Calculation of magnetic moment of inverse-Heusler alloy \( \text{Fe,CuAl} \) via first-principles-based tight-binding model

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Abstract. Heusler alloys have been known since the 19th century and have fascinated researchers because of their wide range of applications, especially related to their magnetic properties. The magnetic moment of a few of these materials can be predicted by simply counting their valence electrons [this is called the Slater–Pauling (SP) rule]. However, this simple counting rule does not work in many other cases. Inverse-Heusler alloys are a sub-class of Heusler alloys, and in many cases also do not follow the SP rule. \( \text{Fe,CuAl} \) (FCA) is an inverse-Heusler alloy for which the SP rule predicts a magnetic moment of 2.00 \( \mu \)B. However, experimental results give a magnetic moment of 3.30 \( \mu \)B. Motivated by this discrepancy, we study this material theoretically to gain a microscopic understanding of how the magnetic moment forms. For this purpose, we construct a first-principles-based tight-binding model incorporating an on-site Hubbard repulsion \( U \) between each \( d \) orbital and a Hund coupling \( J \) between different \( d \) orbitals of a given atom in the system. We use the Green’s function technique and apply the mean-field approximation to solve the model. The results show the magnetic moment of FCA depends on \( U \) and \( J \). We find that the magnetic moment given by the SP rule (2.00 \( \mu \)B) corresponds to a plateau in our magnetic moment vs \( J \) curves for various values of \( U \), and that the experimental magnetic moment (3.30 \( \mu \)B) corresponds to a point on the curves rising above the plateau.

1. Introduction

Heusler alloys have been known since 19th century when Friedric Heusler found that the combination of Cu, Mn, and Al (Cu\(_2\)MnAl) is ferromagnetic although each element alone is not magnetic \cite{1}. Generally, according to the total number of atoms per formula unit, Heusler alloys can be divided into two sub-classes: half-Heusler (XYZ) with three atoms per formula unit, and full-Heusler (X\(_2\)YZ) with four atoms per formula unit. Both have the valence of the \( X \) transition-metal atom, which is greater than the valence of the \( Y \) transition-metal atom. In some special cases of the \( X_2YZ \) structure, the valance of the \( Y \) transition-metal atom may be greater than that of the \( X \) transition-metal atom. This leads to another sub-class of alloys called inverse-Heusler alloys \cite{2}. Because the valance of \( Y \) is greater than that of \( X \), this situation changes the crystal structure from L2\(_1\) to the \( XA \) structure, where the Wyckoff positions of the atoms are \( X_1(0,0,0), X_2(1/4,1/4,1/4), Y(1/2,1/2,1/2), \) and \( Z(3/4,4/3,4/3) \).
of parameters the nearest second term of equation where
The elements of the matrix spin FCA is shown in figure 1b.
FCA orbitals of the Fe
To construct the non-parallel numerical algorithm because
magnetic moment of 2.00 µB, calculate the magnetic moment of Fe
total number of valance electrons per formula unit. In many cases, this simple counting formula predicted
For this situation indicates that the SP simple counting rule is too simplistic to correctly predict the magnetic moment of inverse-Heusler alloys, probably because it neglects the effects of various complexities occurring in the real system.
Motivated by this issue, we propose a theoretical study to calculate the magnetic moment of the inverse-Heusler alloy FeCuAl within a first-principles-based tight-binding model by incorporating on-site Hubbard repulsions and Hund spin-spin interactions in a mean-field framework. We handle the numerical algorithm by using the FORTRAN 90/95 language [4] and perform the computation in a parallel-computing scheme with the Message Passing Interface (MPI) [5].

2. Model
To construct the non-interacting (or the kinetic) part of our model Hamiltonian, we employ 22 basis orbitals of the FeCuAl (FCA) system taken from all the valence orbitals of the primitive unit cell of FCA, listed in table 1. Figure 1a shows the conventional unit cell of FCA. The primitive unit cell of FCA is shown in figure 1b.

