

## Calculated magnetization of iron-cobalt disordered alloys

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The spin polarization of the disordered Fe-Co alloy was calculated using a tight-binding scheme, with single-site, full-orbital interactions treated self-consistently. Disorder is introduced by the use of the virtual-crystal approximation. Excellent agreement with the experimental spin polarization is obtained and the unusual shape of the Fe-Co curve on the Slater-Pauling plot is explained. The magnetization of the Co-rich alloys essentially depends on the number of available  $d$  holes, while the magnetization of the Fe-rich alloys is influenced by a relatively weak electron-electron interaction. The intersection of the two effects occurs at approximately 30 at. % Co and produces a maximum.

### I. INTRODUCTION

One of the most famous plots in the solid-state literature is the Slater-Pauling curve.<sup>1</sup> This plot displays magnetization versus the electron-to-atom ratio for a large variety of chemically disordered transition-metal alloys. One of the most interesting features of the curve is the abrupt change in its slope as it passes through its maximum at approximately 26.3 electrons per atom. Several explanations have been proposed for this feature. Pauling<sup>2</sup> argued that the number of unbalanced  $d$  holes could not exceed approximately 2.4 because the other 2.6  $d$  electrons of each spin belong to a lower band which cannot lose electrons until the upper one is completely emptied. A somewhat different point of view is provided by Williams *et al.*<sup>3</sup> who argued that the only two relevant features are magnetic saturation, which occurs on the Co side of the maximum, and ferromagnetic weakness, which occurs on the Fe side of the maximum. It is noted<sup>4</sup> that this ferromagnetic weakness coincides with the pinning of the Fermi level at a valley in the minority-spin density of states. Finally, one might expect that band narrowing and other complicated band-structure effects, such as those which occur in Ni-Cu alloys,<sup>5</sup> may be causing the maximum.

The uppermost and sharpest maximum on the Slater-Pauling curves is formed by the Fe-Co alloy system. Consequently, one expects that a complete understanding of this alloy would lead to the correct explanation for the Slater-Pauling maxima. Several experimental and theoretical studies have been performed for Fe-Co. Early experimental measurements of the saturation magnetization were made by Weiss and Forrer.<sup>6</sup> Later, after the discovery of an ordered structure near the equiatomic alloy, Bardos<sup>7</sup> remeasured the disordered substance. It is also known<sup>8</sup> that Fe-Co undergoes structural phase transitions with a change in concentration: Iron-cobalt is bcc for 25% or more iron; it is fcc or hcp for less than 10% iron, and there is a mixed phase in between. Meyer and Asch<sup>9</sup> determined the  $g$  factors for the Fe-Co alloys, thus allowing a comparison of the experimentally measured

magnetization with the theoretically predicted spin polarization. Neutron-diffraction<sup>10</sup> studies indicate that the vast majority of the anomalous increase in the magnetic moment is due to an increase in the Fe magnetic moment from  $2.2\mu_B$  to approximately  $3.0\mu_B$ , while the Co magnetic moment remains approximately constant at  $1.8\mu_B$ .

Theoretical results are less numerous. Kaspar and Salahub<sup>11</sup> used the spin-polarized, self-consistent field,  $X\alpha$  scattered-wave method to calculate the magnetic and electronic properties of 15-atom Fe-Co clusters. Unfortunately, results of these authors for the spin polarization differed considerably from experimental bulk values, possibly because Fe "feels" the effect of surfaces quite strongly.<sup>12,13</sup> Schwarz and Salahub<sup>14</sup> used local-spin-density theory to calculate the properties of the ordered FeCo alloy with fair success: Calculated spin polarization is 4.36 per unit cell versus  $4.50 \pm 0.02$  experimentally.<sup>7,9</sup> Victora *et al.*<sup>13</sup> used a tight-binding scheme with single-site, full-orbital interactions treated self-consistently in the Hartree-Fock approximation and obtained somewhat better results: Calculated spin polarization is 4.44 per unit cell for the ordered FeCo alloy. The latter two calculations both demonstrate the correct qualitative behavior, i.e., a large anomalous increase in the alloy magnetization relative to the average of the two elements in their pure bulk form. Desjonquères and Lavagna<sup>15</sup> discuss the differences between the ordered and disordered FeCo alloy: However, their magnetization results appear to contradict experiment.<sup>7</sup>

In this paper we present results of calculations for the magnetic properties of disordered Fe-Co alloys in both the fcc and bcc structures. We use the Slater-Koster parametrized tight-binding scheme in which the one- and two-center integrals are fitted to the bulk band structure. The exchange interaction is treated self-consistently in a single-site approximation. This scheme has previously been used and produced excellent agreement with both experiment and state-of-the-art calculations. Disorder is introduced by the use of the virtual-crystal approximation, an approximation which is suitable here due to the extreme similarity of the iron and cobalt bulk band structures.

