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First principles study on the electronic structure and magnetism of $Fe_{1-x}Co_xSi$ alloys*

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Electronic and magnetic properties of $Fe_{1-x}Co_xSi$ alloys were investigated by using a full-potential linear augmented-plane-wave method based on density functional theory. Electronic structure calculation demonstrates that half-metallic property appears in the Fe-rich region of $0 < x \leq 0.25$, while the alloys turn out to be a magnetic metal for $x > 0.25$. The concentration dependence of the magnetic moment of the alloys can be understood by the fixed Fermi level at minority band in Fe-rich region, as well as at the majority band in Co-rich region. In Fe-rich alloys, the electronic structure and the magnetic properties at Fe site depend mainly on the spin-polarization of nearest neighbouring Co atoms, while in Co-rich alloys, these features at Co site arise mainly from the neighbours of Fe atoms.

Keywords: first principles, disordered alloys, electronic structure, magnetic properties
PACC: 7550B, 7540M, 7120C

The cubic B20 monosilicides FeSi, CoSi and their disordered alloys $Fe_{1-x}Co_xSi$ have been extensively investigated due to their unusual magnetic and transport properties.[1−3] It is surprising that the $Fe_{1-x}Co_xSi$ alloys show long-range magnetic order in a wide concentration range,[4,5] despite the fact that the parent compounds FeSi and CoSi are nonmagnetic. FeSi is a nonmagnetic narrow-gap semiconductor. Mössbauer spectroscopy and nuclear magnetic resonance experiments show the absence of any sort of ordered moments in FeSi alloy.[6] CoSi is a diamagnetic metal with a temperature-independent susceptibility.[7] Recently, these disordered alloys have given rise to a renewed interest due to their remarkable semimetallic and positive magnetoresistance properties.[4,8,9]

Experimental study on $Fe_{1-x}Co_xSi$ system reveals that the magnetic moment, in Fe-rich region, increases almost linearly with Co concentration, suggesting a fully spin-polarized electron gas.[4] The theoretical investigation on the magnetism has been made by Punkkinen *et al*[10] using the exact muffin-tin orbital (EMTO) method with the coherent potential approximation (CPA).[11] Theoretical magnetic moments have been found to agree well with the experimental results up to $x \approx 0.3$, but large deviation appears for $x > 0.3$. Guevara *et al*[12] investigated the $Fe_{1-x}Co_xSi$ alloys using the full-potential linear augmented-plane-wave method with the virtual crystal approximation (VCA),[13,14] as well as supercell calculation (SCC). The VCA results show that the linear dependence of the magnetic moment on x is due to the half-metallic character for $0.08 \leq x \leq 0.25$, but it fails at larger Co concentration. However, the magnetic moment for $0 \leq x \leq 0.5$ obtained by supercell calculation seems to be in agreement with the experimental results. It is important to point out that the commonly used approximation for description of disordered systems, such as VCA or CPA, cannot describe correctly the influence of the chemical and local environment of a given atom.[15]

In this work, we investigate the $Fe_{1-x}Co_xSi$ alloys theoretically with the first-principles calculations in combination with the supercell approach. The study is extended to include the whole concentration of $Fe_{1-x}Co_xSi$ alloys, in order to gain an overall picture about the relationship between electronic structure and magnetic properties of these disordered alloys.

The first-principles calculations are performed using a full-potential linear augmented-plane-wave (FP-LAPW)[16] method as implemented in the WIEN2K code.[17] We use the exchange correlation potential in local spin density approximation (LSDA).[18] Core

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states are treated fully relativistically, while for valence states we adopt the scalar relativistic approximation. Inside the muffin-tin sphere we consider 10 core charges for transition metal (TM) atoms and 4 for Si. The radius of the muffin-tin sphere is 2.2 a.u. for TM atoms and 1.9 a.u. for Si. The cut off energy for plane waves in the interstitial region is chosen to be 17.7 Ry. The number of k points in Brillouin zone is enough to obtain the great numerical precision of charge density in each case, and has been checked by higher cut off energy and more k points.

