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Iron–cobalt alloys: electronic and magnetic structure from SCF $X\alpha$ sw cluster calculations

J Kaspar and D R Salahub

Département de Chimie, Université de Montréal, CP 6210, Succ. A, Montréal, Québec, Canada H3C 3V1

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Abstract. The electronic structures of 15-atom clusters (Fe_{15} , CoFe_8Co_6 , FeCo_8Fe_6 and Co_{15}) in the geometry appropriate to the bulk bcc metals and alloys have been determined from spin-polarised self-consistent field $X\alpha$ scattered-wave calculations. The general features of the results are quite similar to those obtained from band calculations for the bulk alloys. Examination of the local density of states on each atom and in each spin manifold has yielded a consistent and simple picture of the important interplay in these alloys between magnetic and chemical effects, the key factors being the greater electronegativity of Co and the larger magnetic moment and exchange splitting of Fe. The calculations lead to a qualitative explanation for the concentration dependence of the magnetisation, the volume and the thermal expansion coefficient, which show similar (though less dramatic) behaviour to that observed for the fcc Fe–Ni (Invar) alloys. Calculations of the contact hyperfine fields have led to a model in which the core contribution is proportional to the magnetic moment and the valence contribution depends on the moments of neighbouring atoms. The calculations have allowed some comments to be made on the effects of the order–disorder transition of these alloys on the volume, magnetisation and hyperfine fields.

1. Introduction

The binary bcc FeCo alloys exhibit (figure 1) concentration dependences of the lattice constant, the average magnetisation and the thermal expansion coefficient reminiscent of (but less dramatic than) those of the Invar alloys (Nakamura 1976 and references therein). Between compositions of zero and about 30 at% Co both the lattice constant and the average magnetic moment increase, go through a maximum and decrease between 30 and 70 at% Co where a phase transition to the fcc structure occurs (Bozorth 1951, Bardos 1969). The thermal expansion coefficient shows a broad minimum centred at about 50 at% Co (Fine and Ellis 1948).

Polarised neutron diffraction studies (Collins and Forsyth 1963, Spooner *et al* 1971) indicate that the local magnetic moment on the Co atom stays nearly constant over the whole composition range and quite near to the value ($1.71 \mu_B$) for pure hcp Co (Moon 1964) whereas the iron moment ($2.2 \mu_B$ for pure bcc Fe) increases with increasing Co concentration, reaching a maximum value of approximately $3 \mu_B$ at 50 at% Co and remaining constant thereafter. This value is amongst the highest known for iron.

Marshall (1958) discussed the various terms contributing to the hyperfine fields, B_{hf} , at the nuclei of a ferromagnet and presented an analysis in which B_{hf} is proportional to the magnetisation. Such a relationship has been verified, for example, in a study of the

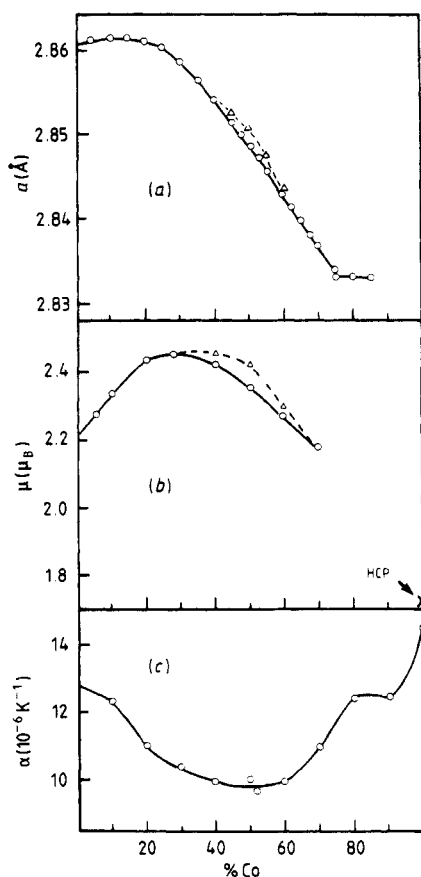


Figure 1. Experimental data on bcc FeCo alloys. (a) Lattice constant for the ordered and quenched alloys at 298 K (Bozorth 1951); (b) average magnetic moment for ordered and quenched alloys extrapolated to 0 K (Bardos 1969); (c) linear thermal expansion coefficient (Bozorth 1951). Δ — Δ , ordered; $\circ$ — $\circ$, quenched.

temperature dependence of B_{hf} for iron (Nagle *et al* 1960) and also holds for series of salts containing ions of common valency (Abragam *et al* 1955, Freeman and Watson 1965, table 14). The FeCo alloys provide a clear example for which this proportionality does not hold. Mössbauer experiments (Johnson *et al* 1961, De Mayo *et al* 1970) have shown that B_{hf} at the Fe nucleus is closely proportional to the average moment rather than the local Fe moment, whereas Arp *et al* (1959) have determined, from measurements of the nuclear contribution to the specific heat, that $|B_{\text{hf}}|$ for Co decreases almost linearly with increasing Co concentration.