## II. CALCULATION

This section describes our calculations. Section II A describes the Hamiltonian and Sec. II B examines the numerical accuracy of our work and the possible errors introduced by our major approximations.

### A. The Hamiltonian

We take our Hamiltonian to be the sum of a one-electron term  $H_0$  and an electron-electron interaction term  $H_{e-e}$ . For  $H_0$  we choose the parametrized tight-binding scheme of Slater and Koster.<sup>16</sup> The Hamiltonian  $H_0$  is written in terms of one- and two-center integrals, which are treated as parameters chosen to fit the bulk band structure. In Co (as in Ni) there is a marked discrepancy between the calculated and the experimentally measured bandwidth (photoemission experiments). For both Co and Fe, we have chosen the calculated paramagnetic band structures of Moruzzi *et al.*<sup>17,18</sup> (see the Appendix), with the belief that discrepancies with photoemission data are caused by additional many-body effects,<sup>19</sup> as has been argued for Ni. We include  $s$ ,  $p$ , and  $d$  orbitals with interactions up to second-nearest neighbors.

For the electron-electron interaction we use a single-site approximation which has been extensively discussed:<sup>20</sup>

$$H_{e-e} = \sum_{i,\sigma,\sigma'} \sum_{\alpha,\beta,\gamma,\delta} U_{\alpha\beta\gamma\delta} c_{i\alpha\sigma}^\dagger c_{i\beta\sigma'}^\dagger c_{i\gamma\sigma} c_{i\delta\sigma}, \quad (1)$$

where  $c_{i\alpha\sigma}^\dagger$  creates an orbital of symmetry  $\alpha$  and spin  $\sigma$  at site  $i$ .

We treat  $H_{e-e}$  in the Hartree-Fock approach; with some approximations we can reduce  $H_{e-e}$  to a simple form for the on-site potential shifts,

$$\begin{aligned} \Delta E_{d\nu\sigma} = & -\frac{1}{2}(U-J)\langle m_{d\nu\sigma} \rangle - \frac{1}{2}J\langle m_{d\sigma} \rangle \\ & + \frac{1}{2}(U-2U'+J)\langle n_{d\nu} - n_{d\nu}^0 \rangle \\ & + V_{sd}\langle n_s - n_s^0 \rangle + V_{dd}\langle n_d - n_d^0 \rangle, \end{aligned} \quad (2)$$

$$\Delta E_{s\sigma} = V_{ss}\langle n_s - n_s^0 \rangle + V_{sd}\langle n_d - n_d^0 \rangle.$$

Here,  $\Delta E_{d\nu\sigma}$  is the on-site potential shift for a  $d$  orbital of symmetry  $\nu$  and spin  $\sigma$ , which is measured relative to the value for the pure paramagnetic metal. By  $m_{d\nu\sigma}$  we denote the spin polarization ( $n_{d\nu\sigma} - n_{d\nu\sigma}^0$ ) in the  $d$  orbital of symmetry  $\nu$  at a given site, and  $m_{d\sigma} \equiv \sum_{\nu} m_{d\nu\sigma}$ . The total  $d$  occupancy at the site is denoted by  $n_d \equiv \sum_{\nu,\sigma} n_{d\nu\sigma}$ , and the value for the respective pure metal is  $n_d^0$ . Quantities for  $s$  and  $p$  orbitals are similarly defined. In (2),  $s$  refers to the entire  $sp$  complex.

We define  $U$  as the on-site direct Coulomb integral between  $d$  orbitals of the same symmetry (rescaled by correlation effects; see below),  $U'$  is the integral between  $d$  orbitals of different symmetry, and  $J$  is the exchange integral. We define  $V_{dd} \equiv U' - \frac{1}{2}J$ , which gives the effective (repulsive) interaction between  $d$  electrons, aside from magnetic effects. We similarly define an effective interaction  $V_{ss}$  between  $sp$  electrons, and  $V_{sd}$  between  $sp$  and  $d$  electrons. We neglect the on-site exchange integrals other than those between the  $d$  orbitals. Atomic symmetry requires that  $U = U' + 2J$ . The ratio  $U:J$  is taken to be 5:1,

as suggested by Herring.<sup>21</sup> The absolute magnitude of  $U$  is scaled to give the correct bulk magnetization,  $\mu = 1.72\mu_B$  for Co and  $\mu = 2.22\mu_B$  for Fe. We use Auger data<sup>22</sup> to set  $V_{dd}$  for Fe and Co. The ratios of  $V_{sd}$  and  $V_{ss}$  to  $V_{dd}$  are taken to be the ratios of the atomic values.

