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The Slater–Pauling curve: First principles calculations of the moments of $Fe_{1-c}Ni_c$ and $V_{1-c}Fe_c$

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We have performed calculations of the electronic structure of the random substitutional alloys $Fe_{1-c}Ni_c$ and $V_{1-c}Fe_c$ using the spin-polarized, self-consistent Korringa–Kohn–Rostoker coherent-potential approximation (KKR-CPA) method. This is a first principles method based on spin density functional theory and a local spin density approximation for the exchange and correlation functional. For fcc $Fe_{1-c}Ni_c$, a range of volumes were considered for $0.25 < c < 1.0$, and it was found that the moments are sensitive to the volume in the Fe-rich alloys near the INVAR concentration. In bcc $V_{1-c}Fe_c$, we find the average moments to decrease linearly with vanadium concentration (in the Fe-rich alloys) and the vanadium moment to be antiparallel to the iron moment. The moments vanish when the vanadium concentration becomes greater than 0.7 which is in good agreement with experiment. In $V_{1-c}Fe_c$, in contrast to bcc $Fe_{1-c}Ni_c$, the bonding–antibonding "valley" of the minority density of states (in which the Fermi level is pinned) persists over a wide range of concentrations.

I. INTRODUCTION

Although the existence of magnetism in binary alloys has been studied for a long time,[1] a first-principles microscopic description has not been developed. All attempts of such a description have omitted one or more key ingredients. The simplest of these attempts is based on the rigid-band model.[2] In spite of some successes, the rigid-band model does not include (and therefore cannot explain) the effects due to chemical differences, other than the electron per atom ratio (e/a), nor due to chemical disorder. Cluster calculations[3] place too much emphasis on local environment effects, neglecting the long-range effects of the electronic structure. These calculations also have a large surface-to-volume ratio, which limits their credibility. Calculations for ordered alloys[4] have been important for understanding chemical effects, but in ordered arrangements bonding may be enhanced. The virtual crystal approximation[5] does average over the chemical species, but it is too crude for an accurate description of many properties especially of the electronic states. Although tight-binding calculations[6] use a sophisticated averaging scheme, parameters are introduced and the electrons are treated in a non-self-consistent manner.

We have embarked on a program to understand magnetic alloys from an *ab initio*, parameter-free description. We use the spin-polarized, self-consistent Korringa–Kohn–Rostoker coherent-potential approximation (KKR-CPA),[7] the multiple scattering version of the coherent potential approximation (CPA).[8] This is a first principles theory of the electronic structure, which uses the CPA mean field theory to average over the chemical disorder. In our first calculations for magnetic alloys,[9] we found the effects of disorder significant in determining the electronic structure and in understanding the stability of magnetism, and therefore the overall stability.

Naively, disorder should be harmful to the existence of magnetism, since disorder smears the sharp structures in the electronic density of states (DOS) and a large $n(\epsilon_f)$, density of states at the Fermi level, is needed to meet the Stoner criterion.[10] However, this argument fails, because the Stoner condition is applied before the exchange splitting of the electron states was included. When no moments exist, electrons of either spin are equally scattered by the disorder. In spin-polarized calculations, it is possible for the effects of the disorder to be confined to electrons of one spin. In previous calculations[9] for $Fe_{0.65}Ni_{0.35}$ we showed that the majority density of states was very sharp, which implies electron states with long lifetimes and with a large spatial extent. These majority electrons are able to hop to *any* site; the minority electrons tend to be confined to one chemical species. The sharpness of the majority density of states implies an energy width ΔE of an electron state that is much smaller than the exchange splitting Δ. If Δ and ΔE are comparable, the moment cannot be sustained, which happens in fcc $Fe_{0.75}Ni_{0.25}$.

II. RESULTS

We have performed a series of calculations on bcc $V_{1-c}Fe_c$ and on both bcc and fcc $Fe_{1-c}Ni_c$. The formalism and calculational method have been described elsewhere.[7,11] These calculations used the local density approximation[12]

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for the exchange-correlation functional. The angular momentum expansion has been truncated at $l = 2$. In solving the fundamental equations of the KKR-CPA, the real-space formalism of Winter and Stocks was used[13] and we have included five shells of neighbors. Sums over energy eigenstates were carried out in the complex plane[14] to facilitate convergence of potentials and charge densities. We have used the experimental lattice constants for $V_{1-c}Fe_c$. To elucidate the sensitivity to the volume seen in previous calculations,[9] we have performed calculations for the fcc $Fe_{1-c}Ni_c$ alloys at three different lattice constants. In the bcc $Fe_{1-c}Ni_c$ alloys, where we do not expect such sensitivity we used one lattice constant, $a = 5.30$ a.u.

