Electronic structure, exchange interactions, and Curie temperature of FeCo

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Fe–Co alloys in the α phase are soft magnetic materials which have high saturation inductions over a wide range of compositions. However, above about 1250 K, an α to γ phase transition occurs. The fcc-based, γ, high-temperature phase is paramagnetic at this temperature. In this work the low-temperature ordered $B2$, or α', phase, as well as the disordered bcc phase of FeCo alloys, have been studied with first-principles electronic-structure calculations using the layer Korringa–Kohn–Rostoker method. The variation of moment with composition (Slater–Pauling curve) is discussed. For equiatomic FeCo, interatomic exchange couplings are derived from first principles. These exchange interactions are compared to those obtained for pure Fe and Co, and are used within a mean-field theory to estimate the hypothetical Curie temperature of the α phase. © *1999 American Institute of Physics.* [S0021-8979(99)76808-8]

INTRODUCTION

Over a wide composition range Fe–Co alloys exist in the α or bcc-based phase. These alloys are soft ferromagnetic materials with large saturation inductions (about 15% greater than Fe). For Co concentrations less than about 17%, the Curie temperature is reached before the α to γ phase transition. However, for greater Co concentrations the phase transition to the nonmagnetic γ phase occurs while the α phase is still ferromagnetic, leading to ''virtual'' Curie temperatures for the α phase which are greater than the α to γ transition temperature. This ''virtual'' Curie temperature is an important parameter, however, in theories which predict the temperature dependence of the magnetic anisotropy and of domain-wall pinning in these materials, for example. The α to γ transition occurs at about 1250 K (although this varies some with composition).[1] FeCo alloys offer significant potential as high-temperature magnets, in such applications as rotors in electric aircraft engines. Extrapolation of specific magnetization versus temperature data for equiatomic alloys suggests a Curie temperature of about 1500 K,[2] one that exceeds that of elemental Co.

This article reports on studies of ordered and disordered FeCo alloys based on first-principles local spin-density electronic-structure calculations. These computations are performed using the layer Korringa–Kohn–Rostoker (LKKR) method within the atomic spheres approximation. Compositional disorder is modeled within the coherent potential approximation (CPA).[3] Details about the LKKR method can be found in Refs. 4 and 5. In the case of equiatomic FeCo, the interatomic exchange interactions are also obtained.

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RESULTS

The first set of calculations presented summarizes the changes in magnetic properties that occur with changes in alloy composition. Figure 1 shows the variation of the Fe and Co moments in the ordered α' and disordered α phases of FeCo. The calculations were performed at that lattice constant that minimized the total energy. These calculations differ from the previous study by Schwartz *et al.*[6] In that work, five ordered FeCo compounds were used to represent points on the FeCo phase diagram. In this work, for the ''ordered'' crystal data, one sublattice is treated statistically, i.e., for the Fe-rich side of the graph, the Fe site is left ordered and the excess Fe is placed on the Co site. The Co sublattice is, therefore, disordered and is treated within the CPA. Conversely, for the Co-rich material, the Co site is ordered with the excess Co placed on the Fe site. The influence of composition is seen to be mainly on the value of the Fe moment,

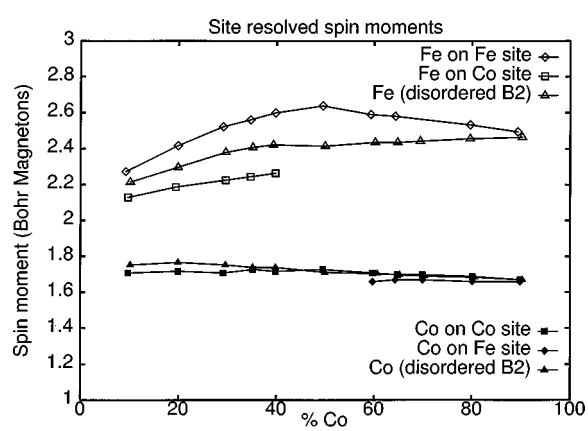

FIG. 1. Variation in Fe and Co moments for α' ($B2$-based) and disordered α (bcc-based) Fe–Co alloys.

