B2 Atomic Disorder in $\text{Co}_2\text{Fe}_x\text{Mn}_{1-x}\text{Si}$ Heusler Alloys

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Co-based full Heusler alloys have attracted significant attention due to their high spin polarisation and successful integration as electrodes in magnetic tunnelling junctions and current-perpendicular-to-plane spin valves (CPP-SV). Further improvement of the CFMS based CPP-SVs requires a fundamental understanding of the effects of atomic disorder within the Heusler alloys. In this work we present a theoretical study of disorder in CFMS alloys using ab initio simulations, guided by images from Z-contrast scanning-TEM of sample films. The simulations are based on density functional theory plus a Hubbard U term, allowing the investigation of the effects of atomic disorder on the spin-polarisation at the Fermi level, and computation of the disorder formation energy. It is found that in order to retain the high spin-polarisation at the Fermi level the integrity of the Co-sublattice should be preserved, but that the effect of mixing between the Fe/Mn and Si sublattices (B2 phase) varies dramatically depending on the precise nature of the disorder and the chemical composition of the CFMS. Calculations of the spin-polarisation at the Fermi energy show that $\text{Co}_2\text{Fe}_{0.5}\text{Mn}_{0.5}\text{Si}$ is especially robust with respect to such intermixing, an observation which may explain the good performance of films in this composition range.

Key words: Heusler alloys, half-metals, thin films, spintronics materials

1. Introduction

Half metallic ferromagnets are 100% spin-polarised materials at the Fermi-level, and for this reason are excellent candidate materials for spintronics devices^{1, 2}. Co-based full Heusler alloys are promising half-metals that have already been used as electrodes in magnetic tunnelling junctions and current-perpendicular-to-plane spin valves (CPP-SVs)³⁻⁶. Co_2MnSi (CMS) and Co_2FeSi (CFS) are of particular interest for such applications because of their low damping constants and high Curie temperatures, both of which are important for applications in current-induced magnetisation switching⁶. Since CMS and CFS share the same crystal structure and similar lattice constants, it is possible to alloy them and the properties of $\text{Co}_2\text{Fe}_x\text{Mn}_{1-x}\text{Si}$ (CFMS) films have been explored recently. By tuning the elemental composition (x), it has been suggested that both the Gilbert damping constant and the half-metallic band gap of CFMS can be improved with respect to both CMS and CFS⁷. Furthermore it is possible to prepare a relatively well-ordered L_{21} phase of CFMS at lower annealing temperatures compared to CMS⁴, a fact which is likely to contribute to the large room-temperature magnetoresistance (MR) of 74% that has been observed in CFMS-based CPP-SVs⁸. Indeed CFMS-based devices have already outperformed the current-perpendicular-to-plane giant magnetoresistance (CPP-GMR) structures based on CMS and Co_2MnGe ^{4, 9},

¹⁰. Nevertheless the theoretical 100% magnetoresistance has not yet been realised in films or devices. A number of studies have investigated the effect of disorder on the half-metallicity of the Heusler alloys^{11, 12}. Recently it has been shown that the integrity of the Co sublattice is crucial for the spin polarisation of $\text{Co}_2\text{Fe}_{0.5}\text{Mn}_{0.5}\text{Si}$ at the Fermi level¹³, and that the Co sublattice is relatively stable. Nevertheless the general effects of atomic disorder on $\text{Co}_2\text{Fe}_x\text{Mn}_{1-x}\text{Si}$ are still poorly understood. In this work we present density functional theory (DFT) + Hubbard U calculations on CMS, CFMS and CFS to explore how the electronic properties are affected by atomic disorder.

2. Atomic disorder

Full Heusler alloys are of the form X_2YZ , where X and Y are d-block elements and Z is a p-block element. They possess a cubic structure comprised of four interlocking fcc cubic sublattices; in the ground-state, fully-ordered L_{21} phase, X occupies two of the sublattices, with Y and Z occupying the other two sublattices, Figure 1. Heusler thin-films often exhibit a degree of *atomic* disorder, in which there is mixing of elements between the sublattices. This atomic disorder can modify the electronic properties of the Heusler alloys significantly, so understanding its origin and effects is crucial¹³⁻¹⁵. Binary mixing is the most common form of atomic disorder, whereby the elements on two different sublattices intermix and depending on

