Ordering and Magnetism in Fe-Co: Dense Sequence of Ground-State Structures

Ralf Drautz,[1] Alejandro Díaz-Ortiz,[2] Manfred Fähnle,[1] and Helmut Dosch[1]
[1]Max-Planck-Institut für Metallforschung, Heisenbergstraße 3, D-70569 Stuttgart, Germany
[2]National Supercomputing Center, CNS-IPICyT, Apartado Postal 3-74 Tangamanga, 78231 San Luis Potosí, S.L.P., Mexico

(Received 11 December 2003; published 2 August 2004)

We discover that Fe-Co alloys develop a series of ordered ground-state structures in addition to the known CsCl-type structure. This new set of structures is found from a combinatorial ground-state search of 1.5×10^{10} bcc-based structures. The energies of the searched bcc structures are constructed with the cluster expansion method from few first-principles calculations of ordered Fe-Co structures. The set of new ground-state structures is explained from the decay behavior of the cluster expansion coefficients which allows us to identify a simple geometric motif common to all structures. The appearance of these FeCo superstructures offers a broader view of the ordering reactions in bipartite-lattice based binary alloys.

DOI: 10.1103/PhysRevLett.93.067202 PACS numbers: 75.50.–y, 61.50.–f, 61.66.–f

In this Letter we predict and explain the existence of a dense sequence of ground states for Fe-rich Fe-Co alloys. The new ground states appear at a composition spacing of $\Delta x = 1/16$, as originating from a quasicontinuous sequence of ground states for $\mathrm{Fe}_x\mathrm{Co}_{1-x}$ alloys with $x \geq 0.5$. Quasicontinuous sequences of ground states in binary-alloy phase diagrams have been discussed in the literature within the context of infinitely adaptive crystal structures [1]. Variation of the alignment of structural units exhibiting different compositions allows such systems to attain a continuous sequence of ground-state structures when the overall composition is changed. Long-range elastic interactions between the interfaces of structural units have been suggested [2] as the driving force behind infinitely adaptive crystal structures. Recently, this suggestion has been confirmed by an *ab initio* analysis [3] of Cu-Au and Ni-Pt. In this Letter, however, we show that alloys of Fe and Co do not require the presence of such repetitive structural units to display a dense succession of ordered ground states.

Consider the hypothetical case of a body-centered cubic (bcc) binary-alloy system with only one attractive nearest-neighbor pair interaction between the A and B atoms [see Fig. 1(a)]. A ground-state (GS) analysis shows three stable states, namely, two pure states and a CsCl-type (B2) ordered state. Structures with energies on or above the tieline joining the AB compound with any of the pure phases are unstable against the two-phase mixture $B + AB$ (or $AB + A$) [4]. Consider now that the system in question is characterized by a set of effective pair interactions (EPIs) of different lengths. What kind of GS phase diagram should be expected from this condition? Aside from the fact that the GS phase diagram should be symmetric with respect to equiatomic composition, a general answer to this question is difficult to obtain [5].

However, if the decay of the EPIs shows a characteristic behavior, general conclusions for the expected GSs can be drawn. Consider a pure-B material with some atoms replaced by A atoms. Assume an EPI distribution that decreases monotonically with distance, where all EPIs remain positive as shown in Fig. 1(b). The material's energy will then be minimized when the different atomic species are arranged in such a way that the distances between A atoms are maximized. If several configurations with identical nearest-neighbor distances between A atoms exist, then the one with the largest second-nearest neighbor distances will have the lowest energy, and so on. If for such a situation the number of A atoms is increased, every additional A atom changes the configuration of all other A atoms, and therefore a continuous sequence of GS's is generated. Deviations from the above-described ideal decay behavior of the EPIs with respect to their lengths will break, in general, the quasicontinuous progression of GSs. The system will then display a discrete

