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Using structural disorder to enhance the magnetism and spin-polarization in Fe$_x$Si$_{1-x}$ thin films for spintronics

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Abstract

Amorphous Fe$_x$Si$_{1-x}$ thin films exhibit a striking enhancement in magnetization compared to crystalline films with the same composition (0.45 < $x$ < 0.75), and x-ray magnetic circular dichroism reveals an enhancement in both spin and orbital moments in the amorphous films. Density functional theory (DFT) calculations reproduce this enhanced magnetization and also show a relatively large spin-polarization at the Fermi energy, also seen experimentally in Andreev reflection. Theory and experiment show that the amorphous materials have a decreased number of nearest neighbors and reduced number density relative to the crystalline samples of the same composition; the associated decrease in Fe-Si neighbors reduces the hybridization of Fe orbitals, leading to the enhanced moment.

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Spintronic (spin-electronic) devices are a potential alternative to standard charge-based devices where the electron spin carries the information instead of the charge. Many proposed spintronic devices require a spin-injector, a material that can produce a highly spin-polarized current, and consequently significant work has gone into identifying these types of materials. Ga$_x$Mn$_{1-x}$As, the canonical dilute magnetic semiconductor, has been touted as a promising material in this capacity. However, the Curie temperature remains low (~150 K), making the material unsuitable for room-temperature spintronic applications. By contrast, Fe$_x$Si$_{1-x}$ alloys are potential candidates given their high Curie temperature and the tunability of their magnetic and electronic properties (including carrier concentration) with changes in the composition ($0.50 < x < 0.75$) of crystalline films [1–5]. This tunability comes in part because there exist three different bcc-like structures (D0$_3$, B2, A2), each with different degrees of chemical order. What has not been considered is the use of structural disorder to tune the magnetic and electronic properties, despite the fact that the mobility of the spin injector is not directly relevant and there are numerous examples of amorphous ferromagnets [6].

In this paper, we will show that amorphous ($a$-) Fe$_x$Si$_{1-x}$ ($0.45 \leq x \leq 0.75$) is not only ferromagnetic but exhibits a significant enhancement in magnetic moment (both spin and orbital components) and spin polarization at the Fermi energy compared to crystalline counterparts. This enhanced magnetism is particularly surprising when considered in the context of magnetism in amorphous transition metals and their alloys, where the moments are strongly influenced by the local chemical environments. In many transition metal–metalloid (TM-M) alloys, the moment extrapolated to a pure amorphous transition metal is essentially the same as for the crystalline metal e.g. 1.7 $\mu_B$/Co in $a$-Co$_{1-x}$P$_1$ and 2.3 $\mu_B$/Fe in $a$-Fe$_y$B$_{1-x}$ as $x$ approaches 1.0, and is reduced for lower $x$ [7]. In addition, magnetic moments are often reduced from the crystalline counterpart by frustrated exchange interactions [7]. For example, vapor-quenched amorphous Fe was found to be ferromagnetic at low temperature but with a decreased average magnetic moment (1.5 $\mu_B$/Fe) [8, 9] attributed to a distribution of interatomic distances leading to both positive (similar to $\alpha$-Fe) and negative exchange interactions (similar to $\gamma$-Fe). Additionally, many amorphous Fe$_y$Z$_{1-y}$ alloys ($Z=\text{Nb, Ta, Y, Zr, Lu}$) are ferromagnetic as $y$ approaches 1, with moments ranging from 0.7–1.8 $\mu_B$/Fe depending on $y$ and $Z$, but all exhibit spin glass behavior with decreasing $y$ ($y=0.64–0.80$) due to frustrated mixed interactions [10–14].

By contrast, limited previous reports on amorphous Fe$_x$Si$_{1-x}$, show the onset of a magnetic moment occurs at $x=0.4$, with a magnetization that increased with $x$ [15–17] (e.g. 1.4 $\mu_B$/Fe for $x=0.62$), and no sign of frustration. However, the origin of the enhanced moment (versus the crystalline materials) was not explained, inhomogeneity was evidenced by the lack of square $M(H)$ curves, and structural analysis showed high local coordination, inconsistent with a ferromagnetic Fe alloy [17]. In this report, we investigate the structural, magnetic, and electronic properties of amorphous Fe$_x$Si$_{1-x}$ and use density, DFT calculations and XAFS experiments to show that the enhanced magnetism is attributable to decreased coordination (below that of either bcc or fcc Fe) and a decrease in Si neighbors around each Fe atom, resulting in reduced $sd$ hybridization.