Fig. 1 Schematic of the fully ordered $L2_1$ phase, and three possible realisations of YZ (B2) disorder. a) Swapping atoms on Y and Z site between neighboring planes; b) Swapping Y and Z atoms within an atomic plane; and c) stacking fault type of neighboring YZ planes. For $\text{Co}_2(\text{Mn,Fe})\text{Si}$ the X site is occupied by Co, Y by Mn/Fe and the Z site by Si.

which sublattices are mixed this can be characterised as XY, XZ, or YZ. For the Co-based Heuslers studied here, a previous investigation showed that XY and XZ intermixing is energetically unfavourable even at elevated growth temperatures and this theoretical prediction is borne out in experimental studies of CFMS films (Fig. 1). In contrast the YZ disorder responsible for the B2 phase of full Heuslers is of low energy, therefore it is expected to be present even for films grown at higher annealing temperatures. Therefore understanding the realisation of the YZ disorder in CFMS across a range of Fe/Mn concentrations is of great interest in order to understand the functionality of devices based on CFMS-type electrodes. Next we discuss the type of YZ disorder considered in this work.

A conventional 16-atom unit cell of a full Heusler alloy comprises 8 X, 4 Y and 4 Z atoms in a cubic arrangement. In the (001) direction the material consists of alternating planes of X and Y/Z atoms, with 4 atoms per plane (Fig. 1a). The atomic positions in each plane form the vertices of a square; in the X planes all vertices are occupied by X atoms but in the Y/Z planes adjacent vertices are occupied by different atomic types. In this unit cell there are thus two distinct types of YZ disorder: mixing between the Y and Z across different YZ planes (Fig. 1a), leading to local violations of stoichiometry; and mixing between the Y and Z within a single YZ plane (Fig. 1b). A particular case of this latter kind of disorder is the YZ-stacking fault. In the fully-ordered $L2_1$ state, the Y/Z planes follow an A-B-A stacking sequence whereby the occupation of any particular vertex alternates between the Y and Z atoms. The alternative A-A-A sequence represents a stacking fault whereby all of the Y-Z planes are identical (Fig. 1c). For the CFMS Heusler that is the focus of this work, there is an additional factor of two in the possible disorder types due to the mixture of Fe and Mn atoms on the Y sites.

3. Methods

To illustrate the YZ ordering in CFMS, we have structurally studied a giant magnetoresistance structure (GMR) based on CFMS films. The GMR structure was deposited on $\text{MgO}(100)$ substrate, and consist of the following layers:

$\text{Ru}(10)/\text{CFMS}(5)/\text{Ag}(5)/\text{CFMS}(20)/\text{Ag}(5)/\text{Cr}(20)/\text{MgO}$

All layers number are in nm. The CFMS layers were deposited using $(\text{Co}-\text{Fe}-\text{Mn}-\text{Si})$ (Co: 45.2%, Fe: 9.7%, Mn: 16.8%, Si: 28.3%) alloyed targets which results in $\text{Co}_2\text{Fe}_{0.4}\text{Mn}_{0.6}\text{Si}$. In order to improve the CFMS crystallinity, top electrode (CFMS, 5nm) and bottom electrode (CFMS, 20nm) were annealed at 350 °C and 500 °C, respectively, in the sputtering chamber. Structural investigation was done by cross section transmission scanning electron microscopy (STEM) using High Angle Annular Dark Field (HAADF) technique which is Z contrast sensitive on JEOL ARM microscope. The cross-section specimens were prepared by conventional methods that include mechanical thinning/polishing and finishing with low energy Ar ion milling¹⁶.

In order to simulate the effect of atomic disorder on the Heusler alloys, *ab initio* calculations were performed using the plane-wave DFT program CASTEP¹⁷. All of the simulations were performed with non-linear core-corrected ultrasoft pseudopotentials, a 650 eV plane-wave cut-off and a Brillouin zone sampling of $0.04 \times 2\pi \text{\AA}^{-1}$ with a Fermi-level broadening of 0.2 eV. These values were chosen such that the force on a displaced atom in an ordered $L2_1$ CFMS ($x=0.5$) cell was correct to better than 1%, and the total energy was converged to within 1 meV/atom.

