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Magnetically induced crystal structure and phase stability in $Fe_{1-c}Co_c$

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We present an *ab initio* determination of the crystallographic phase stability of Fe-Co alloys as a function of concentration, using the coherent potential approximation. A bcc → hcp phase transition is found at a concentration of 85 at. % of Co, in good agreement with the experimental phase diagram. We demonstrate that for the Fe-rich random alloys magnetism stabilizes the bcc phase relative to the close-packed fcc and hcp phases. Magnetism also favors the partially ordered α' phase relative to the random bcc alloy. This unique relation between magnetism and phase stability for the Fe-Co alloys is analyzed by a spin-polarized canonical d-band model. [S0163-1829(96)09326-5]

I. INTRODUCTION

An unusual feature of the Fe-Co phase diagram,[1] shown in Fig. 1, is that Fe-Co forms random, magnetic alloys in the body centered cubic (bcc), the face centered cubic (fcc), and the hexagonal close packed (hcp) crystal structures as well as an ordered α' phase (called B2 or CsCl structure) at different temperatures and alloy concentrations. The corresponding crystal structure sequence of the random alloys, bcc → fcc → hcp, may be viewed as part of the well-known paramagnetic d transition metal sequence hcp → bcc → (fcc) → hcp → fcc.[2–4] To establish this connection, one assumes that the magnetic Fe-Co alloys are completely saturated ferromagnets, i.e., that the spin-up d band is full and does not contribute to the bonding. In this case, the key parameter is the fractional filling of the spin-down d band and if we consider structural energy differences as functions of the spin-down rather than the total d occupation number it is possible to bring the crystal structure sequence of the magnetic $3d$ transition metals, Fe, Co, and Ni, into complete agreement with the sequence obeyed by the paramagnetic $4d$ and $5d$ transition metals.[5] In Fig. 2 we illustrate this by showing the structural trend as a function of band occupation, obtained from canonical band theory. Note that for the spin polarized metals the spin down d-occupation number dictates a bcc structure in Fe and an hcp structure in Co, in agreement with observations. In contrast, paramagnetic Fe adopts an hcp structure.

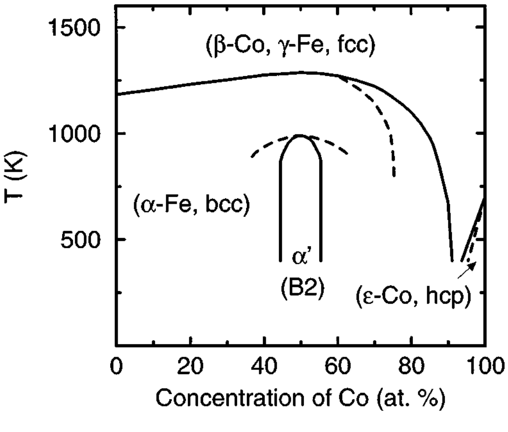

FIG. 1. The low temperature part of the experimental Fe-Co phase diagram, redrawn from Ref. 1.

In the case of elemental metals one may manipulate the d occupation number by application of pressure and thereby accomplish a change of crystal structure. However, transition metals are typically hard and the d occupation changes only

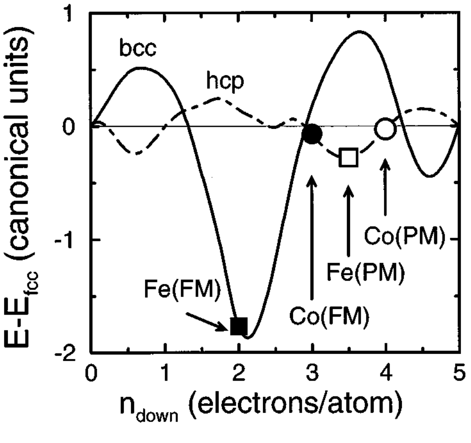

FIG. 2. The energy of bcc (full line) and hcp (dot-dashed line) structures relative to the energy of the fcc structure as a function of the occupation of the canonical spin-down d-band n_{down}.