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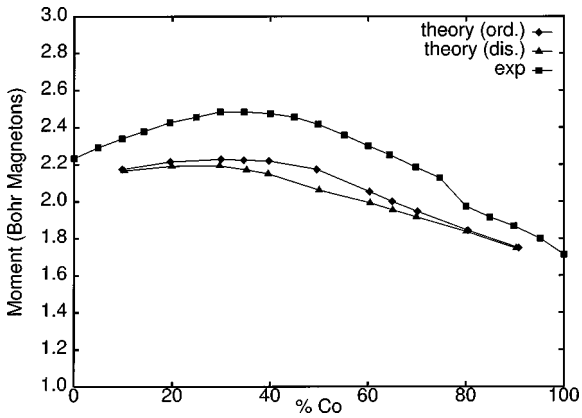

FIG. 2. Calculated and measured Slater–Pauling curves for Fe–Co alloys. The kink in the experimental data at around 70% Co is the result of the appearance of mixed α and γ phases.

with the Co moment remaining approximately constant over the whole range of compositions studied. The largest Fe moment is found for equiatomic FeCo.

Figure 2 shows the variation in the average moment per atom along with the experimental values taken from Bozorth's book.[1] The Slater–Pauling curve seen experimentally is reproduced nicely by the electronic-structure calculations, a peak in the moment is seen at around 30 at. % Co in Fe. The differences between the average moment per atom for ordered and disordered structures are seen to be small. The calculated moments are slightly smaller than the experimental values, the most likely reason for this is that the theoretical values only include the spin contribution to the moment. The orbital moment is almost quenched in transition metal alloys due to the strong crystal-field perturbation on the *d* electrons, however, typical values of the orbital moment are between 0.1 and 0.2 μB.

The density of states for Fe and Co atoms in equiatomic ordered *B*2 FeCo is shown in Fig. 3. As can be seen from Fig. 3, the crystal is a strong ferromagnet with the majority *d* bands of both Fe and Co essentially filled, and only partially filled minority Fe and Co *d* bands. Since Co has one more valence electron than Fe, band-filling arguments would suggest that Co-rich alloys would be expected to have lower

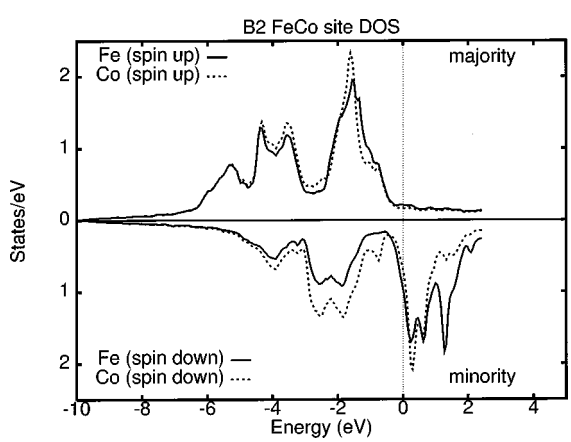

FIG. 3. Spin-resolved density of states for the Fe and Co sites in ordered α' (*B*2-based) FeCo.

moments due to filling minority states. On the Fe-rich side, however, the moment reduction could arise from the changing occupancies of both minority and majority bands. However, this simple picture would predict a maximum in the Slater–Pauling curve at a 50:50 alloy composition, which is not observed experimentally. In fact, the Co moment remains approximately constant over the whole composition range, and only the Fe moment changes significantly. As the Co content of the ordered α' alloy is increased, the alloy remains a strong ferromagnet, and the moment falls primarily due to the filling of minority Fe *d* states as expected from a rigid band model. In contrast, in the high-temperature disordered α phase, the Fe moment increases very slightly with increasing Co content. This was found to be due to the effects of disorder on the electronic structure. The density of states for the Fe site is smoothed due to the disorder at all compositions. The large peak in the unoccupied minority density of states in the disordered alloy remains above the Fermi energy, and does not change its occupancy appreciably.

The variation of the Fe moment on the Fe-rich side is more complex, however, since there is a change in the occupancy of both majority and minority states. In both ordered and disordered alloys, the number of majority Fe *d* states decreases as the Co content of the alloy is decreased, as would be expected in a rigid band model. In addition, we observe that the number of minority Fe *d* states also increases, and this appears to be due to hybridization changes on the occupied states near the Fermi energy. As a result, as the Co content of the alloy is decreased, a more rapid decrease in Fe moment is observed. The Fe site density of states is found to change smoothly to that of bcc Fe, which is no longer a strong ferromagnet. Thus, it is the combination of the roughly constant Co moment and varying Fe moment that accounts for the maximum in the Slater–Pauling curve occurring at around 30 at. % Co, rather than at the equiatomic *B*2 FeCo.