Whereas common semi-local approximations for exchange and correlation such as PBE¹⁸ are sufficient to reproduce the half-metallicity of CMS, they do not reproduce that of CFS, due to the well-known under-localisation of the d-electrons and related fractional state occupation. The half-metallic properties of the bulk Heuslers CFMS are recovered for all $0.0 \leq x$

Fig. 2 (a) Z-contrast (HAADF) image of $\text{Co}_2(\text{Fe,Mn})\text{Si}$ annealed at 350 °C in [110] orientation. (b) Intensity profile along the YZ (Fe/Mn)-Si plane, showing clearly the separation between the L_{21} and B2 ordered regions. (c) HAADF image of $\text{Co}_2(\text{Fe,Mn})\text{Si}$ annealed at 500 °C in [110] orientation. (d) Intensity profile along the YZ (Fe/Mn)-Si plane, showing the presence of an L_{21} phase.

≤ 1.0 by introducing an appropriate Hubbard U term into the electronic Hamiltonian^{13, 19, 20}, which widens the minority spin band-gap in CFS by 0.9 eV. It should be noted that DFT + U is still an approximation, hence the calculated band gaps could still have some discrepancy compared to real band gaps; however, the band gap trends are widely considered to be accurate. For the calculations presented in the rest of this work, we used the PBE exchange-correlation functional with a Hubbard U of 2.1 eV for the Co, Fe, and Mn d-states.

The effects of disorder were studied across a range of chemical compositions from pure Co_2MnSi (CMS) to pure Co_2FeSi (CFS), starting from CMS and generating new compositions by systematically replacing Mn by Fe. Since there are 4 Y atomic sites in the conventional 16-atom Heusler cell, this allowed the study of

$\text{Co}_2\text{Fe}_x\text{Mn}_{1-x}\text{Si}$ (CFMS) for $x=0, 0.25, 0.5, 0.75$ and 1.0.

The disordered simulation systems were constructed by exchanging pairs of atoms in the ordered CFMS unit cells. Since there are four Y sites and four Z sites in the conventional cell, exchanging one pair corresponds to a 25% incorrect site occupation. In this nomenclature, 50% would correspond to “full disorder,” where the correct and incorrect occupations are equally likely. For each new unit cell the lattice and atomic positions were relaxed until the maximum force on any atom was less than 0.04 eV/Å and the stress was under 0.02 GPa.

The PBE + U calculations of the spin DOS for the L_{21} ordered phases of CMS, CFMS and CFS confirmed their half-metallic properties, with 99-100% spin polarisation at the Fermi level and a typical Kohn-Sham band-gap of around 1 eV for the minority spin.

Table 1 Formation energies (eV/atom) of the YZ disorders for 25% disordered $\text{Co}_2\text{Fe}_x\text{Mn}_{1-x}\text{Si}$. For $0 < x < 1$ the disorder energies depend on whether Fe or Mn is exchanged for the Si.

YZ disorder type	Chemical composition (x)				
	0	0.25	0.5	0.75	1
Atomic swap between planes	0.09(6)	0.08(8)-0.09(4)	0.08(7)-0.09(2)	0.08(7)-0.09(1)	0.08(1)
Atomic swap in-plane	0.07	0.06(3)-0.06(6)	0.05(6)-0.06(6)	0.05(4)-0.06(1)	0.04(5)
Stacking fault	0.08(0)	0.07(4)	0.06(1)	0.05(8)	0.04(2)

Fig. 3 Spin polarised density of states for CFMS with a YZ stacking fault, as in Figure 1(c). For pure CMS (left) the disorder introduces states just below the Fermi level, reducing the half-metallicity. For pure CFS (right) the disorder introduces states just above the Fermi level, reducing the half-metallicity. For CFMS ($x=0.5$) the Fermi level is in the middle of the gap, and the half-metallicity is preserved. Calculations were performed using PBE + U (U: Co 2.1 eV, Fe d 2.1 eV, and Mn d 2.1 eV).

4. Results

Due to the Z -contrast mechanism in STEM-HAADF (where Z refers to an element's atomic number) and the relatively large difference in the atomic number on the YZ plane between Fe/Mn and Si it is clear whether ordering on this plane has been achieved in any thin film structures. Figure 2 shows the effect of the annealing temperature of the CFMS films. When annealing is performed at 350 °C the film shows mixed regions of L2₁ and B2 phases (Figure 1a), Increasing the temperature to 500 °C, almost completely removes the YZ disorder (B2 regions) in the film, as illustrated in Figure 2b. Next we present the energy of realisation of different types of YZ disorder in $\text{Fe}_x\text{Mn}_{1-x}\text{Si}$ for x ranging between 0 and 1 with a step of 0.25.