The determined equilibrium lattice constant of FeSi is 4.372 Å with corresponding internal atom-position parameters $u_{\mathrm{Fe}} = 0.1372$ and $u_{\mathrm{Si}} = 0.8410$, while the equilibrium lattice parameters of CoSi are $a = 4.355$ Å, $u_{\mathrm{Co}} = 0.1460$ and $u_{\mathrm{Si}} = 0.8430$. The results we obtained show excellent agreement with previous calculations, either using FPLAPW method[12] or EMTO method[10] with local density approximation (LDA), while underestimate the experimental values[3] by 2.5% for FeSi and 2.1% for CoSi, respectively, since the LDA is generally known to underestimate lattice parameters. Based on spin-polarized band structure calculations, both the parent compounds are shown no magnetic moments. In the case of FeSi, the calculated gap in the middle of the d band is about 0.11 eV, in consistent with the previous results also calculated by the LDA band theory.[12,19,20] The overall shape of total densities of states DOSs for FeSi and CoSi we calculated are in general agreement with those reported by Guevara *et al.*[12]

Both experimental[3,8] and theoretical[10]studies show that it is reasonable to assume a linear dependence of the lattice constant and internal atom-position parameters upon Co concentration for $\mathrm{Fe}_{1-x}\mathrm{Co}_x\mathrm{Si}$ alloys. Thus, the lattice parameters of the $\mathrm{Fe}_{1-x}\mathrm{Co}_x\mathrm{Si}$ alloys are determined by a linear interpolation between those of the FeSi and CoSi compounds. The substitution of Fe by Co in $\mathrm{Fe}_{1-x}\mathrm{Co}_x\mathrm{Si}$ is supposed to occur in a strictly random way. The influence of local environment on the electronic and magnetic properties can be investigated in a way of SCC method in combination with a Boltzmann distribution (for details see Ref.[12]). In the present calculation, one configuration for $x = 0.125$ and 0.875, two configurations for $x = 0.25$ and 0.75, and four configurations for $x = 0.5$ are considered. Each configuration is simulated with single or double B20 unit cells, containing 4 or 8 TM and Si atoms per supercell. The weighted average magnetic moments are obtained by using a Boltzmann distribution, at the experimental annealing temperature,[4] applied to all the considered configurations at a given concentration.

Figure 1 shows the DOSs for selected representative configurations of $\mathrm{Fe}_{1-x}\mathrm{Co}_x\mathrm{Si}$ alloys with $x = 0.125$, 0.25, 0.5, 0.75, and 0.875. In the Fe-rich region ($x \leq 0.25$), both the DOSs for $x = 0.125$ and $x = 0.25$ show half-metallic behaviour (Fig.1).

