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Magnetic moments and coordination symmetry in bcc Fe-M alloys

Brinton W. Corb
Institut für Physik der Universität Basel, CH-4056 Basel, Switzerland

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A directed valence analysis of metalloid (M) atoms in various structures has been performed and discussed in terms of the ligand p-d bond model. It is shown that p-d bonding cannot have a direct effect on the moment of Fe atoms in bcc Fe-M alloys, whereas in most other transition-metal–metalloid (T-M) structures with ferromagnetic T atoms as solvents, it is shown that p-d bonding can reduce the moments of the T atoms. The small moment variations in bcc Fe-M alloys could be caused instead by variations in the intraband exchange splitting, as a result of changes in the lattice constant.

I. INTRODUCTION

It was recently proposed that the saturation magnetic moment reduction in ferromagnetic transition-metal–metalloid (T-M) crystalline and glassy alloys occurs by bonding of the d states of the T atoms with the p states of the M atoms.[1] The model worked sufficiently well with $T=\text{Co}$ and Ni. However, it predicted a much faster decrease in the magnetic moment for bcc Fe-M alloys than that observed. This led the authors of paper I to the conjecture that p-d bonding does not occur with the d orbitals of bcc Fe that are ferromagnetic—i.e., the E_g orbitals. In Sec. II of this work, a directed valence analysis will be applied to the ligand p-d bond model[1] to show that p-d bonding cannot strongly affect the magnetic moment in bcc Fe-M alloys, whereas for other T atoms in other crystalline forms it most likely does. In Sec. III, it will be shown that the small moment variations in bcc Fe-M alloys are a general function of the lattice constant. In Sec. IV the conclusions will be drawn.

II. VALENCE ANALYSIS

A. Ligand p-d bond model

In paper I, the magnetic moment reduction caused by alloying ferromagnetic T atoms with M atoms was considered from the point of view of the local coordination around the M atoms. The model assumes that strong, localized p-d bonds are formed and, thus, it is similar to the approach used in ligand chemistry. The model is not a theory for ferromagnetism; rather, it gives a method of calculating the magnetic moment reduction in an alloy as a result of the formation of non-spin-polarized p-d bonds. An important assumption used in the model is that the p-d bonds are localized within the first coordination shell around the M atoms. The model is easily constructed from Pauling's valence bond theory by assuming that Z_M T atoms surround an M atom in a solid, and Z_M resonating valence bonds, formed with Z_M d orbitals from the T atoms and with the three p orbitals from the M atom, are formed. The remaining number of d orbitals not used in bonding with the M atoms, and which presumably still carry ferromagnetic moments, is $5N_T - Z_M N_M$, where N_T and N_M are the number of T and M atoms in the solid. In paper I the assumption was made that each d orbital used in p-d bonding was magnetic before the bond was formed, and that each bonded d orbital had carried an average of $(n_B/5)\,\mu_B$ (μ_B is the Bohr magneton) per orbital before bonding, where n_B is the moment of the T atom in the pure state. Essentially, it was assumed that the moment of the T atoms is equally distributed over the manifold of d states. Thus, the magnetic moment per T atom is

$$\mu=(5N_T-Z_M N_M)(n_B/5)/N_T \ ,$$

or, with $N_M/N_T=c/(1-c)$, in which c is the metalloid concentration,

$$\mu=n_B-Z_M(n_B/5)c/(1-c) \ , \tag{1}$$

and the average moment per T and M atoms is

$$\bar{\mu}=n_B-\left[\frac{Z_M n_B}{5}+n_B\right]c \ . \tag{2}$$

In paper I the same equation was obtained with the molecular orbital theory (MO) with the assumption that the Z_M d orbitals combine with the three p orbitals from the M atom to form three bonding MO's, three antibonding MO's, and Z_M-3 nonbonding MO's. It was assumed that the MO's are not magnetic. The nonbonding and bonding MO's can be looked at as being essentially equivalent to the Z_M resonating bonds from Pauling's theory.

B. Directed valence analysis

A questionable assumption used in deriving Eqs. (1) and (2) is that the moment of the T atoms is equally distributed over the manifold of the d states and, thus, the d orbitals used in bonding were ferromagnetic before forming the bonds. A directed valence analysis will be applied here to test the validity of this assumption. For an M atom on an fcc lattice there would be 12 valence bonds directed along the $\langle 110\rangle$-type directions towards the first near-neighbor T atoms, and the valence bonds are denoted as Ω_{110}. In the bcc lattice there are eight bonds formed along the $\langle 111\rangle$-type directions, denoted as Ω_{111}, and in the simple-cubic lattice there are six bonds formed along the $\langle 100\rangle$ directions, denoted as Ω_{100}. The latter case also represents the valence bonds between a central atom and its second near neighbors in both the fcc and the bcc lattices. In Table I the basis functions of the irreducible representations necessary to form the valence bonds in O_h point symmetry are listed. For the fcc case, all five d orbitals are used to form the valence bonds, and thus Eqs. (1) and (2) should work for fcc Co-M and Ni-M alloys, as shown in paper I. In the bcc

TABLE I. Irreducible representations (IR) and their basis functions necessary to construct various valence bonds in O_h symmetry. Degeneracies are given in parentheses, and basis-function partners are grouped in brackets.