A summary of the results is given in Fig. 1, where the average and individual moments are plotted as a function of e/a. For bcc $V_{1-c}Fe_c$, the calculations show an almost linear dependence of the average moment in the iron-rich alloys, which is in good agreement with experimental measurements.[15] In spite of this simple behavior of the average moment, both individual moments show a complicated dependence on e/a. As vanadium is added to iron, the iron moment increases slightly before decreasing, which is in disagreement with recent tight-binding CPA calculations,[16] but in agreement with the neutron scattering experiments of Mirebeau, Parette, and Cable.[17] This maximum is due to the filling of the majority d band. The majority d band, as still more vanadium is added, acquires a long extended tail due to disorder whose upper part is unoccupied. The corresponding minimum in $n(\epsilon_F)$ has been seen in specific heat measurements.[18]

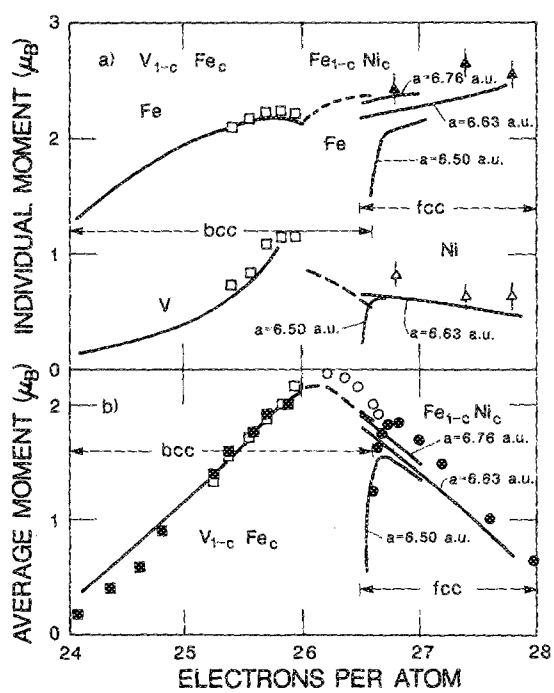

FIG. 1. Individual and average moments plotted as a function of the number of electrons per atom. Note that the vanadium moment is antiparallel to the iron moment. The solid and dashed lines are the results of our calculations. The symbols are experimental results. The shaded and open squares denote the experimental results of Nevitt and Aldred (Ref. 15) and Mirebeau *et al.* (Ref. 17), respectively. The circles and triangles are the measurements of Crangle and Hallam (Ref. 20) and Collins and Forsyth (Ref. 20), respectively.

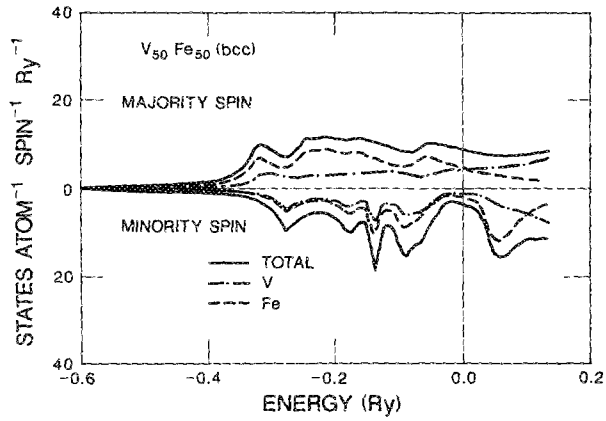

FIG. 2. Density of states for bcc $V_{50}Fe_{50}$ plotted as a function of energy (relative to the Fermi level).