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little under compression, and as a consequence pressure induced structural phase transitions of the transition metals are rarely observed. In contrast, alloy systems offer the possibility of a significant change in the average *d* occupation and, as a result, one can expect several structural phase transitions as a function of concentration. In the case of random Fe-Co alloys the experimentally observed crystal structure sequence appears to follow the predictions of the canonical band model (Fig. 2) but to our knowledge a quantitative study of this has not been carried out so far. Moreover, an analysis of the full concentration dependence of the stability of the partially ordered α' phase has not been undertaken for this system. We have thus been motivated to analyze theoretically the phase stability of the FeCo alloys, in particular the influence magnetism has on the phase stability of this system.

II. CALCULATIONAL

We have used the multisublattice generalization of the coherent potential approximation (CPA) in conjunction with the linear-muffin-tin-orbital (LMTO) method in the atomic sphere approximation (ASA). The LMTO-ASA is based on the work of Andersen and co-workers[6–9] and the combined technique[10,11] allows us to treat all phases on equal footing. To treat itinerant magnetism we have employed the Vosko-Wilk-Nusair parametrization[12] for the exchange-correlation energy density and potential.

We have considered the fcc, bcc, and hcp (with ideal c/a ratio) phases as completely random alloys, while the α' phase for off-stoichiometry compositions has been considered as a partially ordered alloy in the B2 structure with one sublattice (Fe for $c<50\%$ and Co for $c>50\%$) fully occupied by the atoms with largest concentration, and the other sublattice randomly occupied by the remaining atoms.

The k-space integral has been calculated in the irreducible part of the corresponding Brillouin zone at 240 k points of the fcc lattice, 280 k points of the bcc lattice, 225 k points of the hcp lattice, and 120 k points of the irreducible part of the Brillouin zone of the CsCl structure of the α' phase. To improve the accuracy we used the fixed spin moment method[13,14] for those alloys whose ferromagnetic (FM) and paramagnetic (PM) solutions are close in energy. We have studied only these two solutions; no complicated magnetic configurations (antiferromagnetic, local moment disorder, etc.) have been considered. Note however that a number of investigations carried out for the pure Fe and random Fe-based alloys[15–17] have shown that the paramagnetic calculations give a very good estimate of the ground state total energy of the fcc phase with a vanishing mean magnetic moment.

Though LMTO-ASA calculations successfully reproduce crystal structures for the paramagnetic $3d$, $4d$, and $5d$ transition metals,[4] in order to control the accuracy of the ASA in our ferromagnetic calculations for the Fe-Co alloy we have calculated the structural energy differences for pure Fe and Co by a full-potential technique[18] employing the generalized gradient approximation (GGA) (Ref. 19) for the exchange-correlation potential and energy. As one can see in Fig. 3(a), both methods give very similar results and we conclude that the ASA is sufficiently accurate for this system for the complete concentration interval.

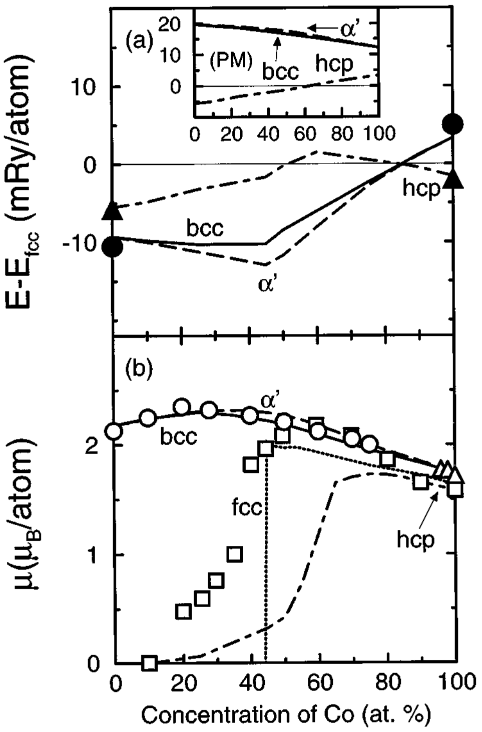

FIG. 3. The energy of bcc and hcp random alloys and the partially ordered α' phase relative to the energy of the fcc phase (a), of the Fe-Co alloy as a function of Co concentration. The corresponding mean magnetic moments are shown in (b). The CPA-LSDA-ASA results are shown as a dashed line for the α' phase, as a full line for the bcc phase, as a dot-dashed line for the hcp phase, and as a dotted line for the fcc phase. The FP-GGA results for pure Fe and Co are shown in (a) by the filled circles (bcc-fcc) and triangles (hcp-fcc). The insert in (a) shows the results from paramagnetic calculations. In (b) experimental mean magnetic moments of Ref. 25 are shown as open circles (bcc), open squares (fcc), and open triangles (hcp).