The FeCo alloys are also of interest since they exhibit an order–disorder transition for compositions between about 30 and 70 at% Co. The ordered state has a larger volume (Bozorth 1951), larger magnetisation (Kouvel 1969) and less negative hyperfine fields at the Fe nuclei (De Mayo *et al* 1970, Montano and Seehra 1977).

In this paper we present results of molecular orbital calculations on small metal clusters aimed at a better understanding of the above properties in particular and of the electronic and magnetic structures of the alloys in general. We find, through comparison with experimental data and band calculations (Schwarz and Salahub 1982) that models

containing 15 atoms for the BCC structure are sufficiently large to yield a qualitative understanding of this type of bulk property. This is in line with previous experience for clusters of the transition metals (Messmer *et al* 1976, Salahub and Messmer 1981, Yang *et al* 1981, Salahub 1981) and Fe-Ni alloys (Kaspar and Salahub 1981). Specifically, these past calculations have shown that clusters in this size range possess a number of properties which are close to those of the bulk solid, namely the general features of the density of states, including spin polarisation, the existence, approximate magnitudes and type of ordering of magnetic moments, spin-density distributions, and the basic description of the chemical bonding. Of course upon more detailed examination, intrinsic cluster properties may be identified, perhaps the most noteworthy being that the central atom of such clusters appears to be the least bulk-like as discussed previously by Yang *et al* (1981) (see also below).

The present results indicate that, similar to the FCC Fe-Ni alloys (Kaspar and Salahub 1981), the variations with composition of the lattice constant, the magnetisation and the thermal expansion coefficient are due to the presence of anti-bonding majority-spin orbitals near the Fermi level for the iron-rich alloys and the destabilisation of these levels for higher cobalt concentrations. The magnetisation of the alloys cannot be understood from the usual Stoner criterion which implies 'rigid band' assumptions. However, a local Stoner criterion can be formulated, which is identical to the usual criterion for the case of an elemental metal. For an alloy, this local criterion allows one to introduce the notion of spin-dependent electronegativities, in terms of which chemical interactions and their effects on the magnetism can be discussed. The behaviour of the hyperfine fields is found to arise from a core-electron contribution which is closely proportional to the local magnetic moment and a more complicated contribution from the valence electrons which depends on the neighbouring atoms and their moments. Finally, the general picture which has emerged from the calculations has allowed us to comment on the possible effects of the order-disorder transition on the local electronic structure and hence on the mechanical and magnetic properties.

2. Method and computational parameters

Non-spin-polarised and spin-polarised molecular orbital (MO) calculations have been performed for 15-atom clusters having the geometry appropriate to the BCC lattice (figure 2) and of composition CoFe_8Co_6 , FeCo_8Fe_6 and Co_{15} . Results for Fe_{15} have been published previously (Yang *et al* 1981). The self-consistent field $X\alpha$ scattered-wave (SCF $X\alpha$ sw) method was used and since this method has been well described elsewhere (Slater 1972, 1974, Johnson 1973) only the input parameters will be given here. These are summarised in table 1. The lattice parameters (second nearest-neighbour (NN) distances) were taken from Bozorth (1951), with that for Co_{15} being derived by linear extrapolation. The muffin-tin spheres were chosen to be of equal size for Fe and Co, non-overlapping, and the outer sphere was tangent to the outermost atomic spheres (see Yang *et al* 1981 for a discussion of the effects of overlapping spheres). Values of α for Fe and Co were taken from the compilation of Schwarz (1972) and an average value, weighted by the number of atoms of each type, was used in the inter-sphere and outer-sphere regions.

A convenient way of analysing the results is to compute densities of states (DOS) from discrete energy levels by replacing each level by a Gaussian of (arbitrarily chosen) width parameter 0.2 eV. Local DOS (LDOS) are generated in a similar fashion by weighting each Gaussian with the charge in a given muffin-tin sphere.