IR	Basis functions	$\Omega_{110}(12)$	$\Omega_{111}(8)$	$\Omega_{100}(6)$
$A_{1g}(1)$	s	1	1	1
$E_g(2)$	$[d_{3z^2-r^2}, d_{x^2-y^2}]$	1	0	1
$T_{2g}(3)$	$[d_{xy}, d_{yz}, d_{xz}]$	1	1	0
$A_{2u}(1)$	f_{xyz}	0	1	0
$T_{1u}(3)$	$[p_x, p_y, p_z]$	1	1	1
$T_{2u}(3)$	f functions[a]	1	0	0

[a] $[f_{zx^2-zy^2}, f_{5xz^2-xr^2}+f_{x^3-3xy^2}, f_{-y^3+3yx^2}-f_{5yz^2-yr^2}]$.

case, however, the only d orbitals that can be used in bonding are the T_{2g} type. Band-structure calculations[2-4] and neutron diffraction studies[5] have shown that the moment in bcc Fe is directed primarily along those directions corresponding to E_g symmetry. Therefore, in the limit of this simple model, p-d bonding cannot directly affect the moment of Fe atoms in bcc Fe-M alloys.

As an example of the effects of p-d bonding, 10 at.% of Si in fcc Co and Ni reduces the moments of the latter atoms by 0.46 and 0.41 μ_B/T at., whereas the same amount of Si in bcc Fe leaves the moment of the Fe atoms virtually unchanged.

In the Fe_3C structure, each M atom forms six bonds with the T atoms that are situated on the corners of a trigonal prism and the valence bonds are denoted as Ω_{Fe_3C}. In the Co_2P structure, the same bonds are formed as above, but three additional bonds are made in directions perpendicular to the faces of the prism. The resulting nine valence bonds are denoted as Ω_{Co_2P}. The hcp structure also has the six valence bonds of the Fe_3C case and has six additional bonds arranged on a hexagon that is perpendicular to the threefold axis of the prism. These bonds are denoted as Ω_{hcp}. Table II lists the basis functions necessary to form the valence bonds in D_{3h} symmetry. Because all five d orbitals can be used in bonding for the above three cases, the ligand p-d bond model should apply to alloys with these structures, as shown in paper I.

As a final example, consider the case where an M atom sits on the largest interstitial position in the bcc lattice, the $(\frac{1}{2},\frac{1}{4},0)$ position. The number of valence bonds is four and the symmetry is C_{2v}. It is easily shown that symmetry allows the magnetic $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ oribtals to be used in p-d bonding. Ray and Hasegawa found that their supersaturated bcc Fe-B solid solutions were composed of $\frac{1}{3}$ interstitial B atoms and $\frac{2}{3}$ substitutional B atoms.[6] Since only the interstitial B atoms can reduce the moment of the Fe atoms, Eq. (2) is used with $Z_M=\frac{4}{3}$ to arrive at $d\bar{\mu}/dc$ of $-2.8\mu_B$. The experimental value is $-3.0\mu_B$.

TABLE II. Irreducible representations (IR) and their basis functions necessary to construct various valence bonds in D_{3h} symmetry. Degeneracies are given in parentheses, and basis-function partners are grouped in brackets.

IR	Basis functions	$\Omega_{Fe_3C}(6)$	$\Omega_{Co_2P}(9)$	$\Omega_{hcp}(12)$
$A_1'(1)$	$s, d_{3z^2-r^2}$	1	2	2
$A_2'(1)$	$f_{3yx^2-y^3}$	0	0	1
$E'(2)$	$[p_x, p_y]$, $[d_{x^2-y^2}, d_{xy}]$	1	2	3
$A_2''(1)$	p_z	1	1	1
$E''(2)$	$[d_{xz}, d_{yz}]$	1	1	1

III. MOMENT VARIATIONS IN bcc Fe-M ALLOYS

It has been recognized that the small moment variation in bcc Fe-M alloys with M content is dependent on the row in