Before further discussions, some comments have to be made concerning pure Fe. We note that Fe is a notoriously difficult element concerning calculations of structural properties, and previous LSDA calculations have either obtained the bcc (Refs. 13,20) or the fcc structure as the stable phase.[21–23] Thus, depending on the computational method the fcc structure may be erroneously stabilized with a few mRy. Here we do not have this problem, the bcc structure is correctly found to have the lowest energy. Moreover, in our investigation we find very good agreement between the present ASA-LSDA and the FP-GGA energy differences. We also obtain very similar results for such a very sensitive quantity as the transition pressure for the bcc-hcp structural phase transition. The ASA-LSDA result (103 kbar) agrees well with both the FP-GGA result (100 kbar) and experiment [130 kbar (Ref. 24)].

III. RESULTS

The calculated energy of the α', bcc, and hcp phases of the Fe-Co alloy relative to the energy of the fcc alloy are presented in Fig. 3(a). In excellent agreement with the experimental phase diagram (see Fig. 1) we have found that the α' phase has the lowest energy up to 85% of Co. At higher

Co concentrations the hcp random alloy becomes stable. The energy difference between the random bcc phase and the partially ordered α' phase is found to be negative over the complete concentration interval indicating an ordering tendency in the bcc Fe-Co alloy for all concentrations. This ordering energy reaches its maximal value at the equiatomic composition and decreases with increasing deviation from the 1:1 stoichiometry. The fcc structure is found not to be stable at zero temperature, but for the Co-rich part of the diagram ($\sim$ 85%) the fcc energy is very close to the energies of all the other phases considered here. This fact is also in agreement with an observation of the direct bcc → hcp transition taking place in the Co-rich part of the diagram at very low temperatures (Fig. 1).

Let us now illustrate that the magnetic properties of the Fe-Co alloy depend strongly on the crystal structure. In Fig. 3(b) we present the mean magnetic moment calculated at the theoretical equilibrium lattice parameter for the α', bcc, fcc, and hcp phases of the Fe-Co alloy in the complete concentration interval, together with available experimental results.[25] Note that there is a very good overall agreement between theory and experiment. We remark here that most of the experimental data for the fcc phase were measured for Fe-Co alloys precipitated in Cu and therefore they probably do not correspond to the values at the equilibrium lattice parameter. In agreement with previous studies of the ordered and disordered bcc alloy[26–28] we find that they are FM for all Co concentrations and the value of the mean magnetic moment is a weak function of concentration which reaches its maximal (saturated) value at about 30% of Co [Fig. 3(b)]. We also find that there is a low-spin (LS)–high-spin (HS) transition at 45% Co, for the fcc alloys. This is a transition of the same kind as has been discussed for the fcc FeNi random alloy.[11,16,17,29] In the fcc phase it is related to the particular shape of the fcc state density and the position of the Fermi level[3,30] which for Fe results in the existence of three (metastable) solutions with different values of the magnetic moments at different Wigner-Seitz radii. In pure fcc Fe the LS solution has the lowest energy, but when one adds Co (or Ni), the energy difference between the HS and the LS states decreases, and for 45% of Co the HS solution becomes more stable. We have found a very close situation for the hcp FeCo alloy. Pure hcp Fe is found to have a zero magnetic moment at the equilibrium Wigner-Seitz radius (calculated to be 2.535 a.u.), but hcp Fe becomes a HS metal at $R_{\mathrm{WS}} > 2.70$ a.u., with a magnetic moment of about 2.7 μ_B. This result for pure hcp Fe agrees well with the results obtained earlier.[3,23] The similarity of the magnetic properties for fcc and hcp structures is to be expected because the canonical state density for the hcp and the fcc phases are also very similar. In the hcp alloy the energy difference between the LS and the HS solutions also decreases with increasing Co concentration, and at 60% the HS phase becomes the lower energy phase. However, the concentration behavior of the fcc and hcp magnetic moments are not quite the same: in the fcc phase a sharp first order phase transition from the LS (PM) to the HS state is observed, while in the hcp phase this transition is smeared out over a longer concentration range.