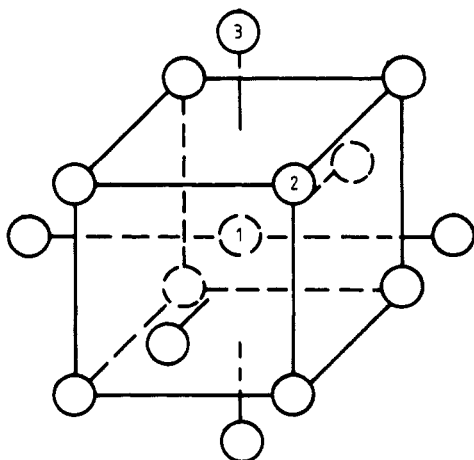


Figure 2. Structure of the 15-atom BCC clusters. The numbers refer to groups of symmetry-related atoms.

3. Results and discussion

3.1. Non-spin-polarised calculations

The total DOS from non-spin-polarised calculations for the clusters are shown in figure 3. The three new cases, CoFe_8Co_6 , FeCo_8Fe_6 and Co_{15} are all similar and show the same basic characteristics as have been discussed previously for Fe_{15} (Yang *et al* 1981). There is reasonable agreement with a typical bulk BCC DOS. The main peaks, labelled 1–5 in figure 3, derive from orbitals of different chemical bonding types. In order of increasing energy these are (1) bonding, predominantly sp orbitals, (2) bonding d orbitals, (3) non-bonding or weakly bonding d functions, (4) anti-bonding d functions, and (5) anti-bonding levels involving s and p as well as d orbitals. In all cases the Fermi level (ϵ_F) lies in the anti-bonding peak and the DOS at ϵ_F is high so that the ‘cluster Stoner criterion’ discussed by Yang *et al* (1981) should be satisfied. Indeed, when spin polarisation is allowed (§ 3.2) all of the clusters become magnetic.

It is only when the LDOS for the various atoms is examined that important differences among the clusters are revealed. The basic chemical interactions at play are represented schematically in figure 4. A Co atomic orbital (AO) is intrinsically more stable (higher electronegativity) than an Fe AO, owing to the increased nuclear charge. Mixing of the AO

Table 1. Computational parameters.

Cluster	Lattice parameter		Sphere radii (Bohr)		$\alpha^{\text{int}} = \alpha^{\text{out}} \dagger$
	(Bohr)	(Å)	Atomic	Outer	
Fe_{15}	5.424	2.870	2.348	7.772	0.71151
CoFe_8Co_6	5.384	2.849	2.331	7.715	0.71089
FeCo_8Fe_6	5.384	2.849	2.331	7.715	0.71076
Co_{15}	5.348	2.830	2.316	7.664	0.71018

$\dagger$ Inter-sphere and outer-sphere α parameter.

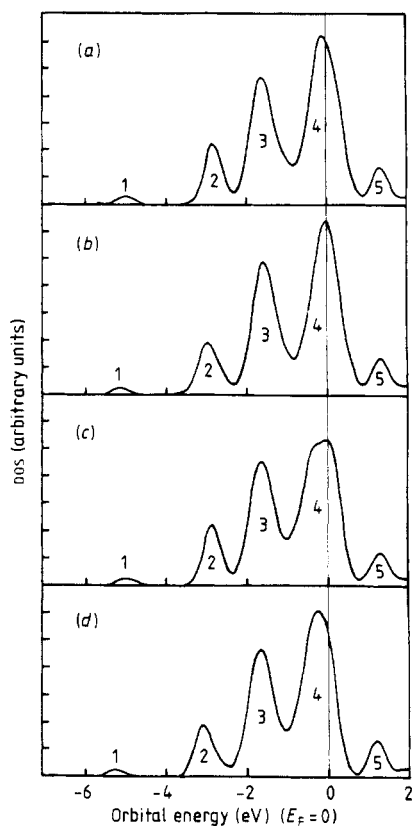


Figure 3. Total DOS for the non-spin-polarised clusters. The curves were generated by replacing each discrete eigenvalue with a Gaussian of width parameter 0.2 eV. (a) Fe_{15} , (b) CoFe_8Co_6 , (c) FeCo_8Fe_6 , (d) Co_{15} .

yields bonding and anti-bonding MO and perturbation theory indicates that the bonding combination will be weighted in favour of Co while the anti-bonding combination is in favour of Fe. Since the d bands are partially filled a somewhat polar bond will result.

This situation is reflected in the LDOS which are shown for the first NN and second NN atoms of the four clusters in the bottom panels (parts (c) and (f)) of figures 5–8. (Data for the central atom are not presented, because, as discussed elsewhere (Yang *et al* 1981) this

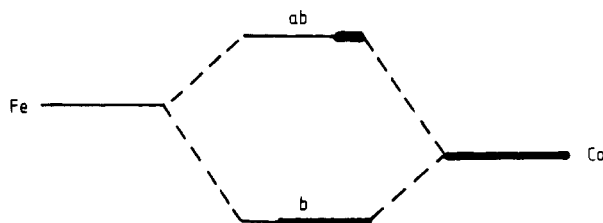


Figure 4. Schematic construction of the non-spin-polarised MO from non-spin-polarised atomic orbitals representing the LDOS. Bold lines represent Co and fine lines Fe. b, bonding; ab, anti-bonding.

