the lowest-energy configuration. Whereas for the BC Fe-Fe pair of the CH structure along the $[01\bar{1}]$ direction, the minority-spin electrons of both B and C Fe ions should occupy the $d_{x^2-z^2}$ orbitals in the lowest-energy configuration. Thus, whichever orbital the minority-spin electron of the B Fe^{2+} ion occupies, the AB and BC Fe-Fe pairs could not adopt the most favorable orbital order simultaneously as illustrated in Fig. 6(b). In other words, there is an orbital frustration in the CH structure. The concept of the orbital frustration is similar to that of the spin frustration in an AFM triangular spin system. Therefore, the origin for the unusual stability of the CA structure in $ZnFeSe_2$ is due to the presence of the orbital frustration in the CH structure. Finally, we want to point out that perfect CA ordering is only available for $x = 0.5$. In general, for alloys away from $x = 0.5$, the maximum ordering parameter is $\eta = \min\{2x, 2(1-x)\}$ [27].

IV. SUMMARY AND CONCLUSIONS

In conclusion, our DFT calculations confirm that the experimentally observed CA order in $ZnFeSe_2$ is the ground state instead of a metastable state. This is opposite to the case of most ternary zinc-blende-based compounds where the CH order is the ground state [11]. The orbital degree of freedom of the high-spin Fe^{2+} ion (d^6) in the tetrahedral crystal field plays a key role in stabilizing this CA order. By considering the isolated Fe^{2+} ion and the NN Fe^{2+} pair, we discover two rules in this system: First, the spin-minority d electron of the Fe^{2+} ion will tend to occupy the $d_{x^2-y^2}$-like orbital instead of the $d_{3z^2-r^2}$-like orbital because of the Coulomb interaction. Second, for a NN Fe^{2+} pair, two spin-minority d electrons tend to occupy the $d_{x^2-y^2}$-like orbitals with the orbital plane containing the Fe-Fe bond in order to lower the electronic kinetic energy. Both conditions can be satisfied in the CA ordered $ZnFeSe_2$ alloy, whereas there is an orbital frustration in the CH structure. Our results, thus, suggest that the orbital degree of freedom provides a new way to manipulate the structure and properties of alloys.

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