

Models of magnetic-moment variation in alloys

R. C. O'Handley and Y. Hara

*Department of Materials Science and Engineering, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139*

(Received 29 October 1986)

Two important new models of alloy magnetism that are based on apparently contradictory assumptions are examined and compared. Reduction to a common set of parameters reveals the strengths and weaknesses of each model as well as their complementarity.

Interpretation and prediction of magnetic moments in alloys and compounds has evolved from simple rigid-band concepts (exemplified by naive interpretations of Slater-Pauling curves), through Pauling radii, virtual bound states, and split-band models to a host of local environment theories based on the early work of Jaccarino and Walker.¹ Concepts of band magnetism or those of localized moments have been individually favored by some models and mixed in others. There now seems to be a renewed interest in models of alloy magnetism due possibly to the remarkable increase in the variety of alloy combinations and extended composition ranges made possible by the fabrication of amorphous alloys over the past two decades. Two of the more recently described models are based on the results of extensive density-functional band-theory calculations² and alternatively on the chemico-physical concepts used in self-consistent-field $X\alpha$, scattered-wave, molecular-orbital cluster calculations.³ Those models are, respectively, the magnetic valence model⁴ (referred to here as the " V_m " model) and the coordination-bond model⁵⁻⁷ (referred to here as the " C " model). These relatively new models have already been widely cited in the literature to interpret variations and trends in alloy moment data.^{8,9} However, these two models appear to be based on mutually exclusive concepts in determining alloy magnetic moment. The V_m model stresses the primacy of average alloy valence, exclusive of local structure, while the C model stresses local coordination and bonding. Yet both models cite two common sets of magnetic data, those of amorphous Co-B alloys¹⁰ and those of amorphous and crystalline Co-P alloys¹¹ as supporting their results.

It is the purpose of this Brief Report to clarify the relation between these two models and thus define more clearly their regions of applicability. We briefly describe each model, leaving it up to the interested reader to refer to the original work for details and supporting data. We then cast the results of the two models in terms of a common set of parameters to allow for quantitative comparison.

The V_m model is based on Friedel's concept of virtual bound states as treated by Terakura and Kanamori.¹² It accounts for the Slater-Pauling-like variation of average magnetic moment with alloy content in a variety of alloys by defining an atom-averaged *magnetic* valence

$$V_m = 2N_d^\downarrow - V, \quad (1)$$

where V is the average *electronic* valence $V = N_d^\uparrow$

$+ N_d^\downarrow + N_{sp}^\uparrow + N_{sp}^\downarrow$ and N_d^\downarrow is the number of majority-spin d electrons. Substitution of the definition for V in Eq. (1) leads to the relation between V_m and the atom-averaged magnetic moment:

$$V_m = \mu_{av} - 2N_{sp}^\uparrow. \quad (2)$$

Equation (2) clearly demonstrates that a plot of μ_{av} versus the atom-averaged magnetic valence V_m necessarily leads to Slater-Pauling-like behavior ($|d\mu_{av}/dx| = 1$) with the x intercept determined by the average number of conduction electrons [Eq. (2)]. Numerous examples of the broad applicability of the model can be found in the original manuscripts.⁴ When the data for a series of alloys deviate from the line of slope 1, it may be the result of a change in conduction-electron concentration or, as is often the case with iron-based alloys, a change from strong to weak ferromagnetism.

In a later addition to this model,¹³ it is pointed out that Slater-Pauling-like behavior is related to the existence of a gap or minimum in the conduction-band density of states. Such a minimum tends to conserve the number of conduction electrons in an alloy series and, therefore, the entire concentration effect is manifest in the d -band occupation or magnetic moment. That is, Eq. (2) reduces to $\mu_{av} = V_m + \text{const}$, and all data should fall on a common straight line.

The essence of the C model⁵ is that for a given metalloid (M) content in a $3d$ -based (T) alloy $T_{1-x}M_x$ the metalloid atom is more or less effective in suppressing the host magnetization depending upon whether M is more or less strongly bonded with T . This bonding is assumed to be proportional to the number of T atoms surrounding an M atom. Hence the magnitude of the average magnetic moment μ per T atom in the alloy is suppressed below that in the pure host μ_0 by an amount proportional to C , the T coordination about the metalloid:

$$\mu = \mu_0(1 - CN_M/5N_T), \quad (3)$$

where N_M/N_T [more commonly written as $x/(1-x)$] is the ratio of the number of M atoms to T atoms. Equation (3) assumes that each of the C nearest-neighbor T atoms forms a bond with the central M atom and therefore loses, on average, one fifth of its moment because one of its five $3d$ -electron orbitals is tied up in a nonmagnetic, covalent bond.

