

Chemical bonding, magnetic moments, and local symmetry in transition-metal—metalloid alloys

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A model is proposed that quantitatively accounts for the moment variation in transition-metal—metalloid (T - M) crystals and glasses. The model, formulated from valence-bond theory, assumes that each T atom surrounding an M atom contributes a d orbital to participate in p - d hybrid bonding. If each bonded d orbital in Co alloys is occupied by $n_B/5$ nonmagnetic holes, then the moment of a Co- M alloy is $\mu(\mu_B/T \text{ at.}) = n_B - Z_M(n_B/5) N_M/N_T$. Here n_B is the effective moment of pure Co in Bohr magnetons, and Z_M is the number of T atoms in the first shell around an M atom. Hence the moment variation in Co- M alloys is determined by the local symmetry of the M atom and not by the valence of M . For Ni alloys it is found that both hybridization and the p valency are responsible for the moment reduction. Symmetry arguments are used to derive the relation $\mu(\mu_B/T \text{ at.}) = n_B - Z_M(n_B/5) N_M/N_T - (V_p N_M)/N_T$ for Ni- M alloys where V_p is the p valency of the metalloid. The models use the hybridization concept of electron sharing rather than electron transfer so that the solid is not ionic. The decrease in magnetization comes from formation of nonpolarizable p - d hybrid bonds from polarizable $3d$ transition-metal states. Therefore the model is in agreement with experiments and theories that indicate a constant number of unoccupied $3d$ levels regardless of metalloid concentration. Excellent quantitative agreement is found when the model is compared with experimental data for crystalline and amorphous Co- and Ni-metalloid alloys. It is found that amorphous alloys retain the same local environment around the metalloid atom as in the crystalline cases, and that the bonding in crystalline alloys and amorphous alloys is equivalent. The bond model predicts zero moment change for dilute bcc Fe alloys because the bonding levels in the Fe band have no uncompensated spin. Reasonable agreement with experiment is obtained for concentrations of metalloid less than 10%, but it is apparent that moment changes in many Fe alloys are caused by more complicated changes in the exchange.

I. INTRODUCTION

Magnetic transition-metal—metalloid (T - M) glasses and crystals are important materials because of their desirable soft magnetic properties; however, little is known about the nature of chemical bonding and how it affects the magnetic moment and the local order of the alloys. In this paper these properties will be related quantitatively to the chemical bonding through the use of a model based on fundamental chemical bonding principles.

The moment variation in T - M alloys has been attributed to electron transfer to the d band of the T atom¹ with little success. Furthermore, Mössbauer work by various authors^{2,3} on Fe alloys has shown that the isomer shift, which depends on the valence of the Fe atom, is constant regardless of metalloid type and concentration. Recent SCF- $X\alpha$ calcula-

tions by Messmer⁴ on Fe-Ni clusters negate any possibility of electron transfer to the T atoms. Instead, it has been proposed^{3,5} that bonds between T and M atoms are responsible for the moment reduction with M content. Calculations by Watson and Bennett⁶ and by Moruzzi⁷ indicate that d - d hybridization between transition-metal atoms may cause reduction in the local moments of T - T alloys.

The purpose of this work is to use a simple model of chemical bonding to account for the moment variation in Co-, Ni-, and Fe- M alloys without the use of complex computer calculations. The model will also reveal the local order of the glasses, since bonding and order are strongly interdependent. The model, and comparison to magnetic data, will yield the extent of T - M bonding which is now believed to be related to the stability of glassy alloys.⁸ The bond model will be developed in Sec. II, and results

for Co, Ni, and Fe alloys with metalloid atoms will be discussed in Sec. III. Conclusions are reached in Sec. IV.

