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Theory of Compositional and Magnetic Correlations in Alloys: Interpretation of a Diffuse Neutron-Scattering Experiment on an Iron-Vanadium Single Crystal

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We describe a first-principles theory for compositional and magnetic correlations in alloys and compare the results of the theory with recent diffuse, unpolarized, neutron-scattering measurements on a single crystal of ferromagnetic $\text{Fe}_{0.865}\text{V}_{0.135}$. The nuclear cross section is described very well by the theory and we are able to connect the q -dependent structure to the underlying electronic structure of the alloy. The magnetocompositional and magnetic correlations may also be obtained for comparison to polarized measurements.

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At the root of alloy theory, and of crucial importance to its subsequent exploitation in the design of new alloys, are the electronic driving mechanisms for particular physical properties.¹ In metallic alloys the electrons cannot be allocated to particular lattice sites nor can their effects be interpreted in terms of pairwise interatomic interactions. It is necessary to solve the many-electron problem as accurately and realistically as possible and to establish a theory for the appropriate correlation functions in terms of this solution. Such correlation functions then reveal, for example, the electronic mechanisms that determine the compositional, or magnetic, ordering in the alloy. At this point the theoretical results can be compared directly with single-crystal, diffuse x-ray or neutron-scattering experiments which probe closely related quantities.² For a wide range of alloys, magnetic and compositional order appear to be strongly interrelated,³ requiring an analysis of their compositional, magnetocompositional, and magnetic correlation functions in terms of their underlying electronic structure. For these systems, polarized neutron-scattering experiments provide the most stringent test of theoretical results.

Here we outline a first-principles theory for compositional ordering in alloys and its dependence on their magnetic structure. It is therefore applicable to alloys in which the compositional phase transition occurs at a lower temperature than the magnetic one. In practice, alloys are typically quenched from high temperatures (T), and, because of the differing response times of the chemical and electronic degrees of freedom, a high- T chemical state is frozen in. If its effective temperature is below the Curie temperature, then its atomic correlations depend upon the magnetically ordered state. Thus, in order to compare our results to the experimental, single-crystal (quenched) data of Cable, Child, and Nakai⁴ in which the effective temperature was estimated to be below the Curie temperature, we apply our theory to a magnetically ordered, iron-vanadium alloy ($\text{Fe}_{0.865}$ -

$\text{V}_{0.135}$). This is the first comparison between the compositional correlation function of a magnetic alloy determined from first principles and that obtained from diffuse nuclear cross-section data. It is made most naturally in reciprocal space, where long-range effects show up as simple peaks. All features of the experiment are reproduced and, moreover, they can be interpreted in terms of the spin-polarized electronic structure of the alloy; i.e., the electronic origins of the ordering mechanisms are identified.

The starting point for the theory is an accurate treatment of the electronic structure of the compositionally disordered, magnetically ordered alloy via the self-consistent field, Korringa-Kohn-Rostoker, coherent-potential approximation (SCF-KKR-CPA) method.⁵ Within the local-spin-density approximation⁶ (LSDA), this method enables the equilibrium properties of such alloys to be described to a similar accuracy as for compositionally ordered systems. For a substitutional alloy, any configuration may be specified by a set of site occupation variables denoted by $\{\xi_i\}$, where, for a binary A_cB_{1-c} alloy, $\xi_i = 1$ (0) for a site i occupied by an A (B) atom. Formally, within the LSDA, the electronic grand potential $\Omega(\{\xi_i\})$ for a system of electrons moving in the fields set up by this arrangement of nuclei can be written down and the statistical mechanics of the compositional fluctuations considered.⁷ Because of differing time scales, the averages over the electronic degrees of freedom may be performed for a given atomic configuration (thus separating the electronic and compositional degrees of freedom) and Ω can then be considered as a compositionally fluctuating alloy Hamiltonian. We briefly describe the contents of the theory below; specific details may be found in Ref. 8.