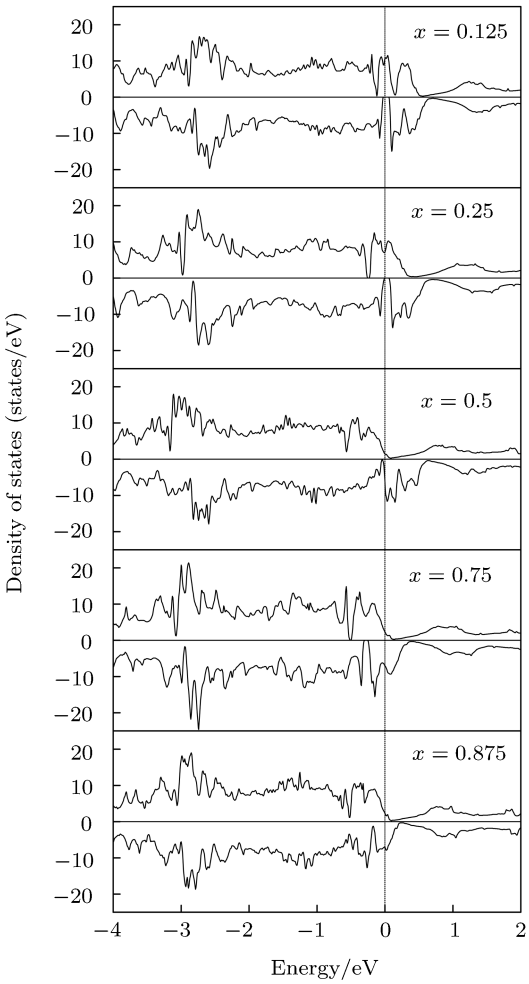


Fig.1. Total density of state for selected representative configuration of $Fe_{1-x}\mathrm{Co}_x\mathrm{Si}$ alloys with $x = 0.125$, 0.25 0.5 0.75 and 0.875.The origin of the energy scale is set at the Fermi level.

The Fermi level E_{F} lies in the gap of minority band as in a narrow gap semiconductor while the majority band is metallic. It can be clearly seen that the E_{F} is fixed in the gap of minority band while the E_{F} in the majority band shifts to higher energy level with increasing x. This leads to a constant occupation number of spin-down d states and an increasing spin-up d electron number, in agreement with the results obtained by Punkkinen *et al*[10] using a simple model. Thus, in the Fe-rich region, the magnetic moment per formula unit increases linearly with Co con-

centration, in agreement with experiments as shown in Fig.2. The half-metallic character disappears in the region of $0.25 < x < 0.5$. The dependence of magnetic moment on Co concentration becomes more complicated, since both the majority and the minority parts of the DOSs shift toward lower energy with increasing x. However, in the Co-rich alloys ($x \geq 0.75$), the E_F in the majority band is fixed and the d electrons from the doping Co atoms mostly fill into the minority band, so the magnetic moment decreases. The weighted average magnetic moments we calculated for samples with $0.5 < x < 0.875$ show slightly higher values than the experimental results, but the difference between the theoretical and experimental moments is smaller than the results obtained by CPA method.[10] This result may suggest that the number of configurations for a given Co concentration is not enough to calculate the average magnetic moment of Co-rich alloys, since the magnetic structure is found to be almost degenerate in this system.[10]

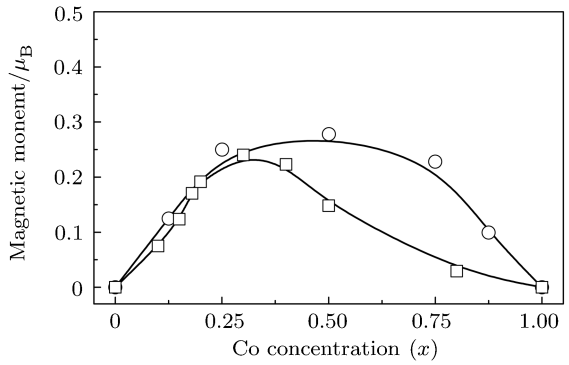


Fig.2. Calculated weighted average magnetic moment per formula as a function of Co concentration in $Fe_{1-x}Co_xSi$ alloys (open circles). The open squares represent the experimental values from Ref.[4].