II. THE BOND MODEL

A. Co-*M* bonding

Hybridization is defined as the linear combination of atomic or molecular orbitals to form new bonding or hybrid orbitals. The bonding orbitals are located between the atoms that donate the orbitals. The electrons that fill the bond orbitals are shared between the atoms. To model the bonding, it is necessary to choose a representative cluster of the solid, because it is generally accepted that the metalloid (*M*) atoms interact predominantly with the closest metal (*T*) neighbors. For dilute *M* in a *T* matrix, a cluster of Z_M atoms of *T* surrounding an atom of *M* will be assumed, with the cluster having the local symmetry of the *M* atom in the crystal. Structural work^{9,10} has shown that *T-M* glasses retain the local environment of the most stable crystal structure.

Messmer's cluster calculations on several *T-M* systems⁴ and Felcher's neutron diffraction study on Ni₃Al (Ref. 11) have yielded some basic information as to how the *T* and *M* orbitals interact. The *d* orbitals on the *T* atoms and the *p* orbitals from the *M* atom combine to form hybrid bonding orbitals by lowering the energies of the atomic orbitals. The *s* orbitals from the *M* atom are deep lying and non-

interacting. It is apparent that the *T-M* bonding interactions are complex. However, it is necessary to make some severe approximations in order to develop a model that is easy to use and understand. From the point of view of the valence-bond theory, each *T* near neighbor will contribute one *d* orbital to the bonded with the three *p* orbitals of the *M* atom.¹² The probable bonding scheme for the Co₆B cluster is shown in Fig. 1. The three *p* orbitals from the *M* atom will combine with three *d* orbitals to form three σ -type bonding and three σ^* -type antibonding orbitals. The Z_M-3 remaining hybrid *d* orbitals will form σ -type levels that are less bonding than the *p-d* bonds. Thus a total of $Z_M d$ orbitals are donated by the Z_M atoms of *T* surrounding *M*. The three *p* orbitals of *M* will be shared between the Z_M orbitals contributed by the *T* atoms to form Z_M valence bonds.

For a solid Co alloy, the levels will broaden as shown in Fig. 1. If there are N_T atoms of *T* and N_M atoms of *M* then there will be $5N_T - Z_M N_M$ unbonded orbitals left on the *T* atoms. The low symmetry of the *hcp* structure and other Co-*M* alloys prevents the identification of one particular *d* state as bonding; thus, it is necessary to assume that the hybridized *d* orbitals in a solid come from the entire manifold of Co 3*d* states. If the *T* atom is strongly ferromagnetic with a magnetization at 0 K of n_B , then each *d* orbital contributed to bonding will carry away $n_B/5$ holes. If the bond orbitals are nonmagnetic,¹¹ then the magnetic moment will be

$$\mu(\mu_B/\text{at.}) = (5N_T - Z_M N_M)(\text{magnetic orbitals})[n_B/5 \text{ (holes/orbitals)}]/[N_T \text{ (T at.)}]$$

or

$$\mu = n_B - Z_M(n_B/5)(N_M/N_T). \quad (1)$$

The moment variation is due to the donation of ferromagnetic states to bonding and has nothing to do with the valence of *M*. Notice that the model does not predict a change in the occupancy of the 3*d* band; rather, it predicts a gradual transformation of spin-polarized *d* levels to bonded nonpolarized *p-d* hybrids. The model is independent of the valence of *M* because the total number of electrons donated to the hybrid orbitals does not exceed the available $\sigma(p-d)$ and $\sigma(d)$ orbitals, as shown for Co-B in Fig. 1. The large number of bonding electrons in Ni-*M* alloys implies that either the antibonding orbitals or the magnetic 3*d* orbitals must fill with electrons as metalloid is added and thus the moment will depend on the valence of *M*. An appropriate expression for Ni alloys will be developed in the following section.