The full Hamiltonian consists of three terms: one representing the kinetic part, one the Hund spin-spin interaction, and the last the Hubbard repulsion:

\[ H = \sum \kappa \epsilon^{\kappa} \left[ H_{0}^{\kappa} (\kappa) \right] \eta_{\kappa} - J \sum \gamma, \alpha, \beta \left\{ \sum_{\gamma} \chi_{\gamma, \alpha}^{(\gamma)} \chi_{\gamma, \beta}^{(\gamma)} + U \sum \gamma, \alpha \eta_{\gamma, \alpha}^{(\gamma)} \eta_{\gamma, \alpha}^{(\gamma)} \right\} \]

(1)
The elements of the matrix \( H_{0}^{\kappa} (\kappa) \) in the first term of equation (1) can in general take the form

\[ H_{0, ij}^{\kappa} (\kappa) = \epsilon_{i} \delta_{i,j} - t_{i,j} \sum_{m,n} \delta^{\kappa}_{m,n} e^{-ik\cdot\delta_{m,n}} \]

(2)
where \( \epsilon_{i} \) denotes the on-site energy of an orbital \( i \), while the Kronecker delta \( \delta_{ij} \) signifies that the on-site energy can only appear when \( i = j \), whereas \( \kappa \) denotes a wave vector in the Brillouin zone. In the second term of equation (2), \( t_{i,j} \) describes the hopping integral between orbitals \( i \) and \( j \) belonging to the nearest-neighbor atoms, with \( \delta^{\kappa}_{m,n} \) denoting the nearest-neighbor translation vectors. All the values of parameters \( \epsilon_{i} \) and \( t_{i,j} \) are obtained by first using density functional theory (implemented, e.g., in the Quantum Espresso package), and then extracting the tight-binding parameters by using another package called wannier90 [6].

| Table 1. Basis orbitals of inverse-Heusler FeCuAl. |
|-----------------------------------------------|
| \( | Fe_{1} - s \rangle \) | \( | Fe_{1} - d_{xy} \rangle \) | \( | Fe_{1} - d_{xz} \rangle \) | \( | Fe_{1} - d_{yz} \rangle \) | \( | Fe_{1} - d_{x^{2}-y^{2}} \rangle \) | \( | Fe_{2} - s \rangle \) | \( | Fe_{2} - d_{xy} \rangle \) | \( | Fe_{2} - d_{xz} \rangle \) | \( | Fe_{2} - d_{yz} \rangle \) | \( | Fe_{2} - d_{x^{2}-y^{2}} \rangle \) |
| \( | Cu - s \rangle \) | \( | Cu - d_{xy} \rangle \) | \( | Cu - d_{xz} \rangle \) | \( | Cu - d_{yz} \rangle \) | \( | Cu - d_{x^{2}-y^{2}} \rangle \) |
| \( | Al - s \rangle \) | \( | Al - p_{x} \rangle \) | \( | Al - p_{y} \rangle \) | \( | Al - p_{z} \rangle \) |

Figure 1. (a) Conventional unit cell of FeCuAl, and (b) primitive unit cell of FeCuAl.
Figure 2. Numerical algorithm

The second term of equation (1) gives the interactions between spins of electrons in different $d$ orbitals of the same atom, with $J$ being the corresponding Hund’s coupling, $\alpha$ and $\beta$ being the components of $d$ orbitals, and $\zeta$ and $\gamma$ denoting the unit cell and site in the unit cell that have the $d$ orbitals, respectively. The last term of equation (1) represents on-site Coulomb repulsive interactions between electrons of the $d$ orbitals in a given atom in the unit cell, where $U$ is the Hubbard repulsion constant, whereas $n_{\nu,\alpha(\beta)}(i)$ denotes the occupation number operator of the electrons. The second and the third terms of equation (1) are treated in the mean-field approximation.

3. Method

$[H_0(\vec{k})]$ is a $(2\times22)\times(2\times22) = 44\times44$ matrix of the form

$$[H_0(\vec{k})] = \begin{bmatrix} [H_0(\vec{k})]_{1,1} & \cdots & [H_0(\vec{k})]_{1,22} \\ \vdots & \ddots & \vdots \\ [H_0(\vec{k})]_{22,1} & \cdots & [H_0(\vec{k})]_{22,22} \end{bmatrix},$$

(3)

where $[H_0(\vec{k})]_{1(i)}$ is a $22\times22$ block corresponding to up (down) spins, which are essentially the same before the interactions are added,

$$[H_0(\vec{k})]_{1(i)} = \begin{bmatrix} H_{1,1} & \cdots & H_{1,22} \\ \vdots & \ddots & \vdots \\ H_{22,1} & \cdots & H_{22,22} \end{bmatrix}. $$

(4)

For further steps of the calculation, we define the “retarded” Green’s function written in matrix form as

$$[G^R(\vec{k}, \omega)] = \left((\omega + i0^+) [I] - [H_0(\vec{k})] - [\Sigma] \right)^{-1}. $$

(5)

The density of states (DOS) of the system can then be calculated through

$$\text{DOS}(\omega) = -\frac{1}{\pi N} \sum_{\vec{k}} \text{Im} \text{Tr} [G^R(\vec{k}, \omega)],$$