The original manuscripts⁵⁻⁷ show the convincing application of this model to metallic glasses as well as to crystalline solid solutions based on a strongly magnetic host, cobalt. The moment reductions observed for amorphous Co-B (Ref. 10) and Co-P (Ref. 11) alloys closely follow the lines determined by Eq. (3) for $C=6$ (based on the Co_3B cementite structure), and $C=9$ (based on the Co_3P tetragonal structure), respectively. For crystalline Co-P alloys¹¹ the data fit the curve defined by Eq. (3) with C varying continuously from 12 (appropriate to hcp solid solutions) at $N_M/N_{\text{Co}}=0$, to $C=9$ (again as in Co_3P) at $N_M/N_{\text{Co}}=0.3$. The implication is that while a boron atom in the glassy alloy bonds with, and therefore suppresses the moment of, six cobalt atoms, a phosphorus atom in the glass bonds with nine cobalt atoms and therefore gives rise to a sharper moment reduction. For the crystalline Co-P alloys the coordination numbers used to fit the data 12 and 9 agree with the results of direct structural determination of C .

The C model can be extended to Ni-base alloys⁶ and, with further assumptions to metal-metal systems.⁷ Thus this simple model provides a clear and easily applied relation between magnetic properties and local atomic structure in crystalline alloys and in metallic glasses.

It may appear at first that the C model, which focuses on the importance of coordination, is orthogonal to the V_m model, which is based on the influence of chemical valence on average magnetic moment. In fact, the C model illustrates a case where metalloid valence seems to play no role in the rate of decrease in magnetic moment.⁵ Al, Si, or P dissolved in a common structure, that of crystalline Co (hcp solid solution, $C=12$) all produce the same moment suppression despite their different valences. Similarly, the valence model plots some data for different structures on a common line implying that magnetic valence and not coordination tells the whole story.

To resolve this conflict we first note that the $\text{Co}_{1-x}\text{B}_x$ data of Hasegawa and Ray¹⁰ and the $\text{Co}_{1-x}\text{P}_x$ data of Pan and Turnbull¹¹ are cited by both models as evidence of their validity. Thus the conflict is due in part to the method of presentation of the data. To clarify this, we point out that the C model plots the variation of moment μ per T atom in terms of the parameter N_M/N_T [which for an alloy $T_{1-x}M_x$ is equivalent to $x/(1-x)$] instead of in terms of the more conventional $N_M/(N_M+N_T)$ (or x) [see Eq. (3)]. The V_m model plots the variation of the moment per average atom μ_{av} in terms of the parameter V_m [Eq. (2)]. For an alloy $T_{1-x}M_x$, with one magnetic species, $\mu_{av}=(1-x)\mu$. Thus, what appears as a shift down along the universal curve in the valence model (e.g., more negative V_m) shows up as a greater slope (T coordination about M) in the coordination model. Specifically, metalloids having greater valence [smaller V_m , thus lower moment, Eq. (2)] are generally more highly coordinated by T atoms [more involved in p bonding, thus lower moment, Eq. (3)]. However, the differences between the models go deeper than this. If we examine the expressions for moment reduction in each model for the Co-B and Co-P systems, the problem becomes clearer.

Equation (3) for the cobalt moment μ in the C model can be written instead to give the atom-averaged moment

$\mu_{av}=(1-x)\mu$ in terms of the metalloid concentration $x=N_M/(N_M+N_T)$:

$$\mu_{av}=\mu_0[1-(5+C)x/5] \quad (4)$$

Equation (4) predicts

$$\mu_{av}=\mu_0(1-2.2x),$$

for amorphous $\text{Co}_{1-x}\text{B}_x$ ($C=6$) and

$$\mu_{av}=\mu_0(1-2.8x),$$

for amorphous $\text{Co}_{1-x}\text{P}_x$ ($C=9$).

Equation (2) for the atom-averaged moment of $\text{Co}_{1-x}\text{M}_x$ in the V_m model can be expressed in terms of x and evaluated using $2N_{sp}^\dagger=\mu_0-1=0.75$ (for cobalt with nine valence electrons $=2N_{sp}^\dagger+N_d^\dagger+N_d^\ddagger$), and $V_m^{\text{Co}}=1$, $V_m^{\text{B}}=-3$, and $V_m^{\text{P}}=-5$ to predict

$$\mu_{av}=\mu_0(1-4x/\mu_0)=\mu_0(1-2.3x)$$

for $\text{Co}_{1-x}\text{B}_x$ and

$$\mu_{av}=\mu_0(1-6x/\mu_0)=\mu_0(1-3.4x)$$

for $\text{Co}_{1-x}\text{P}_x$.

