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THEORETICAL INVESTIGATION OF PHASE STABILITY IN NON-MAGNETIC Fe-V SUBSTITUTIONAL ALLOYS

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The assessed phase diagram of Fe-V exhibits a continuous high temperature bcc solid solution intersected at lower temperatures by a complex sigma phase centered around equiatomic composition [1]. Slow kinetics of the bcc to sigma transformation make it possible to retain the bcc solid solution at low temperature. It has been observed that this metastable solid solution has a tendency to order with a CsCl type structure (B2) below 970 K [1,2]. As a first attempt to describe this behavior from an electronic structure approach, this paper will study the phase stability on the bcc lattice using a realistic tight-binding Hamiltonian. Details of the tight-binding description have been given elsewhere [3]. Main features are as follows: Element and structure specific Slater-Koster parameters are used [4] and lattice parameter effects are incorporated through scaling [5]. Charge transfer is set to zero by rigidly shifting the onsite energies of one constituent. The Coherent Potential Approximation (CPA) is invoked with four levels corresponding to states with s, p, t_{2g} and e_g like symmetry. Effects of off-diagonal disorder (ODD) have not been included, instead, an average alloy Hamiltonian was defined using the Slater-Koster parameters of the components weighted by concentration. At equiatomic composition the effect of this approximation has been evaluated by repeating the electronic structure calculation with inclusion of ODD effects (see also [6]). Effective pair interactions, as defined within the Generalized Perturbation Method (GPM) [7], have been computed and have been used to evaluate the ground states of configurational order on the bcc lattice in the Fe-V system. Furthermore, the theoretically derived energetic properties have been used to determine the phase diagram pertaining to the (metastable) bcc lattice with the Cluster Variation Method (CVM) [8] in the tetrahedron approximation.

The density of states (DOS) for equiatomic V-Fe alloys is shown in figure 1. The bandwidths of V and Fe in the alloy are similar and ODD effects can be expected to be small, as is indeed the case when figures 1a and 1b are compared. The main effect of ODD is to enhance some Fe states near the bottom of the d-band, and to diminish some V states near the top of the d-band. A comparison with the first-principles Korringa-Kohn-Rostoker CPA (KKR-CPA) [9], indicates that taking ODD into account nevertheless improves the agreement with the KKR-CPA results.

Table I gives the effective pair interactions for the first five neighbor shells on the bcc lattice for various V-Fe alloys. The nearest neighbor pair interaction is much larger than the more distant ones. However, those more distant interactions do not diminish rapidly with distance, indicating that beyond the nearest neighbor shell it is not obvious at what shell the GPM expansion for the ordering energy can be truncated.

Despite the fact that ODD has little effect on the DOS, the nearest neighbor pair interaction is reduced dramatically. To understand this, the pair interactions will be examined more closely. Figure 2 shows the first, second, and third nearest neighbor pair interactions as a function of energy. Comparing the cases with and without ODD, the first pair interaction shows the same

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Table I. Effective pair interactions in bcc V-Fe alloys, computed with the GPM with (+) and without (-) ODD (units: mRy/atom).

	VFe +ODD	VFe -ODD	V ₃ Fe -ODD	VFe ₃ -ODD
shell				
1	2.613	6.225	7.210	6.772
2	0.098	0.143	-0.160	0.663
3	0.345	0.301	0.327	0.301
4	0.442	0.423	0.445	0.450
5	-0.457	-0.609	-0.163	-0.944

Figure 1. The DOS of bcc VFe. The dashed (dotted) line represents the states associated with the V (Fe) sites, the solid line indicates the total DOS. (a) without ODD, and (b) with ODD taken into account.

qualitative features, it is negative at the bottom, becomes positive in the center, and is negative again at the top of the d-band, just as is expected from previous tight-binding GPM studies of phase stability in transition metal alloys [7,10], and the nodes of the two curves are very close as well. The main difference stems from the different proportions. The symmetry around half d-band filling in the curve without ODD is not present in the curve with ODD. Likewise, the second nearest pair interaction changes mainly quantitatively when ODD is taken into account., The more distant interactions, as exemplified by the third nearest pair interaction, are barely affected by including ODD.