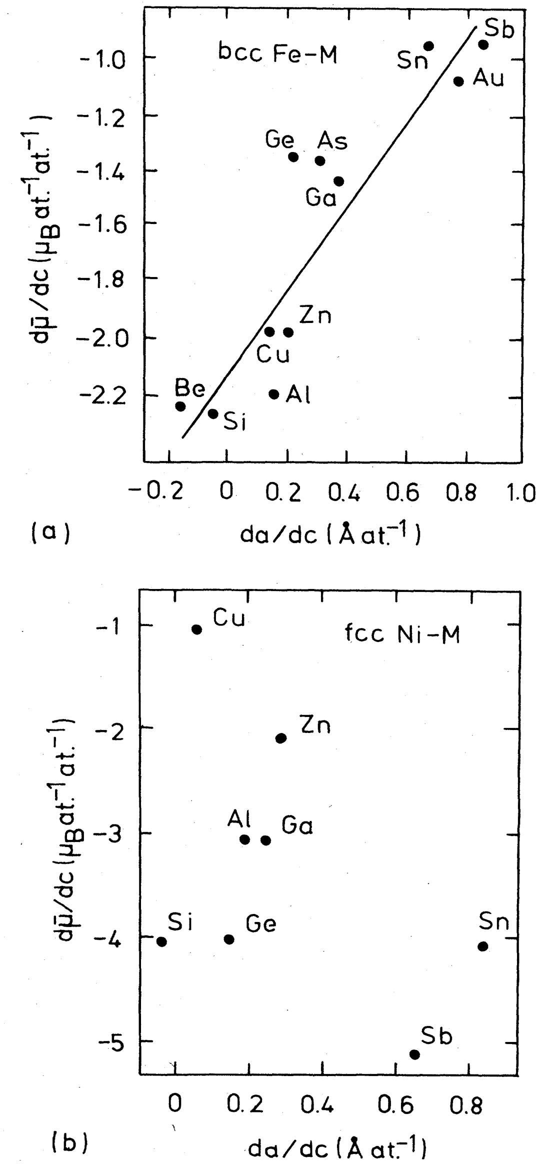

FIG. 1. (a) Concentration dependence of the magnetic moment plotted against the concentration dependence of the lattice constant for various M atoms in bcc Fe. The solid line is the theoretical result from band-structure calculations (Refs. 21 and 22). (b) The same type of plot for fcc Ni-M alloys.

which the M atom occupies in the periodic table, as opposed to the column dependence observed in fcc Ni-M alloys.[7,8] This observation, along with specific-heat measurements[9] and Mössbauer studies,[8,10–12] have tended to discount the electron transfer model and the s-electron polarization model as being responsible for the moment variation with concentration in Fe-M alloys.

Small-angle neutron scattering measurements on bcc Fe-M alloys have shown that the effect of the M atoms on the moment of the Fe atoms is spread out evenly through the solid rather than being localized near the M atoms.[13,14] Thus, localized bonding, as shown in Sec. II B, has little or no effect on the Fe moment.

bcc Fe is a weak ferromagnet in that the spin-up $3d$ band is partially empty. In principle, the small moment variations in bcc Fe-M could be caused by small shifts in the intraband exchange splitting. It is also accepted that the interatomic distance plays a role in determining the spin exchange.[15] Therefore, the moment variation $d\bar{\mu}/dc$ for various bcc Fe-M alloys[7,16–19] have been plotted versus the lattice-constant variation da/dc (Ref. 20) in Fig. 1(a) for metalloid concentrations of less than 10 at.%. Two recent band-structure calculations[21,22] have given $d\bar{\mu}/da$ as $1.59\mu_B$ Å for bcc Fe when the lattice constant is close to equilibrium at $T = 0$ K. This slope is drawn in Fig. 1(a) and the resonable fit to the data suggests that the interatomic spacing plays and important role in the moment variation in bcc Fe alloys.[23]

In contrast, the magnetic moment of strongly ferromagnetic alloys, such as the fcc Ni-M system, is not expected to be dependent on the lattice constant because the spin-up $3d$ band is full and, thus, small changes in the intraband exchange splitting cannot affect the net ferromagnetic moment. The moment variation with concentration for various fcc Ni-M alloys,[24] $d\bar{\mu}/dc$, have been plotted versus da/dc (Ref. 20), and no discernible pattern is seen (taken from data with $0.0 < c < 0.1$).

IV. CONCLUSIONS

A directed valence analysis of metalloid atoms in substitutional bcc Fe-M alloys has shown that the p-d bonds between metalloid and Fe atoms cannot have a direct effect on the moment of the Fe atoms under the assumptions of the ligand p-d bond model.[1] Metalloid atoms in most other structures, however, most likely do affect the moment of the magnetic transition-metal atoms by the formation of localized p-d bonds. The small moment variations of bcc Fe-M alloys appear to be related to the lattice spacing such that $d\bar{\mu}/da = (1.6 \mp 0.4)\mu_B/\text{Å}$ in agreement with recent band-structure calculations.

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