Figure 1 shows these predictions [using $\mu_0(\text{Co})=1.75\mu_B$] along with the data. The theoretical curves are labeled C and V_m for the respective models. Either model comes reasonably close to the data for Co-B alloys. However, in describing the amorphous Co-P data, the C model does better than the V_m model. Beyond the comparison in Fig. 1, it is important to note that the C model predicts a moment suppression proportional to μ_0 while the V_m model does not.

Clearly, for these glassy alloys, the C model gives a

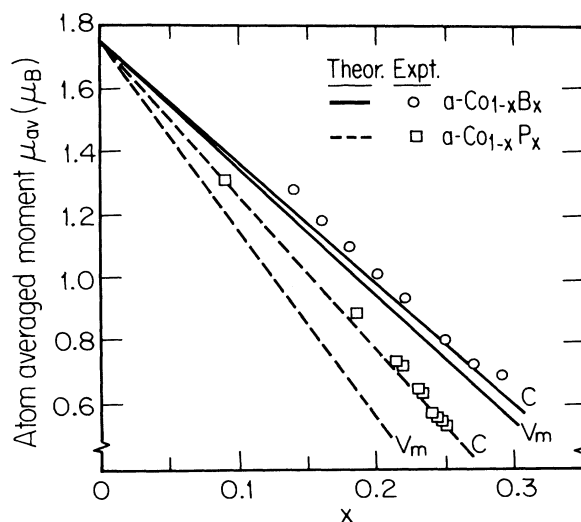


FIG. 1. Experimental data for atom-averaged magnetic moments vs metalloid content in amorphous Co-B (circles, Ref. 10) and amorphous Co-P (squares, Ref. 11) alloys. Theoretical predictions for two alloys Co-B (solid lines) and Co-P (dashed lines) are based on equations and parameters in the text for the two models V_m and C .

more *accurate* fit to the data. However, the V_m model is able to account for general trends in a wider class of alloys⁴ without additional assumptions. Together, these models offer valuable physical insight for understanding alloy magnetism in terms of the impact of bonding and coordination on moment formation, the role of con-

duction-band minima in pinning the Fermi level, and the correlations between metalloid size, coordination, and valence.

This work is supported by National Science Foundation Grant No. DMR 8318829.

-
- ¹V. Jaccarino and L. R. Walker, Phys. Rev. Lett. **15**, 259 (1965).
²V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978), p. 52; V. L. Moruzzi, P. Oelhafen, A. R. Williams, R. Lapka, and H.-J. Guntherodt, Phys. Rev. B **27**, 2049 (1983).
³C. Y. Yang, K. H. Johnson, D. R. Salahub, J. Kaspar, and R. P. Messmer, Phys. Rev. B **24**, 5673 (1981).
⁴A. P. Malozemoff, A. R. Williams, K. Terakura, V. L. Moruzzi, and K. Fukamichi, J. Magn. Magn Mater. **35**, 192 (1983); A. R. Williams, V. L. Moruzzi, A. P. Malozemoff, and K. Terakura, IEEE Trans. Magn. **MAG-19**, 1983 (1983).
⁵B. W. Corb, R. C. O'Handley, and N. J. Grant, J. Appl. Phys. **53**, 7728 (1982).
⁶B. W. Corb, R. C. O'Handley, and N. J. Grant, Phys. Rev. B **27**, 636 (1983).
⁷B. W. Corb and R. C. O'Handley, Phys. Rev. B **31**, 7213 (1985).
⁸R. M. White, *Introduction to Magnetic Recording* (IEEE, New York, 1985), p. 5.
⁹K. Shiba, S. Tsunashima, S. Uchiyama, and S. Yoshimo, IEEE Trans. Magn. **MAG-22**, 1104 (1986).
¹⁰R. Hasegawa and R. Ray, J. Appl. Phys. **50**, 1586 (1979).
¹¹D. Pan and D. Turnbull, J. Appl. Phys. **45**, 1406 (1974).
¹²K. Terakura and J. Kanamori, Prog. Theor. Phys. **46**, 1007 (1971).
¹³A. P. Malozemoff, A. R. Williams, and V. L. Moruzzi, Phys. Rev. B **29**, 1620 (1984).