Since the local magnetic moment of TM atom is strongly dependent upon the local environment, it is necessary to analyse its relationship with the nearest neighbour magnetic atoms. For a given Fe or Co atom, we define NN_{TM} and $\mu(NN_{TM})$ as the number of nearest neighbouring TM atoms and their corresponding total magnetic moment. For $x = 0.125$ a supercell with 8 formula units is considered, which includes 1 Co atom, 7 Fe atoms and 8 Si atoms. The local magnetic moments we calculated of these 7 Fe atoms, as well as the total magnetic moments of their neighbouring TM atoms, are listed in Table 1. It is interesting that the magnetic moment at Fe site, μ_{Fe}, is not larger than $0.1\mu_B$ when there are no Co nearest neighbours, though its neighbouring Fe atoms are in magnetic phase. For a given NN_{Co}, the magnetic moments of different Fe atoms are almost the same. For $NN_{Co} = 1$, the magnetic moment of Fe(4) and Fe(5) is $0.14\mu_B$ and $0.16\mu_B$; respectively; while the total magnetic moments of the neighbouring Fe atoms, $\mu(NN_{Fe})$, are rather different, being $0.56\mu_B$ and $0.70\mu_B$ for Fe(4) and Fe(5), respectively. Figure 3(a) shows that the partial DOSs of d orbitals for these two Fe atoms are almost identical. Furthermore, μ_{Fe} increases linearly with increasing NN_{Co}. The average magnetic moment of Fe atom is 0.05, 0.15, and $0.24\mu_B$ for NN_{Co} =0, 1, and 2, respectively. The average d DOSs of Fe atoms for NN_{Co} =0, 1, and 2 are shown in Fig.3(b) for $Fe_{0.875}Co_{0.125}Si$. It is found that the DOS of the majority d band near the Fermi level increases as a function of NN_{Co} while the occupation number of the minority d band does not change. The results above suggest that, in Fe-rich alloys, the electronic structure, as well as the magnetic properties, at Fe site depends mainly on the spin-polarization of nearest neighbouring Co atoms and the contributions from the neighbouring Fe atoms can be neglected. Similar result is found at Co site in Co-rich alloys that the main contribution to μ_{Co} comes from the spin-polarization of neighbouring Fe atoms. For $x = 0.875$, the average magnetic moments at Co site are 0.03, 0.07, and $0.14\mu_B$ for NN_{Fe} =0, 1, and 2, respectively.

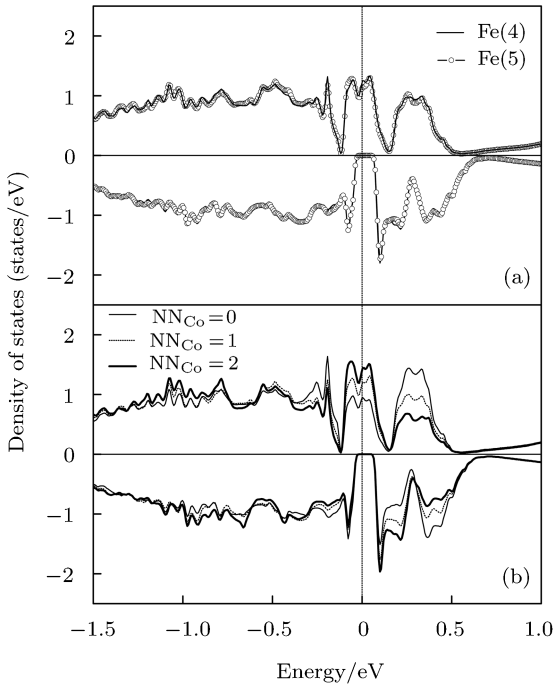


Fig.3. Partial density of states of d orbital for Fe sites of $Fe_{0.875}Co_{0.125}Si$ alloy. (a) DOSs of d orbital for Fe(4) and Fe(5) with $NN_{Co} = 1$. (b) Average Fe d DOS for $NN_{Co} = 0, 1, 2$.

Table 1. The local magnetic moments at different Fe sites in $Fe_{0.875}Co_{0.125}Si$, as well as the number of nearest neighbouring TM atoms NN_{TM} and corresponding total magnetic moments $\mu(NN_{TM})$. The unit for the magnetic moment is μ_B.

Fe site	μ_{Fe}	NN_{Co}	$\mu(NN_{Co})$	NN_{Fe}	$\mu(NN_{Fe})$
(1)	0.00	0	0.00	6	0.59
(2)	0.06	0	0.00	6	0.59
(3)	0.09	0	0.00	6	0.63
(4)	0.14	1	0.17	5	0.56
(5)	0.16	1	0.17	5	0.70
(6)	0.22	2	0.33	4	0.61
(7)	0.26	2	0.33	4	0.62

Finally, the local magnetic moment of different Fe (Co) atoms as a function of NN_{Co} (NN_{Fe}), for all the concentrations and configurations we calculated in ferromagnetic character, is shown in Fig.4. The local magnetic moment at Fe site increases with NN_{Co} in the range of $0 \leq NN_{Co} \leq 3$, while decreases for $NN_{Co} > 3$, leading to the increase of the average magnetic moment of Fe site with increasing Co concentration in the Fe-rich region; while to the decrease in the Co-rich region; as shown in Fig.5. For the Co atoms, μ_{Co} increases slowly with NN_{Fe} for $NN_{Fe} \leq 5$, indicating that the concentration dependence of μ_{Co} is weak.