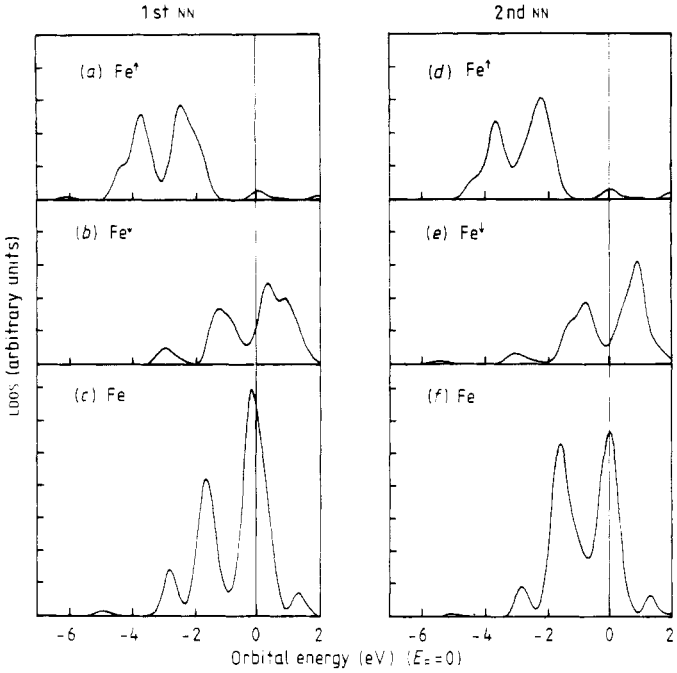


Figure 5. LDOS for the Fe_{15} cluster. (a) Majority-spin first NN, (b) minority-spin first NN, (c) non-spin-polarised first NN, (d) majority-spin second NN, (e) minority-spin second NN, (f) non-spin-polarised second NN.

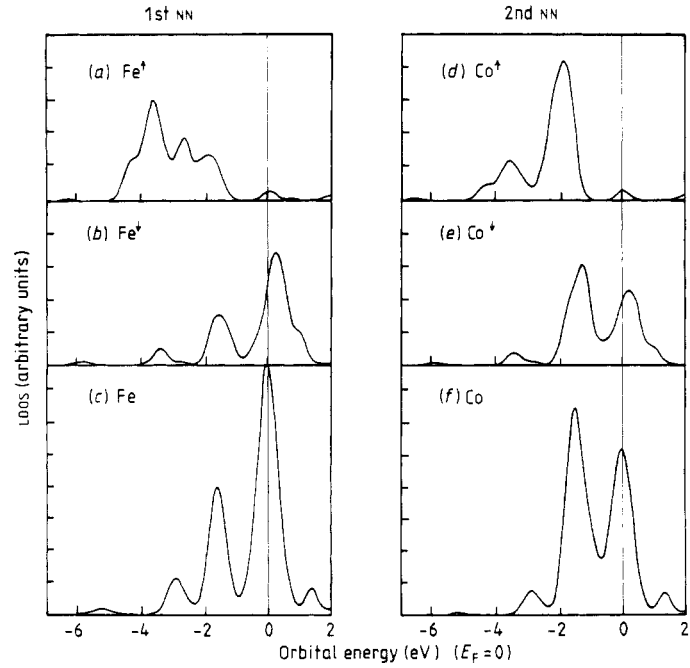


Figure 6. As figure 5 but for CoFe_8Co_6 .

