



Investigation of CoFeBSi alloys composition from molecular dynamics and DFT calculations

R. Mardani^{1*}, M. R. K. Vahdani¹, H. Shahmirzaee¹, P. Daasme²

1-Malek ashtar university, Shiraz, Iran, Mardani_r@birjand.ac.ir

2- National elite's foundation, Shiraz, Iran, p.dasmeh@gmail.com

Abstract

Cobalt based amorphous alloys, in particular CoFeBSi, have been widely used to study the response of *ac*-impedance to the external *dc* magnetic field, i.e., the so called Giant Magneto Impedance (GMI) effect. The utility of CoFeBSi in different applications such as field-sensitive sensors is known and practiced. Despite the wealth of experimental studies on GMI properties of CoFeBSi alloys, no computational approach has yet addressed electronic and magnetic properties of these systems at nanoscale. In this study, we have computed electronic and magnetic properties of amorphous CoFeBSi alloy using a combined molecular dynamics (MD) and density functional theory (DFT) approaches. MD is used to provide a physically realistic sampling of different atomic configurations while the properties such as dipole moments and magnetic susceptibilities are computed using DFT. Our study shows a wide spectrum of electronic as well as magnetic properties for nanoclusters of different sizes which could aim future experimental studies for rational design of Co-based ferromagnetic alloys.

Key Word: Giant Magneto Impedance, CoFeBSi, Density Functional Theory

Introduction

Giant magnetoimpedance (GMI) effect is defined as a large change in the impedance of a soft magnetic conductor which an alternating current flows through in the presence of an applied magnetic field [1, 2, 3]. The amorphous magnetic materials showing considerable GMI effect have important applications in science and industry, in particular in weak magnetic-field sensing [1-3]. This effect was first observed by Panina and Mohri in 1994 [1]. Within classical electrodynamics, GMI is best described as an extension of the skin effect. Theoretical justification of GMI effect and the processes involved in magnetization (e.g., at different *ac* frequencies) have been thoroughly discussed in the literature [4]. However, little is known about molecular architecture of the alloys in GMI studies. Molecular dynamics (MD) and Quantum Chemistry (QC) methods are powerful approaches to study properties of different atomic and molecular systems [5,6]. The QC methods such as the highly accredited Density Functional Theory (DFT), on the other hand, are *ab initio* and therefore independent of external parameterization, however, time- and computational resources-consuming. Therefore, one feasible approach, in particular for metallic clusters, is to use MD for



configuration sampling and DFT for calculation of variety of electronic and magnetic properties [7].

In the current work, we used all atom MD simulation on a super cell containing 1460 atoms of CoFeBSi ferromagnetic alloy using the parameterized Born-Mayer-Buckingham potential function. We report a transition to amorphous state confirmed by calculation of the total radial distribution function (RDF) of the alloy. DFT calculations were further used to calculate dipole moments, isotropic magnetic susceptibility and magnetic anisotropy in nanoclusters with different fractions of metals and metalloids. Our study is thus the first instance that computational approaches are employed to study electronic and magnetic properties of nanoclusters in cobalt based ferromagnetic alloys showing GMI effect.

Results and Discussions

In this work, the interactions between the atoms are described by the Born- Mayer-Buckingham potential function that used to describe physiochemical processes in metallic and intermetallic systems[5]:

$$V(r) = A \exp\left(\frac{-r_{ij}}{\rho}\right) - C \left(\frac{1}{r_{ij}^6}\right) + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (1)$$

In equation 1, A and ρ describe the components of repulsion and, C describes contribution of attraction to potential energy. We calculated interaction potential of Co-Co pair, using DFT as explained in Materials and methods (Fig 1.).