Next, we wish to illustrate that magnetic order plays a most crucial role for the phase stability of the Fe-Co alloy. To do so we present in the insert in Fig. 3(a) the energies of all phases considered here obtained by PM calculations. One can see that the so obtained structural energy differences lead to a completely wrong conclusion about the phase stabilities in the Fe-Co alloy, i.e., the close-packed phases (hcp or fcc, depending on concentration) are found to have the lowest energy, next comes the random bcc alloy, and finally the α' phase has the highest energy. Thus the presence of spin ordering in these materials is critical for the structural properties. To further point out the influence of magnetism on the energies of different Fe-Co phases, we would like to draw the readers attention to the kinks which are seen in both the bcc-fcc and hcp-fcc energy difference curves in Fig. 3(a). This is an effect due to the peculiar magnetic properties of the fcc and hcp phases, and it occurs exactly at the same concentrations where the LS to the HS magnetic transitions take places.

From the discussion presented in the above two sections it is clear that there is an entwined relationship between atomic arrangement and magnetism in this system. This observation is consistent with the picture given by Heine and Samson[31] who demonstrated that ordered phases are to be expected for alloys of transition metals with half-filled bands whereas phase separation would occur in alloys of transition metals with almost filled or almost empty bands. In our paramagnetic calculations the electronic filling corresponds to the case of the almost filled band (7–8 valence electrons occupied in the tenfold degenerate d band) whereas the polarized fivefold degenerate spin down band has 2–3 spin down electrons and therefore is only half-filled (for the spin polarized calculations the spin up band is essentially filled and thus chemically inert).

The possibility of a magnetic stabilization of an ordered phase on a fixed lattice has also been studied in Ref. 32 on the basis of model calculations of interatomic interactions as a function of band filling. Here it was found that different filling of the spin down band in the FM and PM case could lead to a different sign of the most important pair interaction parameter, indicating different ordering tendencies for the FM or PM alloy. Recently it was shown that this is the case for the $\mathrm{Fe}_{50}\mathrm{Co}_{50}$ alloy.[33] Our direct total energy calculations fully support the model of Refs. 31–33 and show clearly that the effect of ordering in the Fe-Co system is opposite in the FM and PM cases.

Finally we will show that the structural stability trend and the correct magnetic behavior of the Fe-Co random alloy can be obtained in the framework of the canonical band model, thus justifying that the observed peculiarities have their origin in the d-band filling. To do so we have used the canonical d-band model of Refs. 3,4 generalized for spin-polarized systems by introducing a spin-dependent shift,

$$\Delta_{\mathrm{ex}} = \mu I_d , \qquad (1)$$

to the LMTO canonical structure constant matrix for the d states, $\mathbf{S}_{lm,lm'}$, and we obtain

$$\mathbf{S}_{lm\sigma,lm'\sigma'} = \begin{pmatrix} \mathbf{S}_{lm,lm'} & \mathbf{0} \\ \mathbf{0} & \mathbf{S}_{lm,lm'} \end{pmatrix} + \begin{pmatrix} -\delta_{m,m'}\Delta_{\mathrm{ex}}/2 & \mathbf{0} \\ \mathbf{0} & +\delta_{m,m'}\Delta_{\mathrm{ex}}/2 \end{pmatrix} . \qquad (2)$$

For a fixed value of the Stoner exchange integral I_d, and d-band filling, n, the magnetic moment μ and the total en-