### B. Accuracy

The numerical accuracy of our calculation is quite high. Approximately 350  $\vec{k}$  points in the irreducible  $\frac{1}{48}$ th wedge of the Brillouin zone are used. Convergence is required to 0.0002 Ry. Estimated accuracy in the spin polarization is 0.005 electrons.

We now recapitulate the most crucial approximations in our Hamiltonian and consider their effects. Our Hartree-Fock approximation necessarily exaggerates the exchange splitting, which is reduced by correlation effects. Our restriction that the elemental Fe and Co have the correct magnetic moment will reduce the possible effects of this error. Nonetheless, it is conceivable that magnetization at intermediate points on the alloy curve will differ from the true value due to the exaggerated splitting.

The use of a tight-binding Hamiltonian should be analyzed with care. This method provides a rather good treatment of the  $d$  band, but the handling of the  $sp$  band is less accurate. Since  $sp-d$  hybridization plays an important role here, the tight-binding approximation introduces some risk of reduced quantitative accuracy.

Finally, it is important to note that the virtual-crystal approximation, in which the Hamiltonian of the two constituent elements is averaged to produce a single alloy "element," in many circumstances is a rather crude approximation. The reason we expect it to be accurate for our particular system is that Fe and Co are very similar elements. They are adjacent on the Periodic Table, and their  $d$ -band widths are identical<sup>18</sup> to within 15%. Furthermore, their large density of states at the Fermi level means that the one-electron difference between them does not offset their  $d$  bands to a very large extent. It is known experimentally that there is only a very small<sup>23</sup> magnetovolume effect (0.25%) and consequently, the averaging of the lattice constants as required by the virtual-crystal approximation should produce only the slightest of errors. It is for these reasons that the calculation of the magnetization for an imaginary element between Fe and Co is expected to give an accurate answer.

Ultimately, we must base our assessment of overall accuracy upon comparison with reported results of fully self-consistent calculations for simple systems, and with experiment. Our Hamiltonian has, on several occasions, been tested this way, and the results suggest that our methods reliably predict the quantitative magnetization of heterogeneous systems.<sup>13,24</sup> We have not previously used the virtual-crystal approximation, but the agreement between this calculation and experiment suggests that again we have a quantitatively reliable calculation.

## III. RESULTS

Calculated results for the spin polarization of the disordered Fe-Co alloy are shown in Fig. 1. Also plotted are the experimental spin polarizations obtained from mag-

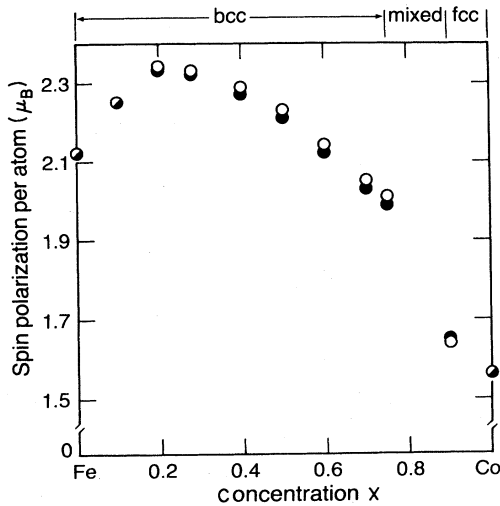


FIG. 1. Spin polarization as a function of Co concentration  $x$  in  $\text{Fe}_{1-x}\text{Co}_x$ . Open circles are theoretical results; closed circles are experimental results taken from Refs. 5 and 7 with  $g$  factors from Ref. 9.

netization and  $g$  factors. The agreement is excellent with a standard-deviation difference of less than 0.02 electrons. This difference is within the experimental error (1%) found in determining the  $g$  factors. Our ability to reproduce accurately this anomalous curve strongly suggests that our calculation includes all of the important physical processes and thus we should be able to understand the physical reasons which cause this unusual shape.

First, one notes that band narrowing, band mismatches, and other band-structure effects of heterogeneous systems cannot be responsible for the shape of the curve because the virtual-crystal approximation does not include them, and yet it reproduces the correct magnetization.

Figure 2 provides an explanation for the curve by plotting the Fe-Co results versus an imaginary "element" described by the Co Hamiltonian, but with a decreasing

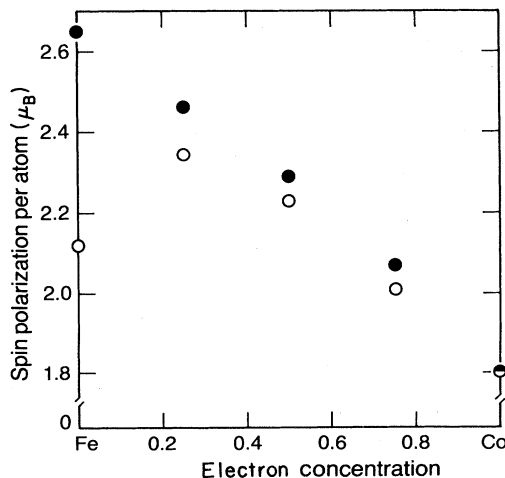


FIG. 2. Spin polarization as a function of electron concentration using a virtual-crystal Hamiltonian (open circles) and a pure Co Hamiltonian (closed circles).