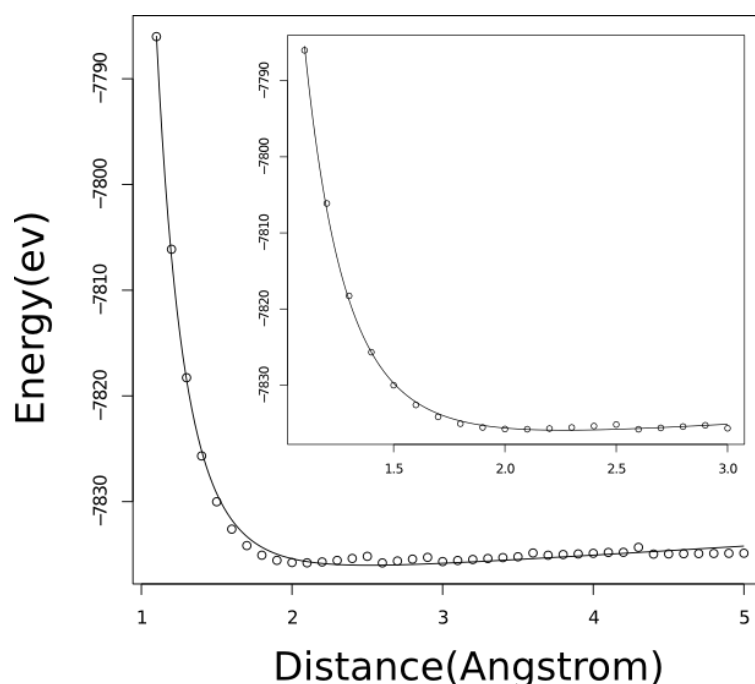


Fig 1. Born-Myer-Buckingham potential fitted to potential energy interaction curve of Co-Co pair generated by DFT (TPSSH+Def2SV).



Then we estimated the energy of different spin multiplicities of interacting pairs as shown in Table 1.

Table 1. Energies of different spin states for interacting pairs in CoFeBSi alloy.

Bond	Spin Multiplicity (Energy in Ha)									
	1	2	3	4	5	6	7	8	9	10
Fe-Fe	-246.436	- ^a	-246.498	-	-246.548	-	-246.619	-	-246.619	-
Fe-Co	-	-268.234		-268.221	-	-268.286	-	-268.275	-	-268.173
Fe-B	-	-148.028		-148.038	-	-148.015	-	-147.954	-	-147.803
Fe-Si	-127.053	-	-127.147	-	-127.133	-	-127.112	-	-127.055	-
Co-Co	-289.782	-	-289.792	-	-289.872	-	-289.829	-	-289.708	-
Co-B	-169.636	-	-169.681	-	-169.651	-	-169.564	-	-169.393	-
Co-Si	-	-148.781	-	-148.769	-	-148.716	-	-148.656	-	-148.415
B-B	-49.371	-	-49.409	-	-49.421	-	-49.115	-	-42.268	-
B-Si	-49.371	-	-49.409	-	-49.421	-	-49.115	-	-42.268	-
Si-Si	-7.589	-	-7.630	-	-7.592	-	-7.459	-	-	-

a: - as not applicable.

From the table, and as an example, the lowest energy in Fe-Fe bond corresponds to the spin multiplicity of seven and the difference in energy of spin states of five and seven is 86.11 kJ/mol, consistent with previous reports [7]. We then performed MD simulation of the system in NVT ensemble using MOLDY software [5] for 1000000 steps comprising total of 1 ns simulation time. To check for convergence and equilibration of the system, we calculated root mean square deviation (RMSD) of each structure to the initial structure at different time points as shown in Figure 2.

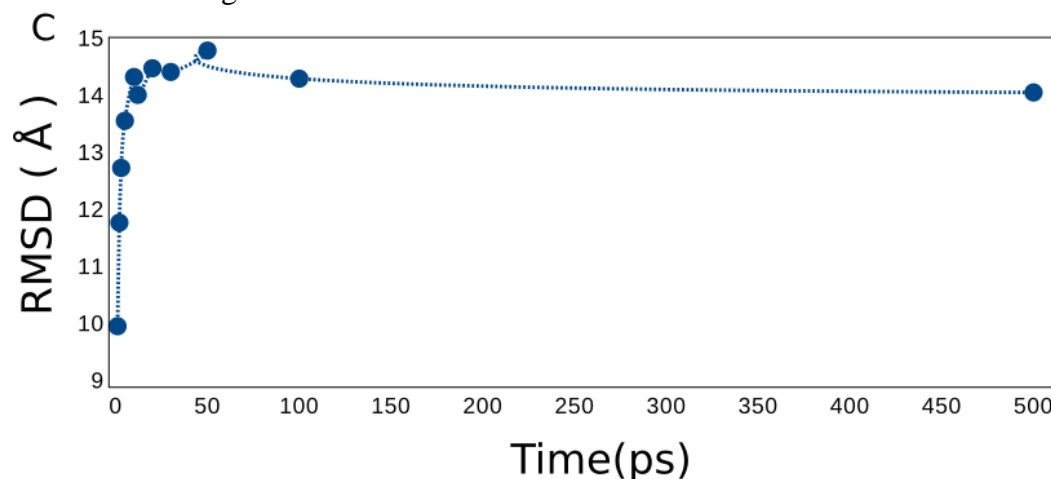


Fig 2. Equilibration of Molecular Dynamic (MD) trajectory from initial to final configuration, confirmed by root mean square deviation (RMSD) profil.



From the figure, an equilibrium is reached at times > 200 ps. As shown in Figure 3, RDF profile shows a typical amorphous structure with no sharp peak compared to the initial configuration.