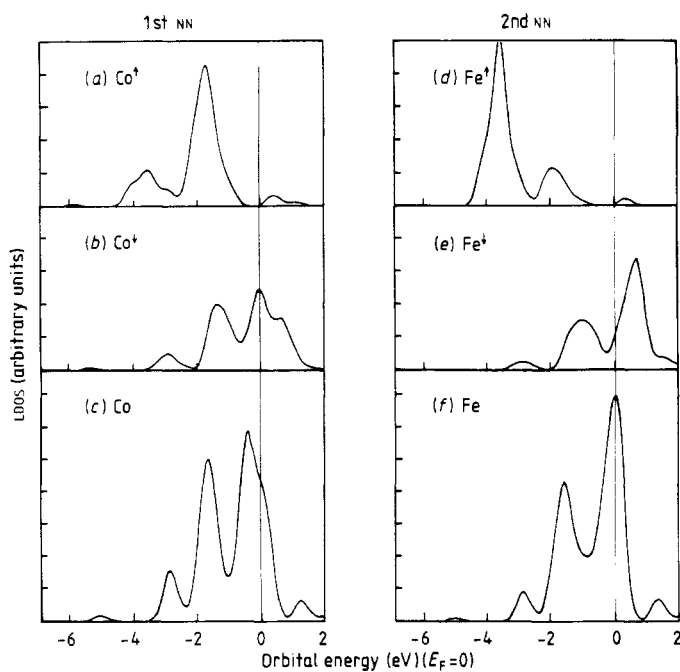


Figure 7. As figure 5 but for FeCo_8Fe_6 .

atom is usually the least bulk-like.) There are pronounced differences in the LDOS for Fe and Co in equivalent positions of the clusters. For example, the first NN Fe in the

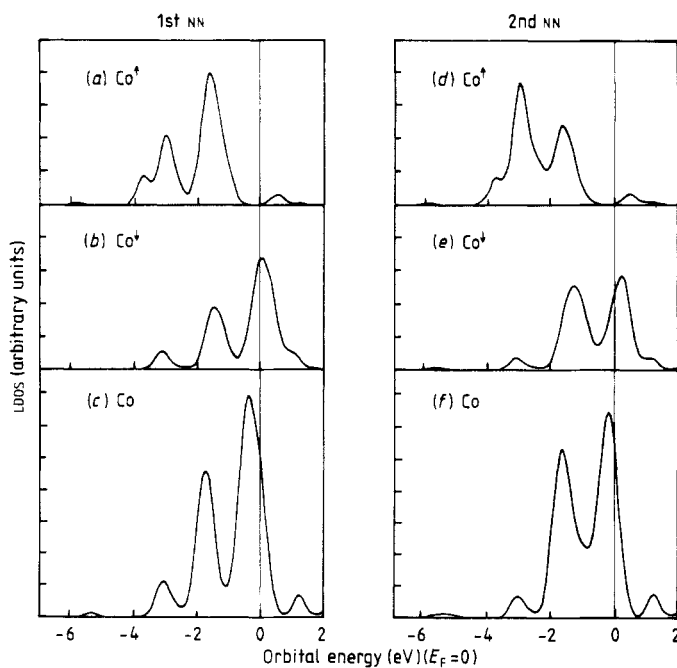


Figure 8. As figure 5 but for Co_{15} .

CoFe_8Co_6 cluster (figure 6(c)) contributes mainly to peak 4 whereas the first NN Co in FeCo_8Fe_6 (figure 7(c)) dominates the lower energy peaks 2 and 3 and that part of peak 4 that lies below the Fermi level. Similar differences can be seen for the second NN atoms (figures 6(f) and 7(f)). As expected, none of these charge transfer effects are present for the pure Co_{15} and Fe_{15} clusters.

The differences in the LDOS for the central atom and its first and second NN are a result of the different degree of binding available to each kind. The atoms with the smallest number of neighbours are the second NN; they contribute strongly to non-bonding orbitals between peaks 3 and 4 and the separation of these peaks is always less pronounced in the LDOS for the second NN than for the first NN. As a consequence, the second NN LDOS is slightly narrower than that of the first NN. This tends to increase the LDOS at the Fermi level. The opposite behaviour is found for the central atom. To the extent that the LDOS at ϵ_F governs the formation and the magnitude of magnetic moments, one would expect the moments to be smallest for the central atom, and larger for the peripheral atoms, a situation which exists for magnetic clusters of only one kind of atom (Yang *et al* 1981, Salahub and Messmer 1981, Salahub 1981). The degree to which chemical effects in the alloys affect this conclusion is discussed in the next section.

3.2. Spin-polarised calculations

3.2.1. Energy levels and magnetic moments. The spin-polarised eigenvalue spectra of the clusters (figure 9, table 2) show the following salient features. All the clusters are magnetic and the d band exchange splitting is largest for Fe_{15} , smallest for Co_{15} and intermediate for the alloys, in agreement with the trends found in band calculations (Moruzzi *et al* 1978, K Schwarz and D R Salahub 1981, unpublished). The general pattern of levels is the same as has already been discussed for Fe_{15} by Yang *et al* (1981). In particular we note that in the majority-spin manifold the main body of the d DOS is separated by a gap of about 1 eV from two levels ($6e_g^\uparrow$ and $7t_{2g}^\uparrow$) which are at the Fermi level (Fe_{15} and CoFe_8Co_6) or above (FeCo_8Fe_6 and Co_{15}). At self-consistency the number of majority-spin electrons is nearly