The energy of each realisation of YZ disorder was computed as the difference between the energy *per atom* of the disordered cell and the fully ordered cell. The calculated disorder energies are presented in Table 1. Previous studies¹²⁾ on CFMS showed that for $x=0.5$ YZ disorder between atomic sites on the same plane had a formation energy of around 0.06 eV/atom, which is confirmed in this work with the Fe-Si atomic disorder about 10 meV/atom more favourable than the Mn-Si

disorder. As the proportion of Fe (x) is increased this in-plane YZ disorder costs less and less energy, with the CFS disorder only 0.04(5) eV/atom. YZ disorder between different atomic planes changes the local stoichiometry and costs more energy, around 0.09 eV/atom. This disorder energy also decreases as x increases, but not as rapidly as the in-plane disorder.

The YZ stacking fault in CMS is intermediate in energy, being 10 meV/atom more energetic than the in-plane disorder but 10 meV/atom less energetic than disorder across YZ planes. However this stacking fault energy decreases more rapidly with x than the in-plane disorder, meaning that it is competitive with the in-plane disorder for $x=0.5$ and 0.75, and for CFS ($x=1$) it is the lowest energy of all the disorders studied.

The results in Table 2 show that both pure phases (CMS and CFS) are sensitive to YZ disorder, losing spin-polarisation at the Fermi-level for all realisations of this disorder. The CFMS phases are most sensitive to mixing between Fe and Si in different YZ planes, with high spin polarisation maintained in the presence of in-plane mixing between Fe and Si, and moderate spin polarisation obtained for mixing between Mn and Si.

The relative robustness of CFMS over CMS and CFS is most striking for the stacking-fault YZ disorder. In pure CMS the incorrect Mn-Si-plane stacking sequence

Table 2 Spin polarisation at the Fermi level for 25% YZ disorder of $\text{Co}_2\text{Fe}_x\text{Mn}_{1-x}\text{Si}$, computed from DOS with 0.3 eV Gaussian smearing. For $0 < x < 1$ the YZ disorder energies depend on whether a Mn or Fe is exchanged.

YZ disorder type	Chemical composition (x)				
	0	0.25	0.5	0.75	1
Mn-Si swap between planes	44%	43%	95%	100%	-
Mn-Si swap in-plane	51%	55%	100%	100%	-
Fe-Si swap between planes	-	21%	84%	84%	23%
Fe-Si swap in-plane	-	72%	100%	96%	83%
Stacking fault	48%	78%	98%	94%	15%

causes a drop in spin-polarisation to 48% at the Fermi level, and in CFS the equivalent Fe-Si stacking fault causes an even larger drop to 15%. In contrast all CFMS compositions studied here retained high spin polarisation in the presence of such stacking faults, with spin polarisations of 78% and above across the chemical range.

The half-metallicity of CFMS for $x=0.5$ and $x=0.75$ is particularly robust to YZ disorder, with high spin polarisations for all the disorder types studied. Both compositions are most sensitive to mixing across Fe-Si planes, in each case lowering the spin polarisation at the Fermi-level to 84%. All other YZ disorder realisations retain high spin-polarisations of 94-100%.

The reason for both the fragility of the CMS and CFS half-metallicity and the robustness of CFMS ($x=0.5$) is apparent from the densities-of-states (DOS). These DOS were computed and analysed using CASTEP and the OPTADOS utility program²¹⁾ with a fixed-width 0.3 eV Gaussian smearing scheme. The DOS for the YZ stacking-fault disorder is shown in Figure 3. For pure CMS, the Fermi-level is located just above the valence band maximum. The YZ stacking-fault disorder shifts this valence edge, causing an increase in the minority spin states at the Fermi level and a loss of half-metallicity. For CFS the extra electrons from the Fe causes the Fermi-level to sit just below the conduction band minimum; here the YZ disorder causes states near the conduction edge, just above the Fermi-level, which again lowers the spin polarisation at the Fermi level. For the CFMS ($x=0.5$) the Fermi-level is situated almost in the centre of the band-gap, meaning that the half-metallicity is robust to small changes in both the valence and conduction edges.

4. Conclusions

Ab initio electronic structure calculations of various YZ disordered phases of CFMS show that the half-metallic property of CFMS is more robust to disorder than that of either CMS or CFS. The disorder energy decreases with increasing x , hence YZ disorder is more likely to occur in films with high Fe concentrations. Films with equal Mn and Fe concentrations ($x=0.5$) are shown to be especially robust, retaining perfect or near-perfect half-metallicity in the presence of all the studied types of YZ disorder. This result may explain the high magnetoresistance experimentally observed in spin valves in CFMS films⁸⁾.

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