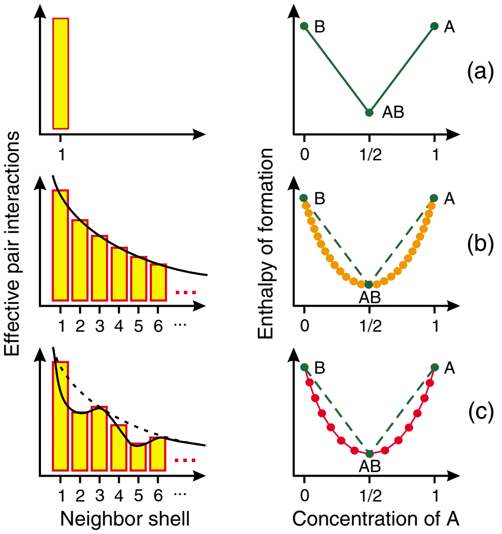

FIG. 1 (color). Schematic representation of EPI distributions as a function of the neighbor shell (left column) and the corresponding GS phase diagram (right column) for bipartite-lattice based A-B alloy systems. Note that a positive EPI describes an attractive interaction between unlike atoms.

number of GSs [see Fig. 1(c)]. A more complicated EPI behavior, for example, oscillating chemical and weak yet long-ranged elastic interactions, can induce a continuous succession of adaptive crystal structures [3] in some part of the phase diagram, while other composition ranges still show a discrete sequence of GSs.

We have found that Fe-Co exhibit a behavior as sketched in Fig. 1(c), i.e., a dense sequence of GSs for Fe-rich alloys. The technological importance of Fe-based alloys is widely recognized in many fields such as superalloys for high-temperature applications [8], soft magnetic materials for magnetic cores in electrical devices [9], permanent magnets for high-performance applications [10], and possible applications in modern spintronic materials [11]. Besides, alloys of Fe and Co possess some additional characteristics, which make them amenable as a prototype system to test our hypothesis of a dense sequence of GSs: The ordered α'-FeCo phase (B2) exists over a considerable range on either side of the stoichiometric composition (30–70 at.% Co) [12]. Moreover, there is the controversial suggestion on the existence of a $\mathrm{Fe_3Co}$ superlattice [13]. Quantum mechanical effects, reflected in the form of magnetism, are of central importance in treating Fe-Co alloys, since the ordering tendencies and energies in these systems are governed by magnetic interactions [19,20]. Neglecting the contribution of magnetism to the energy leads to a postive heat of formation of the B2 structure. Accordingly, a detailed analysis of the energetics and magnetism of $\mathrm{Fe}_n\mathrm{Co}_m$ (with $1 \leq n, m \leq 7$) ordered compounds was carried out using first-principles density-functional electron theory in the generalized-gradient approximation (GGA) for the exchange and correlation energy [21]. For these calculations, we used a spin-polarized mixed-basis plane wave pseudopotential scheme [22], where the wave functions are expanded into plane waves and localized d orbitals for the Fe and Co atoms. In all calculations, we fully relaxed all atomic degrees of freedom, i.e., the unit-cell axis, as well as the positions of the atoms, were varied to find the lowest energy of a given structure. Systematic errors in the computation of the energy of formation $\Delta E(\boldsymbol{\sigma}) = E(\boldsymbol{\sigma}) - xE(\mathrm{Fe}) - (1-x)E(\mathrm{Co})$ (with x the atomic concentration of Fe) were minimized by using equivalent k-point sampling and integration meshes [23].

The calculated energies of formation for 46 bcc-based Fe-Co ordered structures are shown in Fig. 2(a). It is an interesting observation that the energies of many Fe-rich compounds are well below the tieline joining the FeCo-B2 (CsCl-type) and the pure Fe; i.e., they are candidates for GS structures. In particular, our first-principles total-energy calculations show small energy differences