The equilibrium phases in the investigated range of $x$ are D0$_3$ ($x=0.75$) and a large unit cell $\varepsilon$ phase ($x=0.5$) with exotic magnetic and transport properties, which will not be discussed [18]. Non-equilibrium bcc-like structures are possible with thin film growth: A2 (chemically disordered, random bcc solid solution), B2 (partially ordered, CsCl structure with Fe on the cube corner sites and Fe/Si randomly arranged on the body center sites) and finally D0$_3$.
(chemically ordered, Fe on the cube corners and Fe and Si alternating in the body centers with excess Fe ($x>0.75$) or excess Si ($x<0.75$) randomly on the other’s body center sites).

Fe$_x$Si$_{1-x}$ thin films (1300–2200 Å) were grown by electron beam co-evaporation of Fe and Si. Amorphous films ($x=0.45–0.65$) were grown at room temperature on amorphous SiN$_x$ on Si substrates, and epitaxial Fe$_x$Si$_{1-x}$ thin films ($x=0.55–0.75$) were obtained by deposition on (001) MgO at 200 °C for $x>0.65$. For epitaxial samples with $x \leqslant 0.65$, a Cr layer, deposited at 200 °C on (001) MgO prior to film growth, was required to obtain epitaxy. Film number densities, $n_{\text{total}}$, and compositions were measured using Rutherford backscattering spectrometry (RBS). X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) were used to characterize the structure. Room temperature x-ray absorption fine structure (XAFS) was performed at the Fe K-edge at beamline 20-BM at the Advanced Photon Source. Magnetization ($M$) as a function of field ($H$) and temperature ($T$) was measured using a Quantum Design PPMS magnetometer. Room temperature x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) were performed in total electron yield at the Fe L$_{2,3}$-edge in a magnetic field of ±0.5 T at BL 6.3.1 at the Advanced Light Source. The individual spin and orbital moments were calculated using the sum rules [19], where the number of 3$d$ holes was determined from the theoretical calculations. Spin-polarization was measured experimentally by Andreev reflection, based on the methods described in [20]. Conversion electron Mössbauer spectrometry (CEMS) was performed on crystalline ($x=0.77–0.55$) and amorphous ($x=0.67$) Fe$_x$Si$_{1-x}$ thin films at 300 K. Further measurement details and results are discussed in the supplementary material and references [21].

Theoretical calculations were performed on amorphous and crystalline structures. *Ab initio* molecular dynamics (MD) simulations and density functional theory (DFT) were used to simulate the amorphous structure in a cubic unit cell of volume $V$ containing 128 atoms ($128^*x$ Fe atoms and $128^*(1-x)$ Si atoms) using the plane-wave-based Vienna *ab initio* simulation package (VASP) [22], with the projector augmented wave (PAW) method for the description of core-valence interaction [23]. The exchange-correlation functions were treated at the level of generalized-gradient approximation [24]. The structure underwent a melting (2000 K), a quenching (2000–200 K at $3 \times 10^{14}$ K s$^{-1}$), and annealing (200 K, 5 ps) step in a canonical ensemble for the randomization of atomic structural positions. The atomic spacing, positions and $V$ were further optimized before and after the quenching and annealing processes, until forces on each atom were less than 0.01 eV Å$^{-1}$. An energy cutoff of 350 eV was used for the expansion of plane-wave basis functions. While only the $\Gamma$-point was used to sample the Brillouin-zone during the melting, quenching and annealing processes, $3 \times 3 \times 3$ Monkhorst-Pack $k$-points were used for the geometry relaxation and electronic structure determination after the MD simulations. For the crystalline Fe$_x$Si$_{1-x}$ alloys, supercell models with 16 atoms were used. Both D0$_3$ and B2-like structures were investigated for $x=0.75$. For $x=0.625$ and 0.6875, some body center Fe atoms of the stoichiometric D0$_3$ unit cell were replaced by Si, forming off-stoichiometry D0$_3$-like structures; all the body center atoms were randomized to form B2-like structures. The lattice constants of these simulated structures were within 1% of the experimental values. The A2 structure, although not experimentally realized, was also calculated for $x=0.65$. Magnetization, atomic density, electronic band structure, and pair distribution functions were calculated for each structure.