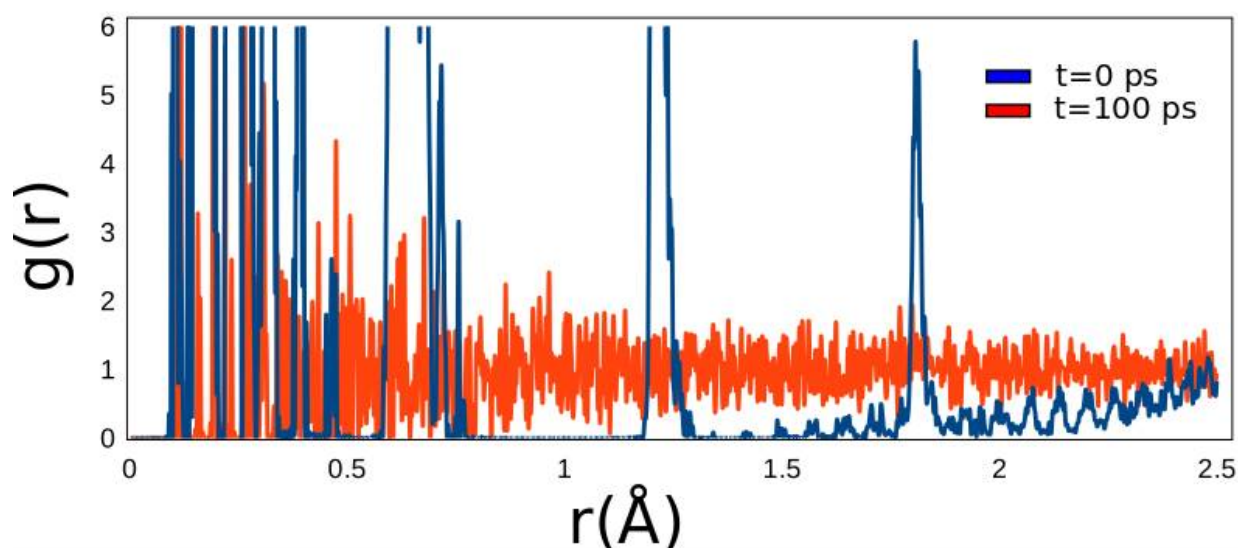


Fig 3. Radial distribution function ($g(r)$) as a function of interatomic distance for two structures A) at the beginning of simulation and B) after 100 ps.

Taken these together our computational approach suggests an optimal composition in CoFeBSi alloys giving rise to soft ferromagnetic features, i.e., high dielectric constants, high magnetic susceptibilities and low magnetic anisotropy [7]. A higher fraction of metals induces a larger magnetic susceptibility in nanoclusters by decreasing magnetic anisotropy that is otherwise enhanced with higher fraction of metalloids. Therefore, metalloids on one hand help amorphizing the alloys and hence decrease magnetocrystalline anisotropy and on the other hand increase magnetic anisotropy through extending the possibility of exchange interaction [7]. The existence of such behavior entails a thorough optimization search for rational composition design of ferromagnetic alloys.

Materials and methods

MD simulations were carried out by the molecular dynamics code MOLDY [Error! Bookmark not defined.]. For DFT calculations, the TPSSH functional [5] and Def2SV basis set [5] were used to calculate potential energy of each pair interaction as shown to outperform other functionals in accurate prediction of spin states and the length of metal-metal bonds [7]. To capture spin crossover upon bond lengthening, we use the following mathematical convention in the fitting process:

$$V(r) = \begin{cases} V_{SB}(r) & r < 3 \text{ \AA} \\ V_{SA}(r) & r \gg 3 \text{ \AA} \end{cases} \quad (2)$$

Here, $V_{SB}(r)$ and $V_{SA}(r)$ are the calculated potentials using bond multiplicity or sum of atomic multiplicities, respectively. Principal elements of magnetic susceptibility tensor for two nanoclusters ($n=7$) in the presence and absence of metalloids shown in table 2. Product of magnetic susceptibility and dipole moments ($\chi.p$) for different sampled clusters along with two clusters was shown in Fig. 4. Components of magnetic susceptibility tensor for different sampled clusters. The coefficient of variation (CV) of components of magnetic susceptibility tensor as a measure of magnetic anisotropy plotted in fraction of metals (Co, Fe) and metalloids (B, Si) for clusters (Fig. 5)

Table 2. Principal elements of magnetic susceptibility tensor for two nanoclusters ($n=7$) in the presence and absence of metalloids.