Decomposing the first nearest pair interaction w.r.t. angular momentum shows that in V-Fe the d-s, p-p, p-s, and s-s components are insignificant, although their role increases slightly when ODD is included. The main components are the d-d and d-p parts. The d-p part shows the same qualitative behavior with and without ODD, however, the magnitude is much larger when ODD is accounted for. The d-d component changes dramatically when ODD is included: the negative region at the bottom of the d-band disappears, the positive region in the center becomes weaker, and the negative region at the top of the d-band becomes much more pronounced. At the Fermi-

slightly of

Figure 2. The first (solid line), second (dashed), and third (dotted) nearest effective pair interactions in equiatomic V-Fe as a function of energy. (a) without ODD, (b) with ODD taken into account.

Figure 3. The angular momentum decomposed first nearest neighbor pair interaction in equiatomic V-Fe as a function of energy. (a) without ODD, d-d: solid d-p: dashed, d-s: dotted, (b) without ODD, p-p: solid, p-s: dashed, s-s: dotted, (c) with ODD, d-d: solid, d-p: dashed, d-s: dotted, (d) with ODD, p-p: solid, p-s: dashed, and s-s: dotted.

level, the d-d part is much less positive, and the d-p part is more positive, although not sufficiently so to compensate for the weakening of the d-d component, when ODD is included. The effect of including ODD is thus twofold, the d-d component is reduced, and the components associated with

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s and p like states are enhanced although not changed much qualitatively. Furthermore, the effects at distant shells appear to be much smaller.

The pair interactions in Table I can be used to determine the ground states of the configurational order on the bcc lattice. Properly representing the ground states in "interaction space" is not a trivial matter. Usually only 3 or 4 interactions can be considered in the evaluation at once [11]. When the first, second, and third interactions are selected for the ground state determination, the following structures are found: bcc, B2, C11_b, and a complicated phase numbered "17" [11]. When instead, the first, second, and fifth (larger than the third) pair interactions are considered: bcc, B2, and phase "9" [11] are found. In both cases a very stable B2 ordered phase results. However, somewhat less stable phases are predicted as well. At present, without a more detailed study it can be remarked that such phases as C11_b, "17", and "9" probably will be stable at relatively low temperature only. Although the values of the pair interactions depend on whether ODD has been included, the findings with regard to the ground states do not change with inclusion of ODD.

The first and second neighbor pair interaction (without ODD) have been used in the tetrahedron approximation of the CVM, to obtain the high temperature portion of the bcc V-Fe phase diagram (figure 4). The maximum order-disorder temperature of the B2 phase is about 1585 K, approximately 600 K above the experimental value. When ODD is considered, the pair interaction becomes more than a factor two smaller, so that in that case too low an order-disorder temperature would be predicted.

Figure 4. The bcc V-Fe phase diagram as calculated with the CVM with interactions computed without ODD.

It appears that the non-magnetic Fe-V system can be described quite well by this tight-binding method. The correct state of order is predicted, and the order-disorder temperature is only about 1.5 times too high. Including ODD appears to correct the previous estimation, and result in a somewhat too low an order-disorder temperature.

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References:

1. J. F. Smith, Bull. Alloy Phase diag. **5**, 184 (1984).
2. K. Bungardt and W. Spyra, Arch. Eisenhuettenwes, **30**, 95 (1959), and T. Naohara and K. Shinohara, Trans. Jap. Inst. Met. **28**, 273 (1987).
3. M. Sluiter and P.E.A. Turchi, submitted to Phys. Rev. B.
4. D. A. Papaconstopoulos, "Handbook of the Band Structure of Elemental Solids," (Plenum Press, New York, 1986).
5. O. K. Andersen, W. Klose, and H. Nohl, Phys. Rev. B **17**, 1209 (1978).
6. M. Sluiter and P.E.A. Turchi, "The Role of Off-Diagonal Disorder on Alloy Phase Stability: An Application to the Ni-Pt System," this volume.
7. F. Ducastelle, "Alloy Phase Stability," NATO ASSI Series E: Applied Sciences - Vol. 163, ed. by G. M. Stocks and A. Gonis, (Kluwer Academic Publishers, Boston, 1989), p. 293.
8. R. Kikuchi, Phys. Rev. **81**, 988 (1951), and J. Sanchez, F. Ducastelle, and D. Gratias, Physica 128A, 334 (1984).
9. P.E.A. Turchi, M. Sluiter, and G. M. Stocks, "A Comparative Study of SRO in Fe-Cr and Fe-V around Equiatomic composition," this volume.
10. A. Bieber and F. Gautier, Acta Met. **34**, 2291 (1986).
11. A. Finel, Ph.D. Thesis, University of Paris VI (Pierre et Marie Curie), Paris (1987).

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