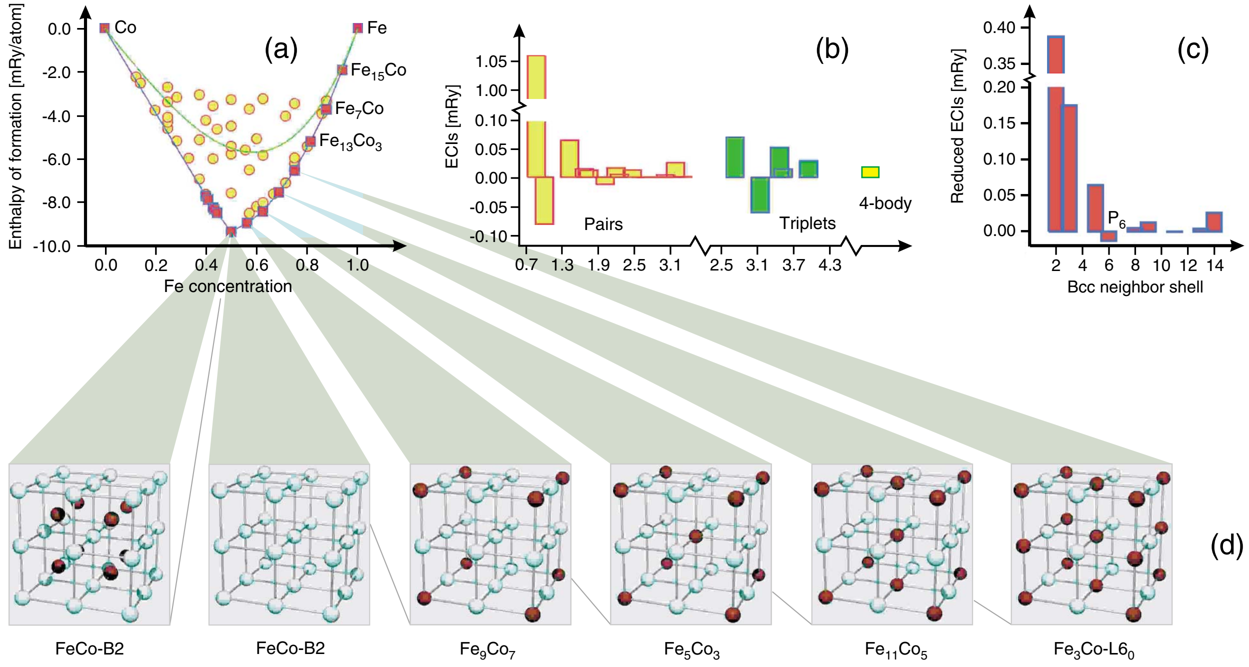

FIG. 2 (color). (a) GS phase diagram for Fe-Co alloys. The *ab initio* results for the energy of formation are represented by circles. The corresponding formation energy for $\mathrm{Fe}_x\mathrm{Co}_{1-x}$ random alloys is represented by the solid line. The results of the direct enumeration GS search are indicated by squares. (b) Effective cluster interactions (ECIs) for bcc-based Fe-Co alloys sorted according to their average bond length. (c) Corresponding reduced effective cluster interactions (RECIs) to the ECIs distribution shown in (b), sorted according to the bcc (original) neighbor shell. (d) Structures found as GSs for Fe-rich Fe-Co alloys. The Fe sc sublattice in the FeCo-B2 (CsCl-type) has been removed from all but the first B2 structure (left) to emphasize that ordering occurs in the remaining sc sublattice. The other three GS structures $\mathrm{Fe_{13}Co_3}$, $\mathrm{Fe_7Co}$, and $\mathrm{Fe_{15}Co}$ are obtained by exchanging Fe and Co atoms on the Co-sc_{II} sublattice.

(~ 0.2 mRy/atom) between the $D0_3$ (Bi_3F-type), a (001) layered Fe_3/Co structure, and the GS $L6_0$ (Ti_3Cu-type) structure for Fe_3Co. Although these energy differences are within our computational error, this illustrates the difficulties in determining the possible existence of Fe_3Co superlattices [13]. The situation for Co-rich compounds is different, since only very few structures have formation energies below the tieline between the FeCo-B2 and pure Co. Also, from the energies of formation of random Fe_xCo_{1-x} [solid line in Fig. 2(a)], it is evident that the GS properties of Fe-Co are not appropriately described by assuming a random occupation of the bcc lattice with Fe and Co.

