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CRYSTAL STRUCTURE AND PHASE STABILITY IN $Fe_{1-x}Co_x$ FROM AB INITIO THEORY

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The crystal structure for many metals is well established, and early research discovered a pattern which was shown to depend on the chemical periodicity of these elements. Particularly for the non-magnetic metals in the $4d$ and $5d$ transition metal series a connection between the atomic number and the crystal structure was recognized[1]. The crystal structure sequence involved more (fcc and hcp) or less (bcc) close-packed structures with high symmetry. The fact that the rare-earth elements show a regular behavior of the crystal structure as a function of atomic number led to the proposal[2]that the occupation of the d states was the important parameter for the crystal structure for these metals. This could then explain the more dramatic behavior of the d transition metals compared to the rare-earths since for the latter the occupation of the d states does not change much over the series whereas for the transition metals the d band is successively being filled when proceeding through the series.

The crystal structure for the magnetic $3d$ transition elements shows, however, a different pattern governed by their magnetic properties. It was shown recently[3] that similar arguments as presented for the explanation of the crystal structure sequence for the non-magnetic metals could be applied also for the magnetic transition metals. Namely, by assuming saturated magnetism (one spin band being completely filled) and only study the remaining spin band, containing at most 5 d electrons, one could use simple models[4] based on canonical band theory to understand the sequence bcc (Fe) → hcp (Co) → fcc (Ni). Also the equilibrium lattice parameter and the bulk modulus are anomalous for these magnetic metals compared to the non-magnetic ones. The lattice parameter is larger and the bulk modulus lower than expected for a non-magnetic transition metal. Again, these anomalous properties could be accounted for by assuming that one spin band is filled and does not contribute to the bonding and therefore only the d states of the other spin contributes. This weakens the chemical bond since only ons spin band participate in the bonding and consequently the lattice parameter becomes larger and the bulk modulus lower.

In the present paper we focus on the alloys between Fe and Co. From the above discussion it is clear that the magnetic properties are very essential for these alloys. Since the occupation of the *d* states is the important parameter for most of the bulk properties for the *d* transition metals including their crystal structure we expect a phase diagram of $Fe_{1-x}Co_x$ which depend largely on the spin-polarization. Although simple canonical band models would give a quantitative picture, we can not assume that it is accurate enough to describe the phase diagram of $Fe_{1-x}Co_x$ qualitatively. Hence we have used a more elaborate method to calculate the spin moment and crystal structure energies which we intend to compare our canonical band results and experiments with.

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 for the local spin density approximation (LSDA) the Vosko-Wilk-Nusair parameterization[12].

We have studied 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 sub-lattice (Fe for $c < 50\%$ and Co for $c > 50\%$) fully occupied by the atoms with largest concentration, and the other sub-lattice randomly occupied by the remaining atoms.

We note that the ground-state of iron is sensitive to approximations commonly used within density functional calculations. For instance, a local approximation for the exchange/correlation functional tend to underestimate the magnetic contribution to the total energy and therefore in certain calculations the non-magnetic fcc phase has wrongly been predicted as the ground-state of Fe[13,14]. However, the present calculations does not suffer from this problem and to check our calculations we have compared our ASA-LSDA calculations with highly accurate full potential calculations which include a gradient corrected approximation for the exchange/correlation functional (FP-GGA)[15]. We find very good agreement between those two methods as regards energy differences and magnetic moments. Both methods correctly predict magnetic bcc Fe as the ground-state and the transition pressure bcc → hcp is in close agreement with each other and experiment ($\sim$ 10 GPa).

Let us turn to the results of our calculations. In Fig. 1 we show our full calculations using ASA-LSDA with the CPA for the $Fe_{1-x}Co_x$ alloys. This is a two panel plot which in the upper panel (a) displays our calculated crystal structure energy differences with respect to the fcc structure energy, which defines the zero energy level. For the pure metals Fe and Co we show full potential results (FP-GGA) as a comparison. Solid circles refers to bcc-fcc energy differences and solid triangles to hcp-fcc energy differences. They are obviously in very good agreement with the ASA-LSDA-CPA results. Experimentally, at low temperatures, there are three phase transitions as a function of alloying, α-Fe (bcc) $\rightarrow \alpha'$ (B2) $\rightarrow \alpha$-Fe (bcc) $\rightarrow \epsilon$-Co (hcp). Our calculations show the same behavior for the $Fe_{1-x}Co_x$ alloys. In the second (b) panel of Fig. 1 our calculated mean magnetic moments are compared to experimental data[16]. Open circles (bcc), open squares (fcc) and open triangles (hcp) refers to the experimental data. The overall agreement between theory and experiment is impressive. For the bcc alloys we note that the magnetic moment is only weakly dependent on the actual alloying. It reaches a maximum value at about 30% of Co which compares well with previous studies[3,17,18]. Notice also that for the fcc and the hcp structures there are transitions from low-spin states to high-spin states, see Fig. 1 (b).