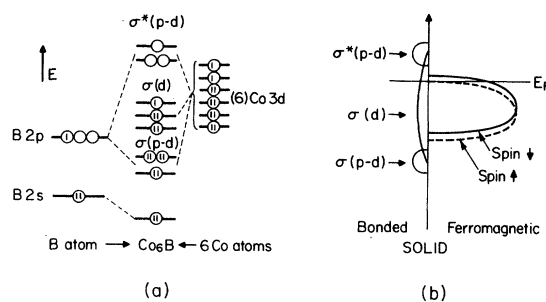


FIG. 1. Approximate orbital energy spectrum in the Co₆B cluster according to the valence-bond theory. Each of six Co atoms contributes one *d* orbital to be bonded with three *p* orbitals from the B atom. Only three *d* orbitals will overlap on average with the *p* orbitals; the other three will be considered nonbonding. The B 2*s* orbital is nonbonding from Messmer's⁴ calculations. Panel (b) shows how these orbitals may spread in a solid of many clusters. The bonded nonmagnetic orbitals are on the left while the unbonded ferromagnetic *d* state of Co are on the right.

B. Ni-M bonding

The bond model for Ni will differ from the case for Co because the high symmetry of fcc Ni alloys allows the symmetry of the bonds to be stated explicitly. An approximate density of states for fcc Ni is shown in Fig. 2. The orbitals near the Fermi energy, which would be magnetic, have T_{2g} symmetry and are responsible for Ni-Ni bonds. The Ni₃Al alloys form an ordered fcc superlattice of the Cu₃Au type, as also shown in Fig. 2. The ordering reaction results in a transformation from O_h to C_{4v} symmetry, and the T_{2g} level splits to form $E(d_{xz}, d_{yz})$ and $B_1(d_{xy})$ orbitals. The E levels are Ni-Ni bonding, whereas the B_1 levels are Ni-Al bonding, as shown by the probable σ bond symmetry planes in Fig. 2. Felcher,¹¹ using neutron diffraction, found that the B_1 bond levels in Ni₃Al fill up with electrons and drop significantly below the Fermi energy when Ni₃Al is formed, while the E type Ni-Ni bonding levels remained partially empty near the top of the band. Since Ni₃Al is nonmagnetic, it follows that the E levels are not spin polarized. This finding is corroborated by the L_{III} absorption-edge results of Pease¹³ on Ni-Al and Ni-Cu alloys. Pease's data indicate that the number of unoccupied 3d states remain constant on Ni atoms regardless of metalloid concentration, even when the moment dropped to zero.

Thus the bond model for Ni alloys must describe d_{xy} - p hybridization, where now the hybridized d_{xy} levels are gradually filled with electrons and lowered in energy as metalloid atoms are added. Formation of Ni-M bonds requires the T_{2g} band to split into filled B_1 -type bands and unfilled but nonmagnetic E -type bands. The d_{xy} levels will fill faster with M atoms that have large p electron valences (V_p). Therefore, Eq. (1) is modified to

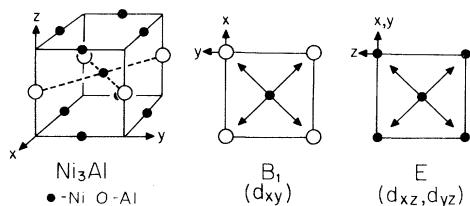


FIG. 2. Bonding in the Ni₃Al alloy. Formation of Ni₃Al crystals from fcc Ni makes the T_{2g} levels split into $B_1(d_{xy})$ and $E(d_{xz}, d_{yz})$ levels, while the E_g levels split into $A_1(d_{z^2})$ and $B_2(d_{x^2-y^2})$ levels. The B_1 are Ni-Al bonding and the E are Ni-Ni bonding. Notice how the B_1 levels are below the Fermi level, and thus have no uncompensated spins, while the E levels are still partially empty, even though the net moment is zero. Conservation of charge requires the E levels to lose electrons as B_1 levels fill up.