Averaging $\Omega(\{\xi_i\})$ over the compositional fluctuations in site and occupation space provides an expression for the free energy F of the high- T , compositionally disordered system. The free energy may be expanded about a

suitable reference alloy Hamiltonian Ω_0 by using the Feynman-Peierls inequality,⁹ $F \leq F_0 + \langle \Omega - \Omega_0 \rangle_0 \equiv \hat{F}$, and statistical averages (denoted by $\langle \dots \rangle$) performed to give a variational upper bound on the free energy, as long as Ω_0 is exactly soluble. It follows that the statistical average for any quantity, e.g., the A -atom occupation probability $c_i \langle \xi_i \rangle$ at site i , may then be obtained. The single-site choice $\Omega_0 = \sum_i f_i(\xi_i)$ for the reference Hamiltonian sets up a mean-field theory¹⁰ in which the functions f_i are found from a functional minimization of \hat{F} . These f_i 's are expressed⁸ in terms of site-restricted averages, namely, $f_i(\xi_i) = \langle \Omega \rangle_0 |_{\xi_i = \xi}$, which are readily available from SCF-KKR-CPA electronic-structure calculations.^{5,8} Hence our choice of reference Hamiltonian underscores the consistency within our approach. Besides depending fully on the alloy electronic structure, note that $\langle \Omega \rangle_0$ depends on the local concentrations $\{c_i\}$ directly, and on the KKR-CPA local moments $\{\mu_i^a\}$ indirectly, where a denotes A or B atoms.

Although, in principle, c_i can vary from site to site in the lattice, we consider only the case of a homogeneous probability distribution (i.e., $c_i = c$, the high- T , randomly disordered state). By considering concentration fluctuations in this state via linear response theory, an expression for the atomic-pair correlation function ($a_{ij} \sim \langle \xi_i \xi_j \rangle - \langle \xi_i \rangle \langle \xi_j \rangle$) is obtained,^{7,8} which depends on the electronic structure of the homogeneously disordered alloy. In reciprocal space, this correlation function (for a binary alloy) may be expressed as

$$\alpha(\mathbf{q}) = 2\beta c(1-c)[1 - \beta c(1-c)S^{(2)}(\mathbf{q})]^{-1}, \quad (1)$$

with

$$S_{ij}^{(2)} = S_{ij}^{c,c} + \sum_I S_{ij}^{c,\mu^A} \gamma_{ij}^A + \sum_I S_{ij}^{c,\mu^B} \gamma_{ij}^B,$$

and $\beta = (k_B T)^{-1}$. The terms $S_{ij}^{c,c}$ and S_{ij}^{c,μ^a} are the variation of $\delta \langle \Omega \rangle / \delta c_i$ (the local chemical potential) with respect to c_j and μ_j^a , respectively, and γ_{ij}^a denotes $\partial \mu_i^a / \partial c_j$. Evidently, magnetic contributions to $S^{(2)}(\mathbf{q})$ arise directly from the spin-polarized electronic structure through $S^{c,c}$ and indirectly from the changes of the local moments due to variations of the local chemical environment through γ^a .⁸

It should be noted that the form of the atomic correlations given in Eq. (1) is quite general within density-functional theory,⁷ and, moreover, $S^{(2)}(\mathbf{q})$ contains interactions to all orders, not just of the pairwise form. However, from our use of KKR-CPA electronic structure and mean-field statistical mechanics (i.e., including only ideal entropy from our choice of Ω_0), $S^{(2)}(\mathbf{q})$ may be considered as the first-principles generalization of the effective pairwise ordering energy $V(\mathbf{q})$ used by Krivoglaz¹¹ and by Clapp and Moss¹² in their pair-potential approach to atomic short-range order.