We would like to emphasize the great importance the magnetism have in the phase diagram of the Fe-Co alloys. For instance, paramagnetic calculations gives total energies for the bcc structure lying about 10-20 mRy higher than the fcc structure energy within the whole concentration range. The paramagnetic results (not shown) are more indicative for the behavior of the 4*d* alloys Ru-Rh or the 5*d* alloys Os-Ir.

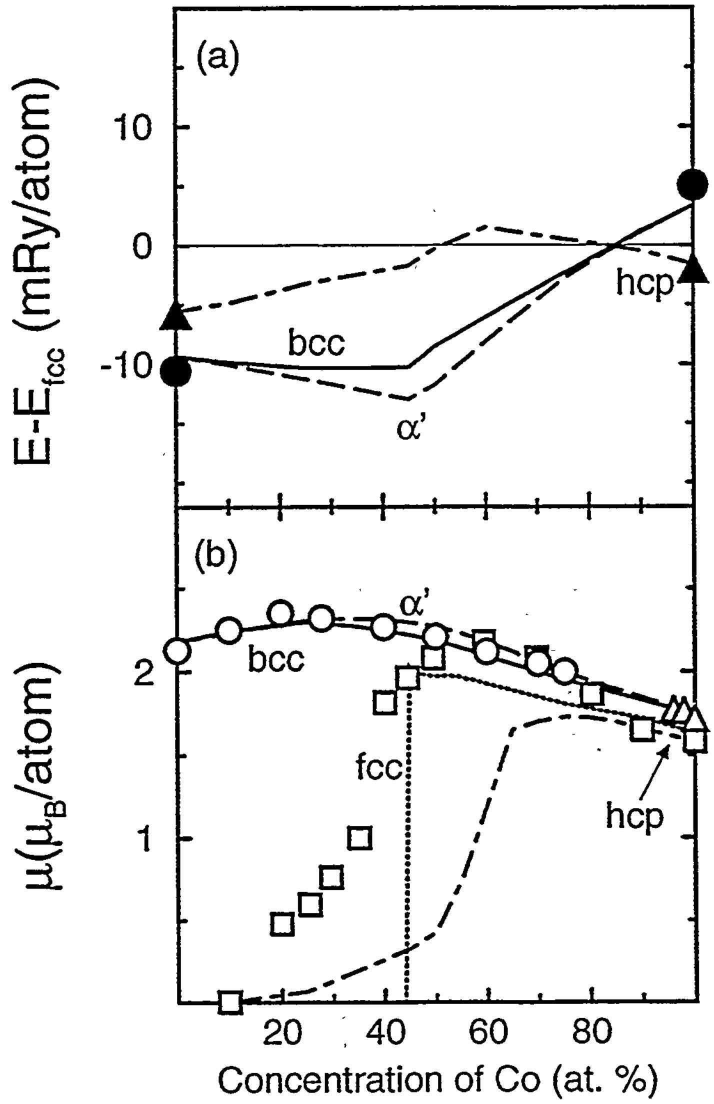

Figure 1. The energy of bcc and hcp random alloys and the partially ordered α' phase relative to the energy of the fcc phase (a), of the Fe-Co alloy as a function of Co concentration. The corresponding mean magnetic moments are shown in (b). The ASA-LSDA-CPA results are shown as a dashed line for the 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). In (b) experimental mean magnetic moments[16] are shown as open circles (bcc), open squares (fcc) and open triangles (hcp).