In our calculations, the Fermi level resides in the bonding–antibonding valley of the minority spin density of states (see Fig. 2). This position of the Fermi level leads to an almost constant number of minority spin electrons in the iron-rich alloys. As suggested by Williams *et al.*,[19] this leads to a moment which is linear function of e/a. The vanadium moment is approximately $1\mu_B$ at small concentrations of vanadium. The self-consistency procedure forces vanadium to form a moment and for it to be antiparallel to that of iron, even though the initial vanadium charge density did not possess a moment. To understand this result, consider the energy levels in a simple tight-binding scheme as pictured in Fig. 3. In the pure systems, the iron levels are exchange split while the vanadium levels are not. By forming an alloy, interactions are introduced, which have a larger effect on the minority spin levels (compared to the majority) since their energy separation is smaller. One of the physical ramifications is that the *minority* electrons will be able to hop to any neighbor while the majority electrons will be confined to one species. This picture cannot be taken too literally, since it does not reproduce the small maximum in the iron moment, which is caused by a subtle interplay between the moments

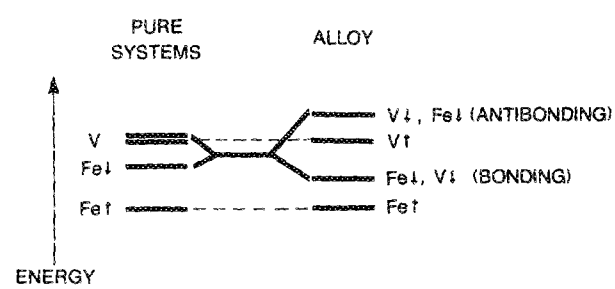

FIG. 3. A schematic picture of the energy levels of the iron-vanadium system. On the left-hand side are the levels for the isolated systems; iron levels are exchange split, vanadium levels are not. On the right-hand side are levels in the alloy. In the minority spin (↓) channel, the levels form bonding and antibonding hybrids. In the former, the electron wave function has a larger amplitude on the iron sites.

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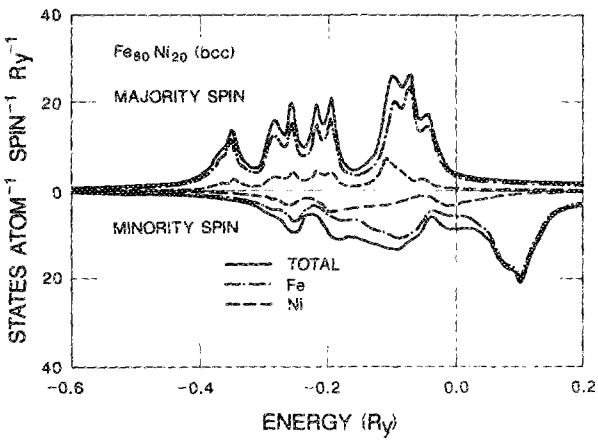

FIG. 4. Density of states for bcc $Fe_{80}Ni_{20}$ plotted as a function of energy (relative to the Fermi level).

and bonding. The moments collapse when the vanadium concentration reaches ~70%.[15] We have not tried to pin down this concentration more precisely, because of the limitations of the mean field approximation inherent in the CPA.

Now consider the bcc $Fe_{1-c}Ni_c$ alloys. In Fig. 1, the majority *d* band fills and the average moment grows with addition of small amounts of nickel, in agreement with experiment.[20] The smearing of the DOS happens in the minority spin channel as in our previous calculations.[9] As small amounts of nickel are added to iron, the bonding–antibonding valley in the minority density of states fills (see Fig. 4), in contrast to the case when vanadium is added to iron. A large number of antibonding states (in the minority spin channel) become occupied, which is destabilizing.

Now we turn our attention to the fcc $Fe_{1-c}Ni_c$ calculations. As shown in Fig. 1, the average moment is linear in concentration as iron is added to nickel. The majority *d* band is filled as long as this linear increase continues. As the iron content is increased, the iron moment slowly decreases and the nickel moment increases. To show the sensitivity of moment as the iron concentration nears 70%, we carried out calculations at three lattice constants, 6.76, 6.63, and 6.50 a.u. At the smallest lattice constant, no magnetic solution to the KKR-CPA equations has been found when the iron concentration is 75%. In contrast to ordered calculations,[4] the Fermi level in the paramagnetic density of states is not near any peaks. As the volume is compressed or as the iron concentration is increased, the Fermi level is pushed into the majority *d* bands and the moment collapses very abruptly, as in pure fcc iron.[21] The top edge in the alloy majority *d* band consists mainly of iron states. Hence, the collapse of the magnetization is precipitated by the collapse of the iron moment.

III. CONCLUSION

We have performed a set of first principles calculations for two magnetic iron binary alloy systems and conclude that our calculations describe and explain the Slater–Pauling curve.

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