9 It was not possible to grow amorphous films at higher $x$ or epitaxial films at lower $x$. 
Figure 1 shows theoretical and experimental spontaneous magnetization, $M_s$, ($M$ at high $H$ extrapolated to $H=0$) at 2 K (a) and $n_{total}$ (b) versus $x$ for crystalline and amorphous films. Square hysteresis loops are observed for all $x \geq 0.55$, indicating the samples are ferromagnetic. The shape of the $M(H)$ curve for the amorphous $x=0.45$ sample is not square; however, magnetic remanence is found and $M$ is larger than a Brillouin function, indicating weak ferromagnetism (see supplementary material). Strikingly, for all $x$ in theory and experiment, $M_s$ of the amorphous samples is very large in comparison to crystalline (B2, D03) samples with the same compositions. The value is dependent on chemical order; the chemically disordered theoretical A2 structure has a significantly larger moment than B2 or D03, which are the same for a given $x$. In the B2 and D03 structures, the nearest neighbor environments are the same and only the second nearest neighbors, which have a smaller effect on $M$, differ. In figure 1(b), as $x$ increases, the theoretical and experimental $n_{total}$ of the crystalline films decreases. By contrast, $n_{total}$ of the amorphous films is constant with composition and significantly (13–17%) lower than the crystalline films at all $x$.

To understand the enhanced magnetism at the atomic level, XMCD (at 79 K, 300 K) was used to experimentally determine the Fe spin ($M_{\text{spin}}$) and orbital ($M_{\text{orbital}}$) moments, which were calculated based on the methods described in references [19, 25]. Figures 1(c) and (d) show $M_{\text{spin}}$ and $M_{\text{orbital}}$, respectively, for both amorphous and epitaxial films. $M_{\text{spin}}$ and $M_{\text{orbital}}$
calculated for epitaxial $x=0.75$ and 1.0 films are in good agreement with previous reports [19, 26]. For all $x$, $M_{\text{spin}}$ tracks the total $M$ and is significantly larger in the amorphous than crystalline films. Even for $x=0.55$, whose spin moments at 300 K are near zero since $T_C$ is near 300 K, measurements at 79 K show that the amorphous film exhibits a much larger $M_{\text{spin}}$ than the epitaxial film. The amorphous films’ $M_{\text{orbital}}$ also increase with increasing $x$ and are larger than the crystalline samples with the same composition, likely due to the lower local symmetry of the amorphous phase.

To explain the enhancement in $M_{\text{spin}}$ we turn to an investigation of the local atomic structure of the amorphous films, which was analyzed in the DFT calculations using pair correlation functions and experimentally by XAFS at the Fe K-edge (see supplementary material). The number of Fe-Fe (Fe-Si) pairs in the $i$ shell of nearest neighbors is defined as $N_{\text{Fe-Fe}}^i$ (and $N_{\text{Fe-Si}}^i$), and the total coordination number in the $i$ shell is $CN^i$. In both theory and experiment, no Fe-Fe pairs were observed in the first shell for $x=0.50$ or 0.55. Fe atoms are completely surrounded by Si but with fewer Si atoms than in the crystalline structures (except for the theoretical A2 phase). As shown in figure 2, for higher $x$, $N_{\text{Fe-Fe}}^i$ increases with $x$ while $N_{\text{Fe-Si}}^i$ decreases causing $CN^1$ to only slightly increase. The total coordination numbers $CN^1(\sim6)$ and $CN^2(\sim12)$ are significantly smaller for all $x$ than the corresponding values, 8 and 14, respectively, in the bcc structure and significantly less than the fcc value ($CN^1 = 12$) suggested previously in $a$-Fe$_x$Si$_{1-x}$ (see supplementary material) [15]. Not just the reduced coordination but also the nearest neighbor species play a crucial role in the magnitude of the moment; notably, it is not the number of Fe nearest neighbors that determines the magnetic moment of an Fe atom but the number of Si neighbors.

This point is elucidated in figure 2, which compares the experimental and theoretical average number of first shell Fe and Si neighbors for selected amorphous and crystalline (A2, B2, D03) compositions. $N_{\text{Fe-Fe}}^1$ (figure 2(a)) in the crystalline materials is greater than in the amorphous materials for all $x$, hence striking and not immediately obvious why the moment in the crystalline systems is LESS than in the amorphous. However, $N_{\text{Fe-Si}}^1$ (figure 2(b)) is also greater in the crystalline materials, for all $x$; therefore, the enhanced magnetism in the amorphous compositions can only be explained by the fact that $N_{\text{Fe-Si}}^1$ is less. As an example, consider $x=0.5$, where both the amorphous and crystalline structures have no Fe nearest neighbors. The B2 phase has no moment while the amorphous films have a significant moment. In the B2 phase, all 8 Fe nearest neighbors are Si, whereas in the amorphous structure, there are only 5 Si neighbors. Only in the hypothetical A2 structure would the moment be expected to be larger than the amorphous structure due to its reduced $N_{\text{Fe-Si}}^1$ relative to the B2, D03, and amorphous structures (as seen in figure 1 for the calculated value of moment for A2 structure for $x=0.65$).