Next we turn to our canonical band results. To do so we have used a generalized canonical band model that includes spin-polarization. Hence we introduce a spin dependent shift,

$$\Delta_{ex} = \mu I_d, \tag{1}$$

to the LMTO canonical structure constant matrix for the d-states, $\mathrm{S}_{lm,lm'}$,

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

Using this model in analogy with previous studies[5] we can calculate a magnetic moment (μ) of the system with fixed Stoner exchange parameter I_d and occupation of the d states. The total energy could then be calculated as the balance between the kinetic energy and the spin-polarization energy:

$$E_{tot} =< T > -\mu^2 I_d/4. \tag{3}$$

The Stoner exchange parameter was chosen so that the magnetic moment behaved similarly to the magnetic moment for the real Fe-Co alloy. These values were, however, close to the calculated (LSDA) correspondence. It is interesting to note in Fig. 2 that the calculated crystal structure energy differences agree fairly well with those calculated from the ASA-LSDA-CPA method. To a large extent this agreement can be understood from the fact that Fe and Co are neighboring atoms 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[3,17,18] However, this split band behavior is more pronounced for states above the Fermi energy, and consequently affects the total energy to a smaller degree.

In summary, we have 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 ~ 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 the fcc and the hcp phases show high spin - low spin magnetic phase transitions.

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 Fe-Co alloy are explained from simple band-filling arguments.

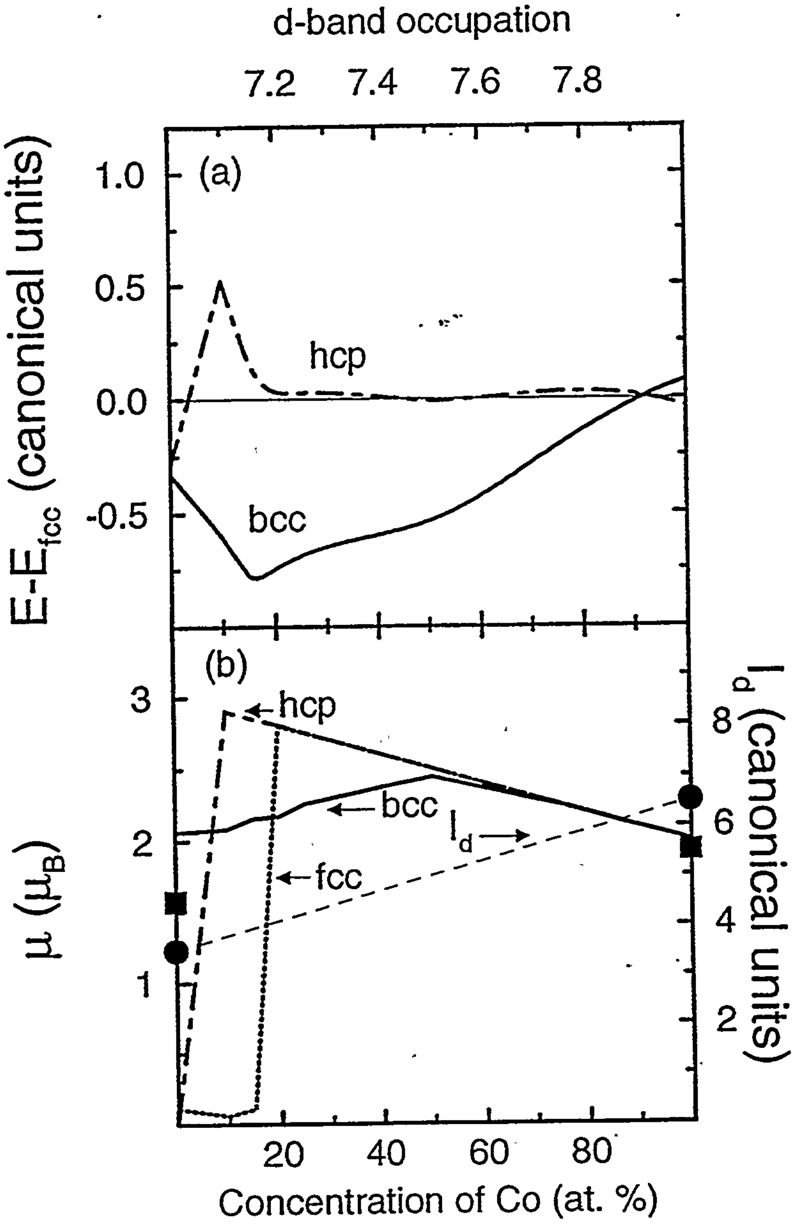

Figure 2. The structural energy difference (a) and the magnetic moment (b) as a function of the occupation of the canonical d-band n corresponding to the Fe-Co alloy. The same lines as in Fig. 1 are used for the different structures. In (b) the concentration dependence of the Stoner exchange integral I_d used for the spin-polarized canonical d-band model calculations is shown as a thin dashed line with the solid 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 solid squares.

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