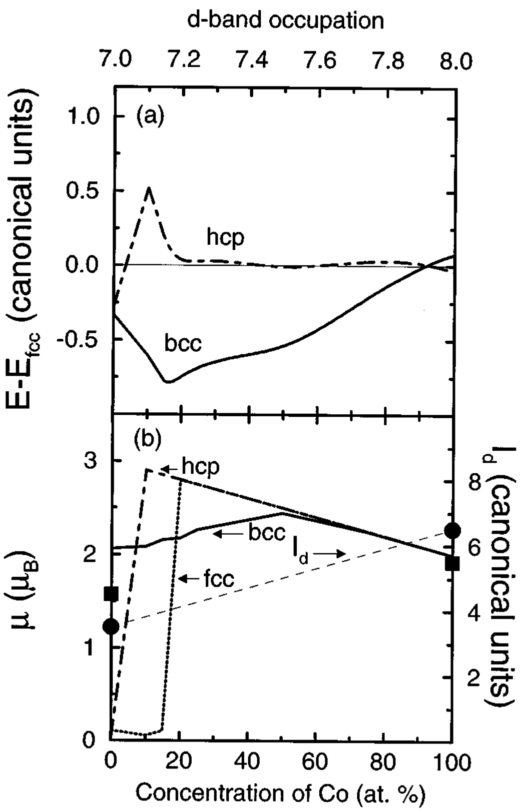

FIG. 4. The structural energy difference (a) and the magnetic moment (b) as a function of the occupation of the canonical d-band n corresponding to the Fe-Co alloy. The same lines as in Fig. 3 are used for the different structures. In (b) the concentration dependence of the Stoner exchange integral I_d used for the spin-polarized canonical d-band model calculations is shown as a thin dashed line with the closed circles. The value of I_d for pure Fe and Co, calculated from LSDA and scaled to canonical units, are also shown in (b) as closed squares.

ergy for a Stoner ferromagnet can be obtained. We note however that the total energy has no strict meaning in a canonical band model but we make an analogy to a real (LSDA) system by defining a kinetic energy as obtained from the eigenvalue sum corrected for the double counting. The total energy E_{tot} is then a sum of the kinetic energy, $\langle T\rangle$, and the spin polarization energy $\mu^2 I_d/4$, i.e.,

$$E_{\text{tot}}=\langle T\rangle-\mu^2 I_d/4. \tag{3}$$

In Fig. 4(a) we show the calculated energy difference between the fcc, bcc, and hcp structures as a function of d-band filling appropriate for the Fe-Co alloy. The concentration dependent value of I_d is chosen in such a way that the self-consistent canonical band magnetic moment reproduces approximately the behavior of the magnetic moment for the real Fe-Co alloy. The so chosen Stoner exchange integral is very close to calculated values of I_d in Fe and Co [transformed to canonical units by scaling of the real (LSDA) and canonical band widths], and is shown in Fig. 4(b). From this figure one can also see that the magnetic moments calculated from our simple model agree reasonably well with both the LMTO-CPA calculations and experiment [Fig. 3(b)]. Even the intricate magnetic behavior of the fcc and hcp structure (LS to HS transition) is present in our canonical band results. Note that this fact is not trivial, because a single value of I_d was used for all structures at a given concentration. Note also that not only the magnetic moment of our model, but also the calculated structural stabilities [Fig. 4(a)] agree fairly well with the complete first-principles calculations [Fig. 3(a)]. Much of the reason for the observed agreement between Figs. 3 and 4 is due to the fact that Fe and Co are neighbors in the Periodic Table. The alloy electronic structure exhibits an almost common band behavior for the spin up band, while a split band behavior, due to large difference in magnetic moments on the Fe and Co sites, occurs for the spin down band.[26–28] However, this split band behavior is more pronounced for states above the Fermi energy, and consequently affects the total energy to a smaller degree. The latter observation indicates that one must be careful in applying similar arguments to other systems, and also that one should not compare quantitatively the canonical band results with the results of complete calculations. In particular the canonical band model predicts the transitions from the LS to the HS state in the fcc and the hcp phases to take place at lower Co concentrations and to have more abrupt character compared to the LMTO-CPA result. Also in the bcc alloy the magnetic moment is saturated at about 30% of Co, while the canonical band calculation moves this concentration to 50%.

IV. CONCLUSIONS

We have here demonstrated the possibility of calculating the phase stability of a magnetic random alloy from first principles by means of LMTO-CPA theory. Our calculated phase diagram is in good agreement with experiment and shows a transition from the partially ordered α' phase to an hcp random alloy at $\sim$ 85% Co concentration.

We have also shown that the structural and phase stability in the Fe-Co alloy is induced by magnetism and have pointed out that it can be understood from the fractional filling of the polarized, minority spin d band. Likewise, the magnetic properties are demonstrated to be determined by the atomic arrangement. That is the bcc phase has a stable magnetic moment in the complete concentration range, while our calculations show a high spin–low spin magnetic phase transition taking place in the fcc and the hcp phases at 45% and 60%, respectively.

We observe that for the Fe-Co system a simple spin polarized canonical model is able to reproduce qualitatively the results obtained by LMTO-CPA calculations. Despite the simplicity of this model the structural properties of the FeCo alloy are explained from simple band-filling arguments.

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