The magnetocompositional correlation function ($\langle \xi_i \mu_j \rangle - \langle \xi_i \rangle \langle \mu_j \rangle$), obtained from the moments' dependence on the local chemical environment, may be written

as $Y(\mathbf{q}) = \alpha(\mathbf{q})\gamma(\mathbf{q})$, where

$$\gamma(\mathbf{q}) = (\mu_A - \mu_B) + c\gamma_A(\mathbf{q}) + (1-c)\gamma_B(\mathbf{q}). \quad (2)$$

$\gamma_a(\mathbf{q})$ is the Fourier transform of γ_{ij}^a and is dependent upon details of the KKR-CPA electronic structure. In real space, these "local" magnetochemical response functions γ_{ij}^a measure the effect of changes in the chemical environment upon the magnitude of the moments.⁸ For instance, they may be used to investigate the variations of site magnetizations upon chemical ordering transitions or, possibly, within metallic multilayers.

Finally, the magnetic correlation functional ($\langle \mu_i \mu_j \rangle - \langle \mu_i \rangle \langle \mu_j \rangle$) within this approach gives a susceptibility $\chi(\mathbf{q}) = \alpha(\mathbf{q})[\gamma(\mathbf{q})]^2 + \bar{\chi}(\mathbf{q})$. $\bar{\chi}$ diverges at the analog of the Stoner criterion for an alloy, while the first term describes the coupling of compositional and magnetic correlations.⁸

Most importantly, these functions are closely related to those used to interpret x-ray, neutron-scattering, NMR, and Mössbauer spectroscopic measurements. In particular, polarized neutron-scattering differential cross sections² may be written as

$$\left(\frac{d\sigma}{d\omega} \right)_{\zeta} = \frac{d\sigma^N}{d\omega} + \zeta \left(\frac{d\sigma^{NM}}{d\omega} \right)_{\zeta} + \frac{d\sigma^M}{d\omega}, \quad (3)$$

where $\zeta = +1$ (-1) if neutrons are polarized parallel (antiparallel) to the magnetization. On the right-hand side of Eq. (3), the nuclear, nuclear-magnetic, and magnetic contributions are proportional to $\alpha(\mathbf{q})$, $Y(\mathbf{q})$, and $\chi(\mathbf{q})$, respectively. The first direct q -dependent comparison of an experimental and *ab initio* theoretical cross section for a magnetic alloy is now presented.

Iron-vanadium alloys are particularly suitable for a comprehensive theoretical and experimental study. Ferromagnetic bcc solid solutions form over a wide range of concentrations.¹³ The Fe and V atoms are of similar size but are quite different in their neutron-scattering amplitudes ($b_{Fe} - b_V = 0.99$) and the diffuse scattering is consequently relatively intense with little distortion from static lattice-displacement effects.⁴ Also, with extensive Mössbauer and NMR studies¹⁴ of Fe-V magnetic multilayers available, tests for the theoretical study and design of such structures via the γ_{ij}^a 's are possible.

Recently, Cable, Child, and Nakai⁴ have reported unpolarized diffuse neutron-scattering measurements on a quenched, single crystal of $\text{Fe}_{0.865}\text{V}_{0.135}$ in which the nuclear cross sections for directions [001], [011], and [111] were extracted. This alloy has a Curie temperature of 1180 K. The sample was water quenched after being annealed at 1270 K and Cable, Child, and Nakai estimated (based on an approximate quench rate and the rapidity of atomic diffusion) the effective quench temperature relevant to the compositional fluctuations in the bulk crystal ($\sim 1.5 \text{ cm}^3$) to be 900 K. Then, assuming this estimated temperature is accurate insofar as it lies below the Curie temperature, the atomic short-range order is