We mapped the *ab initio* calculated energies of the various Fe-Co structures into a cluster expansion [24]. The cluster expansion (CE) describes the energy of formation

$$\Delta E(\boldsymbol{\sigma}) = \sum_{\alpha} D_\alpha J_\alpha \phi_\alpha(\boldsymbol{\sigma}) \tag{1}$$

of an alloy with configuration $\boldsymbol{\sigma} = \{\sigma_1, \sigma_2, \ldots, \sigma_N\}$, via pair and multibody ECIs J_α. Here, the multiplicity of the geometrical different clusters α is denoted by D_α, while the cluster functions $\phi_\alpha(\boldsymbol{\sigma})$ are calculated from the set of occupation variables σ_i for all lattice sites i ($\sigma_i = \pm 1$ for an Fe or a Co atom, respectively). The ECIs were constructed by defining a set of geometrical cluster figures, which was then optimized to best reproduce and predict the *ab initio* calculated energies using Eq. (1). The ability of the numerical values obtained for the expansion coefficients J_α to predict the energies of structures not contained in the set of *ab initio* calculated structures, was ascertained by systematic direct comparison of the predicted cluster-expanded energy for an ordered compound, not initially included in the expansion, with the corresponding GGA total-energy calculation. We have obtained a very robust and accurate CE for the energy of formation (average fit error: ~ 0.15 mRy/atom, average predictive error: ~ 0.29 mRy/atom) using 46 fully relaxed input structures requiring 15 pairs, 5 three-body, and 1 four-body interactions. It is clear from Fig. 2(b) that the energetics in Fe-Co are dominated by a strong attractive nearest-neighbor pair interaction. The remaining pair interactions are considerably smaller. Three-body interactions are small yet significant for the phase equilibria in Fe-Co, since they are responsible for the asymmetry shown by the GS phase diagram—tilted toward Fe-rich alloys, as seen in Fig. 2(a).

We applied the expansion of Eq. (1) to a direct enumeration GS search. In this combinatorial approach, the formation energy of bcc supercells was evaluated for cells of different shape and containing up to 32 atoms. Our exhaustive search resulted in 13 ordered structures, out of the $\sim 1.5 \times 10^{10}$ scanned configurations, as bcc-based GSs in the Fe-Co system. These GSs, depicted in Fig. 2(a) with red squares, proved to be stable against phase separation into structures of neighboring compositions. For Co-rich alloys, the GSs occur at non-Daltonian compositions. A different and unexpected situation is revealed for Fe-rich Fe-Co alloys, where the GSs occur in a regular fashion and at well-defined stoichiometries. As a matter of fact, a new ordered structure appears every 1/16 in Fe concentration from the equiatomic alloy. This is a surprising result that has an even more surprising, in its simplicity, explanation. We advanced at the beginning of this Letter that the particular distribution of the ECIs is solely responsible for the number and structure of the GSs. From Fig. 2(b) we see that the ECIs distribution is dominated by a strong, attractive nearest-neighbor pair interaction that is almost an order of magnitude larger than the rest of the ECIs. This dominant nearest-neighbor interaction "locks" the Fe atoms to one of the simple-cubic sublattices sc_I of the bcc lattice, hence stabilizing a CsCl-type motif. Thus, an increment of the Fe concentration in FeCo-B2 leads to an increment of Fe atoms in the second simple-cubic sc_{II} sublattice. For this reason, we assume for the moment that the Fe-sc_I sublattice does not change for all GSs with $x \geq 0.5$ [20]—this assumption will be justified later. Hence, the occupation of all sites contained in sc_I is $\sigma_i^{(I)} = 1$. This allows to considerably simplify the cluster functions in Eq. (1). For example, a three-body cluster formed by one sc_I site and two sc_{II} sites is effectively broken down into a pair cluster formed by the two sc_{II} sites. The expansion coefficient of the original three-body cluster is subsumed (multiplicities have to be taken into account) with the original expansion coefficient of the pair cluster formed by the two sc_{II} sites.