(6)

where $N$ is the total number of $\vec{k}$ points in the Brillouin zone of the system. Finally, the magnetic moment per unit cell of the system can be calculated by using

$$m = n_\uparrow - n_\downarrow,$$

(7)

where $n_\uparrow$ ($n_\downarrow$) denotes the electron occupancy per unit cell for up (down) spins, which can be obtained by using

$$n_{\uparrow(\downarrow)} = \int_{-\omega}^{\omega} d\omega \text{DOS}_{\uparrow(\downarrow)}(\omega)f(\omega, \mu),$$

(8)

where $f(\omega, \mu)$ is the Fermi–Dirac distribution function, with $\mu$ being the chemical potential of the system. The entire algorithm relies on the mean-field self-consistency scheme that can be summarized in the flow chart of figure 2.
4. Results and discussion

4.1. Density of states

We use 16x16x16 $\bar{k}$ points in the Brillouin zone to obtain the non-interacting or “bare” DOS (figure 3) and the DOS (figure 4) of the FCA system. The bare DOS, as depicted in figure 3, show that the DOS for both the up and down spins are exactly the same when the interaction terms remained turned off. The green-dashed line denotes the chemical potential position with the value of $\mu = 13.22$ eV. At this stage, the $U$ and $J$ values are set to be zero, so there is no Coulomb repulsion or spin-spin interactions between the electrons. This implies $n_\uparrow = n_\downarrow$, leading to zero magnetic moment per unit cell.

Next, we turn on the interaction terms of the system by varying the values of $U$ and $J$. For a particular pair of values $U = 4.00$ eV and $J = 0.60$ eV, leading to $m = 3.20 \mu_B$. Figure 4 shows the resulting interacting DOS. Because the experimental data reported by Gasi et al. give a magnetic moment for FCA of about $3.30 \mu_B$ [3], we conjecture that the $U$ and $J$ values used herein for FCA may be close to the real values.
Figure 5 displays our calculated magnetic moments for FeCuAl (FCA) for various values of $U$ and $J$. Overall, the results show that the system requires a minimum value of either $U$ or $J$ to have a nonzero net magnetic moment per unit cell. The magnetic moment generally increases with $U$ or $J$. In a special situation, we find that the magnetic-moment curves form a plateau corresponding to the SP-rule magnetic moment $m = Z_t - 28 = 2\mu_B$, with $Z_t = 30$ for FCA. In this situation, the magnetic moment is independent of $U$ and $J$. This may indicate that the Slater–Pauling magnetic moment rule is implicitly based on the assumption that $U$ and $J$ for the system are within the moderate range of values. However, since the experimental value turns out to be significantly greater than $2\mu_B$, it is likely the real situation is the combined $U$ and $J$ values are significantly greater than this moderate value.

4.2. Magnetic moment
Figure 5 displays our calculated magnetic moments for FeCuAl (FCA) for various values of $U$ and $J$. Overall, the results show that the system requires a minimum value of either $U$ or $J$ to have a nonzero net magnetic moment per unit cell. The magnetic moment generally increases with $U$ or $J$. In a special situation, we find that the magnetic-moment curves form a plateau corresponding to the SP-rule magnetic moment $m = Z_t - 28 = 2\mu_B$, with $Z_t = 30$ for FCA. In this situation, the magnetic moment is independent of $U$ and $J$. This may indicate that the Slater–Pauling magnetic moment rule is implicitly based on the assumption that $U$ and $J$ for the system are within the moderate range of values. However, since the experimental value turns out to be significantly greater than $2\mu_B$, it is likely the real situation is the combined $U$ and $J$ values are significantly greater than this moderate value.

5. Conclusions
We have developed a first-principles-based tight-binding model incorporating on-site Coulomb repulsions and Hund spin-spin interactions, which we treat within mean-field self-consistency scheme. According to our results, the magnetic moment of the inverse-Heusler alloy FeCuAl (FCA) depends on $U$ and $J$. By using our method, we observe that the situation leading to the Slater–Pauling prediction of the magnetic moment ($2\mu_B$) corresponds to a plateau region in which the magnetic moment is independent of $U$ and $J$, provided that they remain in a moderate range of values. The fact that the experimental value ($3.30 \mu_B$) is significantly larger than the SP-rule prediction makes us conjecture that the real situation for FCA corresponds to $U$ and $J$ values being greater than these moderate values, with some possibility being close to $U = 4.00$ eV and $J = 0.60$ eV. Our results demonstrate that the complexity of the system, as well as the strength of the charge and spin interactions between the electrons, contributes to determining the net magnetic moment of the system.

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