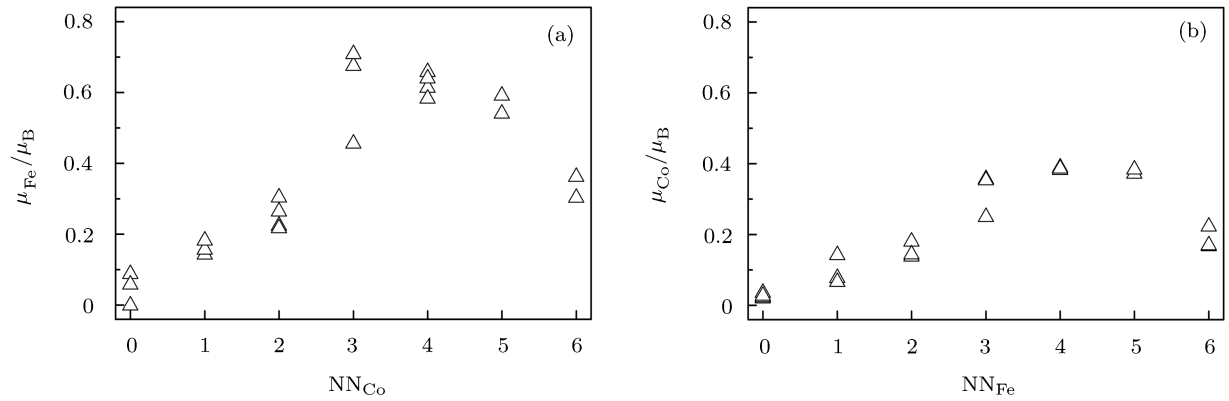


Fig.4. Local magnetic moments at Fe site NN_{Co} (a), and those at Co site versus NN_{Fe} (b), for all the concentrations and configurations we calculated in ferromagnetic character (NN_{Co}+NN_{Fe} = 6).

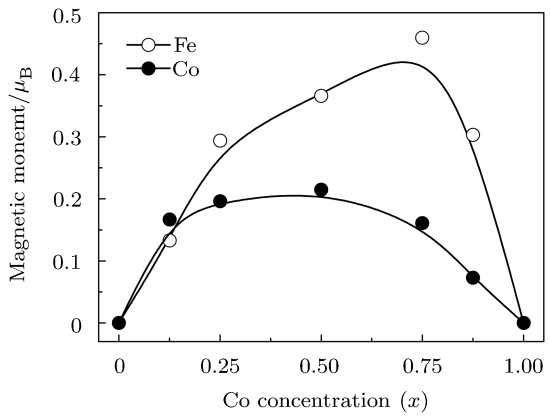


Fig.5. Calculated weighted average magnetic moment of Fe and Co sites per formula unit as a function of Co concentration in $Fe_{1-x}Co_xSi$ alloys.

In conclusion, we have performed a detailed investigation on the electronic and magnetic properties of the $Fe_{1-x}Co_xSi$ alloys. Half-metallic property appears in the Fe-rich region ($x \leq 0.25$), while the alloys turn out to be a magnetic metal for $x > 0.25$. The concentration dependence of the magnetic moment of the alloys can be understood by the fixed Fermi level in the minority band in Fe-rich region, but in the majority band in Co-rich region. The dependence of the local magnetic moment at TM site on its local environment has been investigated. In Fe-rich alloys, the electronic structure and the magnetic properties at Fe site depends mainly on the spin-polarization of nearest neighbouring Co atoms, while in Co-rich alloys, these features at Co site arise mainly from the neighbours of Fe atoms.

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