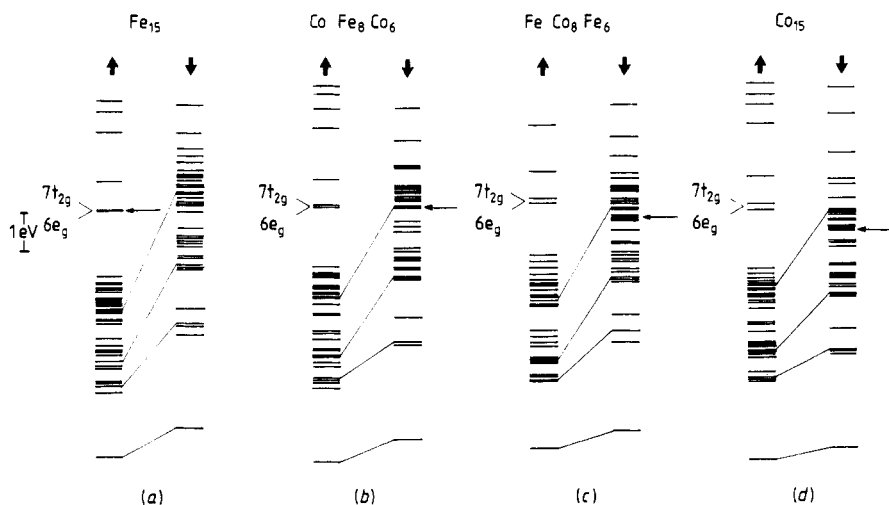


Figure 9. Spin-polarised orbital eigenvalues for (a) Fe_{15} , (b) CoFe_8Co_6 , (c) FeCo_8Fe_6 , (d) Co_{15} . The Fermi level is indicated by a horizontal arrow. For clarity only a few lines connecting corresponding spin-up and spin-down orbitals are shown.

Table 2. Global magnetic properties of the clusters and experimental bulk magnetisation.

	Fe ₁₅	CoFe ₈ Co ₆	FeCo ₈ Fe ₆	Co ₁₅
% Co	0	47	53	100
$n^{\uparrow a}$	215	214	214	214
$n^{\downarrow b}$	175	183	184	191
$(n^{\uparrow} - n^{\downarrow})$	40	31	30	23
$\frac{1}{15}(n^{\uparrow} - n^{\downarrow})$	2.7	2.1	2.0	1.5
μ (μ_B)	2.1 ^c	2.3 ^d		1.9 ^e
Typical exchange (d) ^f	2.5	2.3	2.1	1.7
splitting (eV) (sp) ^g	0.7	0.6	0.5	0.3

^a Number of majority-spin electrons.^b Number of minority-spin electrons.^c Experimental magnetisation including a g' factor of 1.919.^d Experimental magnetisation including a g' factor of 1.916.^e Extrapolated from alloy data (Bardos 1969)—uncorrected for orbital angular momentum.^f Visual average for d levels of figure 9.^g Splitting of lowest valence levels (high sp character) of figure 9.

the same for all of the clusters (215 for Fe₁₅, 214 for the others), leading to the average net-spin electron numbers shown in table 2. Also in table 2 are the observed average magnetic moments for bulk Fe, the 50–50 alloy, and an extrapolated value for BCC Co. The values for Fe and the alloy have been corrected for the small orbital angular momentum contribution using the observed magnetomechanical ratios, g' , of Scott and Sturmer (1969) (1.919 for Fe and 1.916 for FeCo). The average spin moments calculated for the clusters agree with their experimental bulk counterparts to within a few tenths of a Bohr magneton, the largest discrepancy being found for Fe₁₅. It should be noted that changing the spin of a single electron in these 15-atom clusters leads to a change in the average moment of $0.13 \mu_B$. To attain a better quantitative account would require larger clusters and also a closer study of the effects of our particular choice for the exchange-correlation potential as is discussed elsewhere (Yang *et al* 1981, D R Salahub, B N McMaster and J Kaspar 1982, unpublished). More important than these quantitative considerations are the qualitative conclusions concerning the interplay of magnetic, chemical and mechanical effects in the alloys, which can be drawn from a more detailed analysis of the cluster electronic structures.