Our initial choice of cluster figures [Fig. 2(b)] results in reduced effective cluster interactions (RECIs) that contain only pairs [25]. The RECIs acting on the sc_{II} lattice are presented in Fig. 2(c). A strong, attractive reduced nearest-neighbor pair interaction (second nearest-neighbor with respect to the original bcc lattice) dominates the ordering tendencies. Inspection of the RECIs in Fig. 2(c) unveiled an important feature: A characteristic minimum of the RECIs is observed for the sixth pair interaction (P_6) in the original bcc lattice. The range of this interaction is such that it stabilizes Fe-Fe pairs of length $2a$ in the Co-sc_{II} sublattice, thereby forming a sc lattice with lattice constant $2a$. This completes the mechanism underlying the GS sequence of Fig. 2(a): The strong nearest-neighbor pair interaction favors the FeCo-CsCl structure and locks the Fe atoms to one of the sc sublattices (first motif). Increasing the Fe concentration from 50% leads to the replacement of Co atoms on the Co-sc_{II} sublattice by Fe atoms. The distances of the extra Fe atoms that are built into the sc_{II} sublattice are determined by the distance of the RECI P_6. Accordingly, upon increasing the Fe concentration from 50%, the Fe atoms form a sc Fe sublattice with lattice constant distance $2a$ on the Co-sc_{II} (hereafter, the second-motif sublattice). When all sites of the second-motif sublattice are occupied at a concentration of $x = 9/16$, further Fe atoms are placed on the bcc positions of the second motif, thereby forming an interpenetrating second second-motif sublattice in addition to the first second-motif sublattice. In this way, all GSs in the concentration range $\frac{1}{2} \leq x \leq 1$ can be found from arrangements of interpenetrating second-motif sublattices [Fig. 2(a)] at concentrations $x = n/16$, $n = 8, 9, \ldots, 16$. All Co atoms in all GSs are surrounded by eight Fe atoms on nearest-neighbor sites. Also, the Co atoms are located on the Co-sc_{II} sublattice. This justifies the assumption of a perfect Fe-sc_I sublattice.

The numerical values of the RECIs suggest that the ordering transitions of the new GSs appear at such low temperatures that ordering will be nearly impossible to observe experimentally due to very low diffusion rates. However, the second motif as the common characteristic of all GSs favors an arrangement of the Co and Fe atoms on the Co sublattice in such a way that predominantly second nearest-neighbor bonds between unlike atoms are formed. This should be reflected in the short-range order coefficient for the second nearest-neighbor shell in the B2-ordered region of the phase diagram (above the ordering temperature of the predicted GSs). Experimentally, this can be checked in diffuse scattering experiments. Moreover, we speculate that the “550 °C anomaly” [13] which recently also has been found at lower temperatures in small FeCo clusters [26] is related to a transition into the newly found GSs.

To conclude, we have shown that a dense sequence of ground-state structures may occur in a (nonfrustrated) bipartite binary alloy for a rather general class of decay behavior of the effective pair interactions. The new structures found for Fe-rich Fe-Co alloys shed new light onto the ordering reactions occurring in bcc alloys, and more general, in bipartite-lattice based systems. These new ground-state structures may affect the low-temperature mechanical and electronic properties of Fe-Co alloys and may be relevant in nanoscale applications that exploit the magnetic properties of FeCo clusters. We expect that Fe-Co is not the exception, but just one example of a probably large class of alloys which exhibit such a dense sequence.

This work was supported in part by CONACyT (Mexico) through Grant No. 39577-F. The authors acknowledge helpful discussions with D. G. Pettifor. Computational resources from the Supercomputing Center CNS-IPICyT are also acknowledged.

---

[1] J. S. Anderson, J. Chem. Soc. Dalton Trans. **10**, 1107 (1973).

[2] C. Kittel, Solid State Commun. **25**, 519 (1978).

[3] M. Sanati, L. G. Wang, and A. Zunger, Phys. Rev. Lett. **90**, 045502 (2003).