Cluster	Cluster 1		Cluster 2	
	+(B, Si) ^a	-(B, Si) ^b	+(B, Si)	-(B, Si)
χ_{xx} ^c	1034.826 ^e	552.1594	452.8855	574.9491
χ_{yy}	2180.8536	561.6690	-382.4767	500.5295
χ_{zz}	1794.9899	540.2679	170.6050	488.5508
Dipole ^d	2.11	0.85	3.24	0.37

a, b: +(B,Si) and -(B,Si) stands for the cluster with the presence and without the presence of metalloids respectively. c: χ_{xx} , χ_{yy} and χ_{zz} correspond to XX, YY and ZZ components of magnetic susceptibility tensor. Istropic susceptibility is the average of these values. d:Dipole moments are reported in debye. e: Magnetic susceptibilities are in $\text{cm}^3 \cdot \text{mol}^{-1}$.

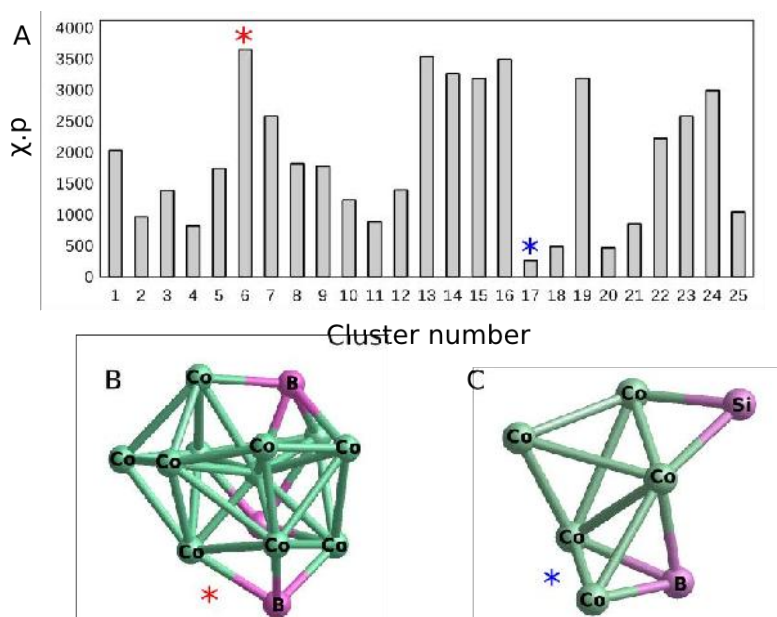


Fig 4. A) Product of magnetic susceptibility and dipole moments ($\chi.p$) for different sampled clusters along with two clusters with B) maximum $\chi.p$ and C) minimum $\chi.p$.

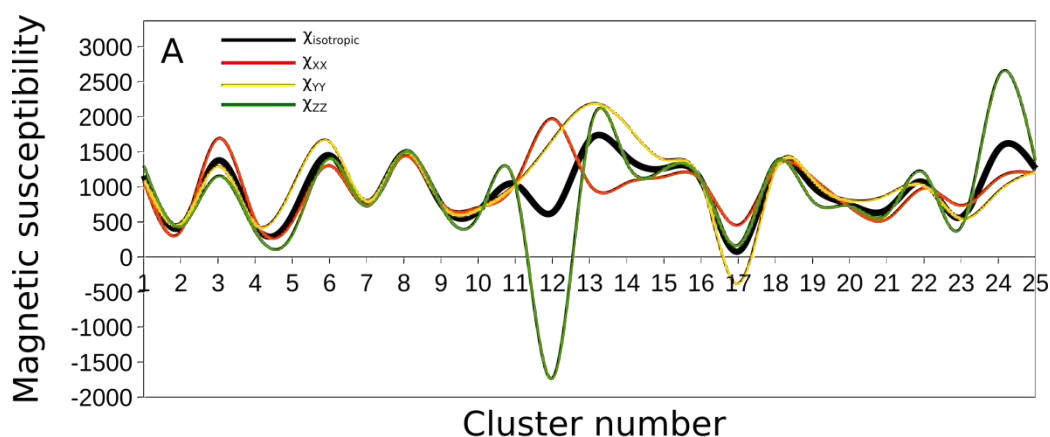


Fig 5. A) Components of magnetic susceptibility tensor for different sampled clusters. The coefficient of variation (CV) of components of magnetic susceptibility tensor as a measure of magnetic anisotropy plotted against B) fraction of metals (Co, Fe) and C) metalloids (B, Si) for clusters.

Results and Discussion

In this work, the interactions between the atoms are described by the Born- Mayer Buckingham potential function. This potential is among the only pair potentials that has been successfully used to describe physiochemical processes in metallic and intermetallic systems in particular Co containing systems. Principal elements of magnetic susceptibility tensor and dipole moments for different sampled clusters has been computed.

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