number of electrons as one approaches the Fe side of the plot. This imaginary element differs from the Fe-Co alloy in that it possesses a much stronger electron-electron interaction than that associated with iron.<sup>25</sup> The plot demonstrates that the effect of this strong interaction is to raise drastically the Fe magnetization and remove the intermediate maximum. On the other hand, it causes little change on the Co side of the curve, suggesting that in this range saturation has been reached, i.e., all possible  $d$  holes are already magnetized. A reasonable conclusion is that the anomalous Fe-Co curve is dominated by magnetic saturation except in those regions of low Co content where an electron-electron interaction insufficient to cause saturation is more important.

Figure 2 also demonstrates that Pauling's explanation of the Fe-Co curve is not to be taken literally. Although we do find that for concentrations of Fe greater than 80%, the Fermi level lies in a minority-spin-density-of-states valley as Pauling's argument predicts, it is clear from Fig. 2 that if the electron-electron interaction to bandwidth ratio had not decreased as the Fe concentration increased, then the Fermi level would have been at its normal strong ferromagnetic position above all of the majority states and hence would have arbitrarily cut the minority density of states. This can be restated in the language of Pauling by noting that the spin polarization at the Fe end of the curve, 2.65, requires an emptying of 2.4 "upper-band" states and 0.25 "lower-band" states. In conclusion, it is clear that a decreasing electron-electron interaction to bandwidth ratio is at least as important as any band-splitting effects.

Finally, one notes that Fig. 2 displays a prediction for the spin polarization of bcc Co. This phase of cobalt has been experimentally constructed by Walmsley *et al.*<sup>26,27</sup> They find a magnetization equal to normal hcp cobalt with 10% error bars. Thus, our value for the spin polarization, 1.80, when combined with a  $g$  factor of 2.10, would be within the error bars of Walmsley *et al.* However, these authors find their bcc Co to have a much smaller lattice constant than one would expect from either extrapolating the Fe-Co lattice-constant curve or multiplying local-density minimal-energy results by a factor accounting for the usual underestimation of magnetic transition-metal lattice constants. This reduced lattice constant can be expected to increase the bandwidth and thus decrease the magnetization. Thus our calculation almost surely overestimates the spin polarization of the bcc Co found by Walmsley *et al.*

#### IV. CONCLUSION

We have calculated the spin polarization of the disordered Fe-Co alloy using a model which depends solely on the elemental properties. Agreement with the experimental curve is excellent and its anomalous behavior is fully reproduced. In the Co-rich region, the Fermi level lies above the majority density of states and the magnetization essentially depends on the number of available  $d$  holes. In the Fe-rich region, a relatively weak electron-electron interaction allows the Fermi level to lie in a valley separating the minority bcc density of states into an upper and

lower band. The intersection of this weakly ferromagnetic region with the saturated region of the Co-rich alloys produces a maximum in the magnetization at approximately 30 at. % Co.

It is likely that our conclusions for the Fe-Co system have application to many other transition-metal alloys. For example, Fe-Ni demonstrates the same sort of maximum at approximately 10 at. % Ni. Other alloys such as Ni-Cr, Ni-V, Co-Cr, and Co-Mn display magnetization curves at right angles to the saturation line. It is possible that this too is the result of a weak electron-electron interaction. However, the testing of these suggestions may need to be performed within an approximation more accurate than the virtual crystal, because of the increasing dissimilarity of the band structures.

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#### APPENDIX

The fcc Co and bcc Fe band structures are taken directly from Ref. 17. The bcc Co and fcc Fe band structures are obtained from the bcc Fe and fcc Co structures by scaling the bandwidths and band centers as suggested in Ref. 18. Unfortunately, the local-density band structures are not given at experimental lattice constants. Consequently, the band structures used in this calculation were evaluated at 3.41, 2.72, and 2.72 Å for fcc Co, bcc Co, and bcc Fe, respectively. Actual lattice constants are 3.54, 2.82, and 2.87 Å, where the bcc Co lattice constant is a result of extrapolating the Fe-Co lattice-constant curve. Thus, theoretical lattice constants are 0.963, 0.964, and 0.948 of the experimental lattice constants. This should make no difference since the strength of the electron-electron interaction has been scaled to give the correct magnetization at the bulk elements and, consequently, intermediate alloys should be well represented. Note that bcc Co and fcc Co have nearly identical (0.963 versus 0.964) lattice ratios and consequently, there should be little error in using the same electron-electron interaction strength for both.

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