[4] F. Ducastelle, *Order and Phase Stability in Alloys* (North-Holland, Amsterdam, 1991).

[5] An analysis of the GSs in a bcc lattice including first- and second-nearest neighbor interactions leave us with four distinct structures (after the $A \leftrightarrow B$ symmetry is taken into account): pure A, B2 (CsCl), B32 (NaTl) and $D0_3$ (Bi_3F) [6]. To the best of the authors' knowledge, the most extensive study in bcc lattices is due to Finel and Ducastelle [7], and it included pair interactions up to fifth-nearest neighbors. Fourth-nearest neighbor interactions brought frustration effects that were difficult to handle, and therefore they were excluded in Finel and Ducastelle's analysis.

[6] J. Kanamori, Prog. Theor. Phys. **35**, 16 (1966).

[7] A. Finel and F. Ducastelle, in *Phase Transformations in Solids*, edited by T. Tsakalakos (North-Holland, Amsterdam, 1984), p. 293; A. Finel, Thèse de Doctorat d'Etat, Université Paris VI, 1987 (unpublished).

[8] C. T. Sims, N. S. Stoloff, and W. C. Hagel, *Superalloys II* (Wiley, New York, 1987).

[9] M. Soinski and A. J. Moses, in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (Elsevier, Amsterdam, 1995), Vol. 8, p. 325.

[10] K. H. J. Buschow, in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (Elsevier, Amsterdam, 1995), Vol. 8, p. 463.

[11] M. Baibich *et al.*, Phys. Rev. Lett. **61**, 2472 (1988).

[12] T. Nishizawa and K. Ishida, *Phase Diagrams of Binary Iron Alloys*, edited by H. Okamoto (ASM International, Materials Park, OH, 1993).

[13] Specific heat measurements by Masumoto *et al.* [14] and electrical resistivity measurements by Viting [15] suggested the existence of Fe_3Co and $FeCo_3$ superstructures (see also Ref. [16]). Neutron diffraction studies [17], on the other hand, indicated evidence against the existence of the superlattices in question. Recent NMR studies on deposited Fe_xCo_{1-x} thin films [18] showed characteristic Fe environments with two and four Co atoms on nearest-neighbor sites at $x = 0.14$ and $x = 0.24$.

[14] H. Masumoto, H. Sato, and M. Shinozaki, Sci. Rep. Res. Inst. Tohoku Univ. **6**, 523 (1954).

[15] L. M. Viting, Zh. Neorg. Khim. **2**, 845 (1957).

[16] A. A. Goldenberg and Y. P. Selissky, Fiz. Met. Metalloved. **15**, 717 (1963).

[17] H. Asano, Y. Bando, N. Nakanishi, and S. Kachi, Trans. Jpn. Inst. Met. **8**, 180 (1967).

[18] M. Wojcik *et al.*, Z. Phys. B **103**, 5 (1997).

[19] R. J. Hawkins and J. M. Sanchez, J. Phys. F **18**, 767 (1988); I. A. Abrikosov *et al.*, Phys. Rev. B **54**, 3380 (1996).

[20] Magnetism is also crucial in the case of atomic defects for the B2 phase of Fe-Co, where the magnetic interactions stabilize the system against a spontaneous formation of antistructure atoms; see M. Neumayer and M. Fähnle, Phys. Rev. B **64**, 132102 (2001).

[21] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[22] B. Meyer, C. Elsässer, F. Lechermann, and M. Fähnle, “FORTRAN90 Program for Mixed-Basis Pseudopotential Calculations,” Max-Planck-Institut für Metallforschung,
Stuttgart (unpublished).

[23] Z. W. Lu *et al.*, Phys. Rev. B**44**, 512 (1991).

[24] J. M. Sanchez, F. Ducastelle, and D. Gratias, Physica (Amsterdam) **128A**, 334 (1984).

[25] This is not a standard behavior of the RECIs and, in general, for other systems one can expect to find RECIs comprising pairs and many-body interactions.

[26] Z. Turgut *et al.*, J. Appl. Phys. **83**, 6468 (1998).