set up by the magnetically ordered electronic structure. A comparison of our first-principles calculation of $\alpha(\mathbf{q})$ with these data is given in Fig. 1. We have used the same values of $b_{\text{Fe}} - b_{\text{V}}$ and background (incoherent and multiple scattering) cross sections (0.154 b/sr/atom). The calculated average magnetic moment of $1.78\mu_B$ ($2.18\mu_B$ on Fe sites and $-0.81\mu_B$ on V sites) compares well with the experimental estimate of $1.78\mu_B$ ($2.18\mu_B$ on Fe sites and $-0.82\mu_B$ on V sites).¹⁵ (The calculated Slater-Pauling curve for a range of Fe-V alloys is compared to experiment in Ref. 16.) Our calculations were performed above the theoretical chemical-transition temperature (~ 975 K) but below the theoretical magnetic-transition temperature (~ 1400 K) (our mean-field theory typically overestimates these temperatures by 20%-30%) and successfully reproduce the main features of the experiment. The dominant peaks at $\mathbf{q}=(100)$ and (111) , indicative of a β -CnZn-type ordering tendency, are evident in both the theory and experiment, as is the peak at $(\frac{1}{2} \frac{1}{2} 0)$. The experimental data are not symmetrical about the $(\frac{1}{2} \frac{1}{2} 0)$ point as the symmetry of the lattice dictates, which either results from displacement effects or suggests an inaccuracy in the subtraction of the two Bragg peaks along this direction. Particularly striking is our reproduction of the double-peak structure in the [111] direction which was proposed as a specific challenge to the theory.⁴

A least-squares fit with $S^{(2)}(\mathbf{q})$ yields Fourier coefficients (real-space interactions) which reproduce our q -space results accurately, but only if many real-space neighbor shells are used, in accordance with the findings of Cable, Child, and Nakai.⁴ Below we describe the origins of the correlations in FeV and show that they arise mainly from short-ranged interactions. As a result, a comparison of interactions from a few neighbor shells may be valid. For the first three neighbor shells, the theoretical ($S_1 = -68$, $S_2 = -39$, and $S_3 = 16$ meV) and experimental⁴ ($S_1 = -68$, $S_2 = -44$, and $S_3 = 8$ meV) interactions compare favorably. Note that the experimental (0.63) and theoretical (0.57) ratios of S_2/S_1 lie properly below the value $\frac{2}{3}$ that defines the stability limit for β -CuZn-type ordering.

We now isolate the mechanisms responsible for driving the ordering—the ultimate aim of an alloy theory. We find that the prominent q -dependent features are produced by the majority-spin electronic structure which is strongly affected by disorder, whereas, the minority-spin electrons contribute little to the ordering or the cross section since they “see” little difference between the Fe and V sites.¹⁶ The half filling of the majority-spin states¹⁶ (roughly split into bonding Fe states and antibonding V states) accounts for the ordering tendency, in contrast to Ni-rich NiFe alloys.¹⁷ This highlights the importance that the exchange splitting can have in driving compositional order. Along the various directions, the overall structure of $\alpha(\mathbf{q})$ results mainly from first-nearest-