Charge and spin density information for each type of atom in the clusters is given in table 3. As usual (Yang *et al* 1981, Salahub and Messmer 1981, Salahub 1981) the central atoms are the least bulk-like, having excess electron density and small magnetic moments (actually negative, i.e. antiferromagnetically aligned for CoFe₈Co₆) and we shall not discuss them further. For first and second NN atoms the local moments on Fe are large (2.70 – $2.97 \mu_B$) and somewhat greater for equivalent positions in the mixed clusters compared with Fe₁₅. The Co moments are smaller (1.51 – $1.78 \mu_B$) and increasing the Co concentration leads to higher values. These values may be compared with those deduced from polarised neutron scattering (table 4). The neutron data indicate an increased moment on Fe for the alloys and a Co moment which is quite near to the value for pure Co ($1.71 \mu_B$ for pure HCP Co (Moon 1964), $1.9 \mu_B$ extrapolated from the BCC alloy data). If the extrapolated value for pure BCC Co is used then the experimental values for μ_{Co} show a slight, but definite, increase with increasing Co concentration. The exact values of the

Table 3. Charge and spin analysis of the clusters^a.

	Fe ₁₅	CoFe ₈ Co ₆	FeCo ₈ Fe ₆	Co ₁₅
Central atom	Fe	Co	Fe	Co
d	7.09	8.14	7.10	8.09
s	0.48	0.51	0.45	0.49
p	0.46	0.48	0.42	0.45
μ_d	1.26	-0.095	0.24	0.15
μ_s	-0.052	-0.054	-0.037	0.033
μ_p	-0.057	-0.059	-0.044	0.038
μ	1.15	-0.21	0.16	0.08
1st NN	Fe	Fe	Co	Co
d	6.44	6.38	7.54	7.49
s	0.35	0.34	0.38	0.35
p	0.18	0.16	0.17	0.17
μ_d	2.71	2.76	1.55	1.63
μ_s	-0.010	0.008	-0.009	-0.007
μ_p	0.001	-0.004	-0.013	-0.017
μ	2.70	2.76	1.52	1.61
2nd NN	Fe	Co	Fe	Co
d	6.35	7.53	6.29	7.42
s	0.36	0.35	0.32	0.33
p	0.12	0.12	0.13	0.13
μ_d	2.80	1.55	2.96	1.80
μ_s	-0.007	-0.043	-0.007	-0.018
μ_p	0.004	0.002	0.010	0.000
μ	2.81	1.51	2.97	1.78
(II + III) ^b	15.258	14.846	14.931	14.645
$\mu(\text{II} + \text{III})^c$	0.419	0.020	-0.144	-0.633
$\frac{1}{15}\mu(\text{II} + \text{III})$	0.028	0.001	-0.010	-0.042

^a Atomic quantities are integrals within a given muffin-tin sphere.^b Number of electrons in inter-sphere and outer-sphere regions.^c Integrated spin density for inter-sphere plus outer-sphere regions.

moments deduced from the neutron measurements are quite sensitive to the method of analysis and we note in particular that Spooner *et al* (1971) propose very large local moments (3.38 μ_B for Fe in the ordered 50 at% alloy) and a large negative non-local moment (a few tenths of a μ_B). On the other hand, in the clusters the only contributions which can reasonably be considered 'non-local' (μ_{sp} and $\mu(\text{II} + \text{III})$) are at least an order of magnitude smaller. This is probably a reflection of the fact that first and second NN atoms are missing neighbours which they would have in the bulk and, even though the negative spin density is remarkably well described in the regions between the atoms (see figure 10 of Yang *et al* 1981), the external parts of the peripheral atoms are poorly described, being dominated by lobes of positive spin density pointing away from the cluster. Overall, the general tendencies of the moments ascribed to Fe and Co are reasonably well interpreted by the cluster calculations, the absolute values of the moments differing by a few tenths of a μ_B from those observed for the corresponding bulk alloys.

Table 4. Experimental values for the magnetic moments in Fe-Co alloys (in μ_B).

Reference	% Co	μ_{Fe}	μ_{Co}	μ_{av}^{local}	$\mu^{non-local}$	μ_{av}
Collins and Forsyth (1963) ^a	30	2.77	1.71	2.47		2.47
	50	3.00	1.77	2.41		2.41
	70	3.00	1.83	2.18		2.18
Spooner <i>et al</i> (1971) ^b	50	3.38	2.20	2.79	-0.36	2.43
	(ordered)			2.59 ^c	-0.16 ^c	2.43
	50	3.12 ^d	2.23 ^d	2.68 ^d	-0.43 ^d	2.25 ^d
	(disordered)			2.73	-0.37 ^c	2.36

^a Polarised neutron diffraction; annealed samples; pure metal form factors. Any 'non-local' moment is included in the values of μ_{Fe} and μ_{Co} .

^b Polarised neutron diffraction, (+2) ion form factors; analysis allows for 'non-local' contribution.

^c Values from Fourier analysis (Moon 1971).

^d There is an inconsistency in these data. One or more of the values for μ_{Fe} , μ_{Co} and $\mu^{non-local}$ would have to be modified by about 0.1 μ_B to yield the correct bulk magnetisation.