$$\mu(\mu_B/\text{Ni at.}) = n_B - Z_M(n_B/5)(N_M/N_T) - V_p(N_M/N_T)$$

or equivalently as

$$\mu(\mu_B/\text{Ni} + M \text{ at.}) = n_B - (n_B + Z_M n_B/5 + V_p)c, \quad (2)$$

where $c = N_M/(N_M + N_T)$. Equation (2) says that the moment reduction in Ni alloys is dependent on the number of d_{xy} Ni-M bond orbitals formed and the rate which the hybridized d_{xy} - p orbitals are filled. It does not imply an electron transfer from the M atom to the Ni atom because the electrons occupy shared hybrid orbitals. Since the hybridized d_{xy} - p orbitals are filling with electrons, conservation of charge requires the E orbitals to empty by an equivalent ($V_p c$) amount; thus, the moment goes down with increasing c , but the total number of unoccupied 3d states remains constant.

C. Fe-M bonding

In Fe the T_{2g} levels and the E_g spin \uparrow levels are occupied while the E_g spin \downarrow levels are empty; thus, only the d orbitals with E_g symmetry contribute to ferromagnetism. However, it can be seen that the d orbitals with T_{2g} symmetry are bonding orbitals in the bcc structure, so that little or no moment reduction (per Fe at.) is expected for dilute bcc Fe-M alloys. However, Fe is weakly ferromagnetic with a partially empty spin \uparrow band so that the moment is extremely sensitive to changes in the Fe-Fe exchange. Thus the bond model is not expected to have much success with Fe-M alloys, except for the special case of dilute bcc alloys.

III. RESULTS AND DISCUSSION

A. Cobalt alloys

Magnetic-moment data^{14,15} for dilute hcp substitutional alloys of P, Si, and Al in Co are shown in Fig. 3, along with the results of the model using Eq.

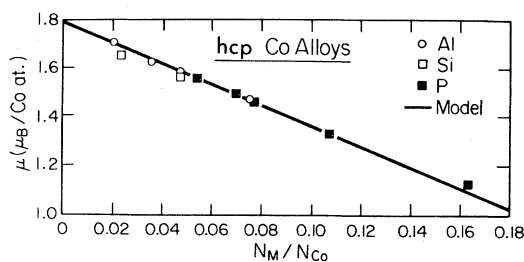


FIG. 3. Magnetic moments for dilute hcp solid solutions of Al, Si, and P in Co. The solid line is from Eq. (1) using $Z_M = 12$.

(1) with $Z_M = 12$. The excellent fit of this line to the data indicates that the moment variation is dependent on the local M environment and not on the valence of M . n_B was taken as 1.79 Bohr magnetons for all Co alloys.

For Co-B glasses,¹⁶ it was assumed that the local environment was similar to that for the stable crystalline Co_3B which has the DO_{11} or Fe_3C structure.¹⁰ Since each B atom would have six Co neighbors, $Z_M = 6$ was used in Eq. (1) and the fit to the experimental points is good, as shown in Fig. 4. Results for amorphous Co-P alloys^{17,18} are also shown in Fig. 4, along with the result of the model assuming that the local environment of the glass is similar to the stable Co_2P crystal, which has the C23 or the PbCl_2 -type structure¹⁰ with $Z_M = 9$. For crystalline Co-P alloys,^{15,17,18} P is soluble in Co up to about 12 at.%, so in this regime $Z_M = 12$ was used in the model. With higher concentrations of P, Z_M was varied from 12 to 9 according to the lever rule for a mixture of the hcp solid solution and the Co_2P phase. The resulting curve for the model fit the data well. It is thus concluded that glassy Co- M alloys retain the same local environment around M as the stable Co_xM -type crystal structure.

$$\mu(\mu_B/T \text{ at.}) = (5N_{\text{Co}} - Z_M N_{\text{Co}} N_M / N_T) n_B / 5N_T + [5N_{\text{Ni}} n'_B - (Z'_M n'_B + V_p) N_{\text{Ni}} N_M / N_T] / 5N_T, \quad (3)$$

where $N_T = N_{\text{Ni}} + N_{\text{Co}}$, $N_M / N_T = 0.25$, $n_B = 1.79$, $n'_B = 0.616$, and $Z_M = Z'_M = 9$. The model predicts moments of 0.25, 0.49, and 0.74 for $x = 20, 40$, and 60. The experimental moment values²² for these