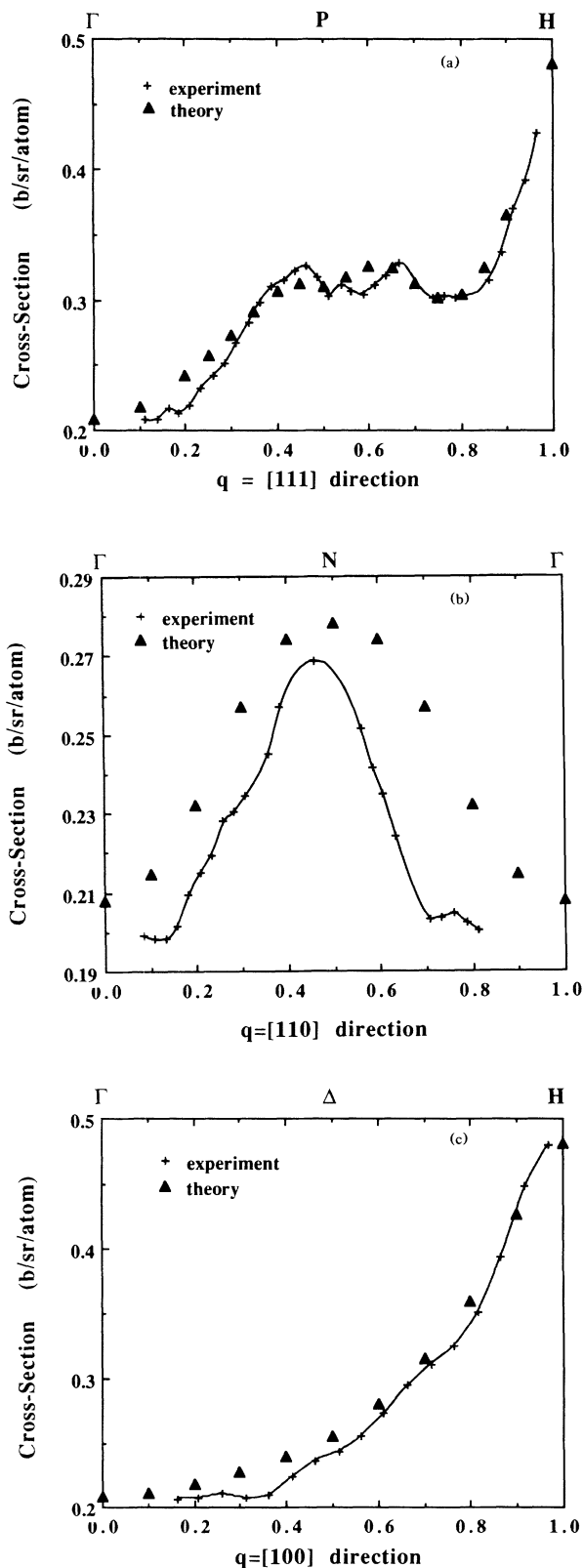


FIG. 1. Comparison of the calculated and experimental nuclear cross sections for bcc $\text{Fe}_{0.865}\text{V}_{0.135}$ along the (a) [111], (b) [110], and (c) [100] wave-vector directions. Note the different scale for (b).

neighbor interactions [$S^{(2)}(\mathbf{q}) \approx S_1 \exp(i\mathbf{q} \cdot \mathbf{R}_{01})$] and reflects the symmetry of the bcc lattice. Of most interest are the two peaks along the [111] direction which have separate origins. The first peak along Γ - P - H is due to short-ranged interactions strictly and requires at least the second- (S_2) and third- (S_3) neighbor interactions. The second peak arises from a locus of diffuse intensity which crosses the (111) symmetry line due to a "2 k_F (111)" nesting vector ($|2k_F| \approx 2.46$, in units where Γ - Δ - H is 1) in the majority-spin Fermi surface. These loci of diffuse intensity also cross the P to N symmetry line about midway along. These nested sheets of alloy Fermi surface are remnants from that of bcc iron. With increasing V content, the Fermi-surface-derived peak should shift due to changes in the electron number and should disappear due to increased disorder broadening. Calculations are planned to confirm this suggestion. An independent experimental investigation of these features and the electronic structure is also desirable. It is interesting to note that the Fermi surface of bcc iron calculated from models of the paramagnetic state¹⁸ maintains vestiges of this structure.¹⁹ We conjecture that this feature would persist even for samples with higher effective quench temperatures.

This comparison between the calculated and experimental nuclear cross sections is the first of its kind, and is both qualitative and quantitative. Moreover, our results underscore the importance for direct q -space comparisons between the two. For instance, extracting real-space interactions requires further approximations and is not necessary for interpreting the ordering mechanisms. In $\text{Fe}_{0.865}\text{V}_{0.135}$, the structure of the nuclear cross section results predominantly from short-range interactions, which give rise to the β -CuZn-type ordering tendency. But, Fermi-surface-driven (long-range) interactions give rise to the second peak along the [111] direction. Finally, polarized neutron scattering has been carried out mainly on polycrystalline alloy samples (see, e.g., Ref. 14). Here essentially the spherical average of $Y(\mathbf{q})$ is measured, making $\gamma(\mathbf{q})$ difficult to extract. We look forward to comparing the magnetocompositional description within our theory, i.e., $Y(\mathbf{q})$ and $\gamma(\mathbf{q})$, and polarized measurements on single crystals. If the $Y(\mathbf{q})$ is described as successfully as the $\alpha(\mathbf{q})$, then a fruitful collaborative study of the ordering processes for a variety of magnetic alloys is feasible, with the possibility of designing compositionally modulated alloys or multilayers with specific magnetic properties.

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