Utilization of amorphous Fe$_x$Si$_{1-x}$ thin films as spin injectors also requires consideration of the electronic structure and spin polarization. Figure 3(a) displays the calculated electronic density of states, $D(E)$, for both up (↑) and down (↓) spins for various $x$ in the amorphous structures, and figure 3(b) shows $D(E)$ for the D03, B2, A2 and amorphous structures with compositions near $x=0.65$. Spin-splitting is observed in the amorphous bandstructures, although the vanishing of $D\downarrow(E)$ near $E_F$ seen in both B2 and D03 is lost. Sharp features in the B2 and D03 structures (figure 3(b)) are significantly broadened in the chemically disordered A2 phase, and further broadened in the amorphous structures.
Figure 2. Average (a) $N_{\text{Fe-Fe}}^1$, (b) $N_{\text{Fe-Si}}^1$ and (c) $CN^1$ for amorphous and crystalline (A2, B2/D0$_3$) materials with various $x$. Open symbols are experimental data, and closed symbols are theory. The lines are a guide to the eye. In (c) the A2 and B2/D0$_3$ data points for $x=0.65$ lie on top of each other (i.e. all bcc-like structures have 8 nearest neighbors).
The spin polarization at $E_F$, $|P|$, is defined as
\[
\left[ \frac{D \uparrow (E_F) - D \downarrow (E_F)}{D \uparrow (E_F) + D \downarrow (E_F)} \right]
\] and was determined both theoretically from $D(E)$ and experimentally by Andreev reflection (see supplementary material). For the theoretical amorphous structures, $D \uparrow(E_F)$ is relatively insensitive to composition, $D \downarrow(E_F)$ changes only slightly; $P$ is negative and does not significantly change with composition (inset figure 2(a)). As shown in the inset of figure 3(b), the calculated spin polarization in the amorphous material ($x = 0.65$) is larger than the A2 structure; it is nearly as large (although of the opposite sign) as the B2 structure. The experimental spin polarization is also shown in the inset of figure 3(b) for an amorphous film ($x = 0.65$) and epitaxial film ($x = 0.65$). $|P|$ measured is

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**Figure 3.** Calculated density of states for (a) amorphous structures with various compositions ($x = 0.5\text{--}0.75$) and (b) crystalline and amorphous structures near $x = 0.65$. Insets: absolute value of spin-polarization $|P|$ at $E_F$ from (a) theoretical calculations (black squares) for amorphous structures with various $x$ and (b) theoretical calculations (black squares) and Andreev reflection (open circles) for crystalline and amorphous structures with $x \sim 0.65$. Note that experimental and theoretical values of $|P|$ for the B2 structure are the same. The D0$_3$ open circle in the inset of (b) is an experimental Andreev reflection data point for D0$_3$ $x = 0.75$ from [27].
larger in the amorphous film than the epitaxial film. In fact, the spin polarization is larger than a previously reported value for a D03 \( x = 0.75 \) epitaxial film [27].

In summary, structural disorder was used to tune the magnetic and electronic properties of Fe\(_x\)Si\(_{1-x}\) thin films. Enhanced magnetic moment and spin polarization were observed for all amorphous films compared to crystalline films of the same composition. Experimental and DFT results showed decreased number densities and coordination numbers in the amorphous structures in comparison to the crystalline phases. The reduced coordination and density of the amorphous Fe-Si structure preserves a ferromagnetic Fe-Fe exchange coupling with no frustration, unlike other amorphous Fe-based materials. The local atomic structure in the amorphous materials has fewer Fe-Si pairs than in any chemically ordered crystalline material but with interatomic distances that are comparable to bcc structures, resulting in the observed moment enhancement and ferromagnetic exchange interactions. This local structure in the amorphous system also preserves a surprisingly robust spin-polarization. Remarkably, disorder significantly enhances the magnetic properties in this amorphous structure, making this material potentially relevant as a spin injector.

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