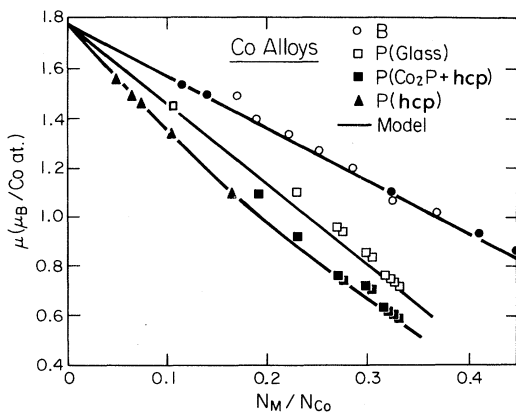


FIG. 4. Magnetic moments for amorphous (open symbols) and crystalline (closed symbols) Co- M alloys where M is P or B. The solid lines are from Eq. (1) with $Z_M = 6$ for Co-B and $Z_M = 9$ for amorphous Co-P. For crystalline Co-P alloys, Z_M was taken at 12 for dilute hcp solutions with less than 12 at.% P. For more concentrated Co-P crystals, Z_M was varied continuously from 12 to 9 according to the lever rule for a mixture of Co_2P crystals with hcp solid solution.

B. Nickel alloys

Magnetic-moment data for dilute fcc substitution Ni alloys is shown in Fig. 5 for Al, Si, Sn, Zn, and Ge (Ref. 19) and for Cu (Refs. 19 and 20). The results of Eq. (3) with $Z_M = 12$ and $n_B = 0.616$ and with the appropriate values of the p valency V_p are also shown. The fits are reasonably good. Zn and Cu have been treated as metalloids by assuming that the $3d$ bands for these atoms are filled and noninteracting. $V_p = -1$ was taken for Cu because it only has one $4s$ electron. A more complete set of Ni-Cu data along with the bond model for Ni-Cu is shown in Fig. 6.

Figure 6 shows the magnetic-moment data for Ni-B alloys²¹ that have crystallized in the hcp Ni and Ni_3B phases. B is not soluble in Ni and the Ni_3B crystals have the Fe_3C structure so that the model [Eq. (3)] was used with $Z_M = 6$ and $V_p = 1$. The fit is good. Application of the bond model to amorphous Ni alloys may be released in the near future.

The bond model should also work for ternary magnetic alloys. For example, the bond model for the $\text{Co}_x\text{Ni}_{80-x}\text{P}_{20}$ system would be

concentrations are 0.12, 0.48, and 0.77. Further applications of the bond model to ternary magnetic systems is under investigation.

C. Iron alloys

The magnetic moments for dilute bcc Fe alloys with Ga, Ge, Sn, Sb, and As,²³ with B,²⁴ with Al,¹⁴

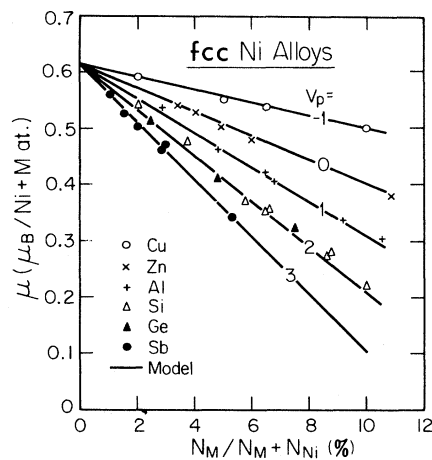


FIG. 5. Magnetic moments of dilute fcc alloys of Ni. The result of the bond model using $Z_M = 12$ and p valences V_p from -1 to $+3$ are also shown. Notice how well the model fits the data for an element with the same value of V_p .