This behavior is in agreement with the neutron diffraction experiments of Collins and Forsyth.[7] Their experiments, using polarized neutrons, revealed that the Co moment was relatively invariant with composition in the Fe–Co binary alloy series, while the Fe moment varied from 2.2 μB for pure Fe, to over 3.0 μB for equiatomic alloys, and for alloys with >50 at. % Co.

The interatomic exchange coupling for the equiatomic ordered and disordered FeCo has been calculated from first principles using the method suggested by Liechtenstein *et al.*[8] This methodology has also been used by several other groups.[9,10] This formalism, worked out for three-dimensional KKR theory, can be simply implemented within the framework of the LKKR method.[11] Within this approach, interatomic exchange parameters J_{ij}, that would appear in a Heisenberg model, can be obtained by considering the change in energy associated with the rotation of spins at sites *i* and *j* in the otherwise perfect structure. This small energy change can be expressed in terms of the change in the one-electron eigenvalue sum.

Values of these exchange interactions for the first five shells of atoms are given in Table I. Note that the magnitude

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TABLE I. Exchange interactions in meV for a Co atom at the origin (first set of J_{ij}), and an Fe atom at the origin (second set of J_{ij}) for $B2$ FeCo. The third set of J_{ij} are those for the random alloy. n_j is the number of neighbors in the shell.

Shell	(n_j)	J_{ij}	$\Sigma_j n_j J_{ij}$	J_{ij}	$\Sigma_j n_j J_{ij}$	J_{ij}	$\Sigma_j n_j J_{ij}$
1	8	25.1	201	25.1	201	23.8	191
2	6	0.14	202	1.02	207	1.34	199
3	12	0.49	208	0.60	214	0.95	210
4	24	1.58	246	1.60	253	1.19	239
5	8	−2.87	223	−0.59	248	−1.71	225

of the moment has been folded into the interaction, so that the Heisenberg Hamiltonian, $H=-\Sigma_{ij}J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j$, has unit spin vectors $\{\mathbf{S}_i\}$. Estimates of the exchange interactions $J_i=\Sigma_i J_{ij}$ in ordered FeCo are 210 and 250 meV for rotating a spin on the Fe and Co sites, respectively. The average of these exceeds that for the disordered lattice, which is 217 meV. These exchange couplings are significantly larger than those found for Fe and Co, which are 170 and 180 meV, respectively. The latter is close to that of 190 meV, found by Sabiryanov *et al.*,[12] for Co. Within a mean-field model, with the magnitudes of the moments folded into the exchange interactions, $kT_c=\frac{2}{3}J\gamma$. The factor γ is given by $S(S+1)/S^2$ for quantum spins and 1 for classical spins. Empirically, it is found that choosing $\gamma=1$ leads to closer agreement with experiment.[8] This is found to be the case in this work, too.

Using this formula, mean-field Curie temperatures of about 1310 and 1370 K are estimated for Fe and Co. The corresponding experimental values are 1043 and 1390 K. The predicted value for Fe is too large, as is found by other groups,[9,10] while the value for Co is much closer to the measured value. An alternative description of the Curie point, based upon the disordered local moment picture by Staunton *et al.*[13] predicted a similar value for the Curie temperature (1280 K), which is also too high. Peng and Jansen[14] adopted a slightly different approach and obtained Heisenberg exchange interactions by fitting the total energy of several candidate magnetic structures. The mean-field Curie temperature obtained from this work is about 1100 K. While the value of the Curie temperature estimated here for FeCo may not be exact, it is clear that the exchange interactions are significantly larger than those of Fe or Co, when the number of neighbors is factored in, and thus, its Curie temperature should exceed both. The exchange interactions in FeCo are quite short ranged, and if we truncate at nearest neighbor, then a mean-field Curie temperature of greater than 1500 K is expected, a value which is consistent with the extrapolation of the magnetization versus temperature data.

CONCLUSIONS

In summary, we have calculated the variation in moment for a series of Fe–Co alloys. Calculated values agree quite well with measured values. The Fe moment on the Co-rich side decreases primarily due to the filling of Fe minority d states, while the decrease on the Fe-rich side is more complex due to the participation of both spins. The Co moment remains almost constant as a function of composition. Theoretical exchange couplings show strong ferromagnetic coupling and an estimated Curie temperature (>1500 K) for $B2$ FeCo that exceeds that of elemental Co, a value consistent with extrapolation of the magnetization versus temperature data.

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