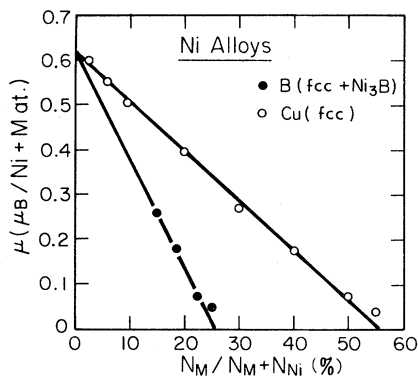


FIG. 6. Magnetic moments of Ni-Cu disordered solid solutions and Ni-B with equilibrium phases of pure fcc Ni and Ni₃B. The solid line is the result of the model using $Z_M = 12$, $V_p = -1$ for Cu and $Z_M = 9$, $V_p = 1$ for B.

and with Si (Refs. 14 and 25) are shown in Fig. 7. The bond model roughly predicts zero moment change per Fe atom because the d orbitals involved in bonding have no uncompensated spin. Good agreement is seen for Si and for Al; but the heavy d -core metalloids slightly increase the moment while B atoms decrease the moment. This effect could be related to the relative size of the metalloids, because the large metalloid atoms tend to swell the lattice which could increase the Fe exchange to expose more ferromagnetic holes. The small B atoms tend to contract the lattice²⁴ and thus could decrease the exchange coupling.

An interesting feature in the Fe-Si and the Fe-Al alloys is the sharp drop in the moment²⁵ as the alloy begins to form the ordered bcc phase (DO_3). The transition from disordered bcc to DO_3 does not affect the degeneracy of the d levels so that the model predicts zero moment change. Thus the moment drop in these systems is caused by changes in exchange coupling rather than the formation of p - d hybrid bonds.

IV. CONCLUSIONS

Co appears to bond strongly to all metalloids implying maximum p - d overlap according to the valence bond theory. The moment variation is caused by hybridization of d states with metalloid p states in which the hybridized orbitals are nonmagnetic. The amount of hybridization is determined solely by the local M environment and not by the valence of M . The electrons in the hybrids are shared between the atoms so that there is no net

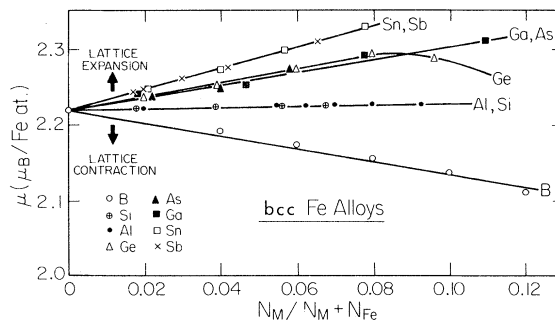


FIG. 7. Moment distribution for various dilute bcc alloys of Fe. The bond model predicts zero change. Exchange increases are possibly caused by lattice expansion, while exchange decreases are possibly caused by lattice contraction.

electron transfer; thus, the number of unoccupied states remains constant regardless of metalloid content or net magnetic moment.

The moment variation in Ni alloys is caused by hybridization of d states with B_1 symmetry. Forming d_{xy} - p hybrid bonds requires the formation of nonpolarizable d states with E symmetry. The moment reduction is caused by the hybridization and filling of the d_{xy} orbitals, so for Ni the moment reduction is also dependent on the valence of the metalloid as well as the local metalloid coordination. For both Co and Ni there is no net electron transfer so that the number of unoccupied d states remains constant even when the net moment is zero.

The bond model predicts about zero moment change for dilute bcc Fe- M alloys. Experimental results are in approximate agreement with the model; but, the model does not account for changes in Fe atom exchange.

The local M environment in magnetic T - M glasses is similar to the M environment in the stable crystalline forms in agreement with structural work.^{9,10,26} T - M bonding is equivalent in the crystalline and in the glassy states.

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