Recent band calculations (Schwarz and Salahub 1982) with the augmented spherical wave (ASW) method (Williams *et al* 1979) using the exchange-correlation potential of von Barth and Hedin (1972) yielded an average spin moment of 2.18 μ_B for the 50-50 alloy (a value quite similar to those found for the alloy clusters (table 2)) and individual moments of 2.68 μ_B (μ_{Fe}) and 1.67 μ_B (μ_{Co}). The calculated average moment is about 0.15 μ_B smaller than the observed value (corrected for the orbital contribution) of 2.33 μ_B . The average moment found in the band calculations is quite similar to that found for the mixed clusters (2.1 μ_B for $CoFe_8Co_6$, 2.0 μ_B for $FeCo_8Fe_6$); however, the distribution between Fe and Co is somewhat different, the cluster moments being slightly larger for Fe and smaller for Co. Reasons for this are discussed in the next section. While the level of agreement with experiment found in the band or cluster calculations is impressive and the trends are clear, the remaining discrepancy will have to be accounted for before a quantitative treatment of the variations of the moments in the series of alloys can be claimed. The source of this small discrepancy may lie in the details of the ASW method or of the exchange-correlation potential or indeed in the one-electron band approximation itself. One interesting possibility for increasing the moments, which arises from the cluster results, is that quite localised majority-spin anti-bonding orbitals exist near the Fermi level. The MO states do not have strict Bloch-wave counterparts and in that language would have to arise through mixing of Bloch states, which would be allowed if the wavefunctions were not constrained to reflect the full translational symmetry of the crystal. These orbitals are discussed further in § 3.2.3.

3.2.2. LDOS, Stoner criterion and chemical effects. The clue to a greater understanding of the trends in the local moments discussed in § 3.2.1 may be found in the LDOS (figures 5-8). For minority spin in the mixed clusters (parts (b) and (e) of figures 6 and 7) the same features are found as in the non-magnetic calculations (parts (c) and (f) of figures 6 and 7) namely, more weight is found for Co in the lower-energy bonding region and more for Fe in the anti-bonding region above ϵ_F . This effectively transfers minority spin from Fe to Co, leading to higher Fe moments and lower Co moments in the alloys compared with the pure clusters. The majority-spin LDOS show the reverse situation (parts (a) and (d) of figures 6 and 7). The low-energy, bonding majority-spin MO are characterised by a charge transfer

to Fe, those lying higher by a charge transfer to Co. To a rough approximation these two effects cancel in computing the moments since all of the states involved are below ϵ_F . Hence the major effect on the local moments arising from changes in shape of the LDOS is that occurring in the minority-spin manifold. Quite similar effects in the LDOS were found in the ASW band calculations (Schwarz and Salahub 1982), except that there the majority-spin LDOS are very similar for Fe and Co indicating more covalent (less polar) interactions. It is clear from both the cluster and band results that rigid band arguments are not appropriate for this system. While the changes in the form of the DOS account quite nicely for the trends in the local moments, they do not of themselves yield an explanation for the increase in the average moment of the alloy compared with the elements. More detailed considerations are necessary for this. A possible mechanism based on the cluster results is discussed in § 3.2.3.

As for the non-magnetic alloy (figure 4) one can account for the general shape of the spin-polarised LDOS in a schematic fashion (figure 10) by considering the relative spin-orbital electronegativities of Fe and Co. Co has a higher electronegativity than Fe and this is reflected by its lower non-spin-polarised energy level in figure 10, where a single line is used to represent an average energy level for the atoms in a bulk environment (the centre of gravity of the LDOS). The next outermost columns of figure 10 represent the effects of spin polarisation on the Fe and Co levels. Fe moments and exchange splittings are larger than those for Co and for the clusters this brings the spin-up Fe level below that for Co, i.e. the spin-orbital electronegativities are reversed. For minority spin the opposite holds and the electronegativity difference between Fe and Co is enhanced. Finally in the central column the Fe–Co interactions are taken into account leading to the situation described above. The difference between figure 10 and a similar diagram applicable to the band calculations is that for the latter, the $\text{Fe}\uparrow$ and $\text{Co}\uparrow$ levels should be nearly degenerate, leading to non-polar interactions and a very similar majority-spin DOS for Fe and Co.

The discussion can have a more formal basis through consideration of a local version of the Stoner theory. The non-spin-polarised MO of the alloys, $\psi_{\text{MO}}^{\text{NSP}}(\mathbf{r})$, are constructed from atomic orbitals, $|d_A^m(\mathbf{r})\rangle$, whose relative energies determine the electronegativity differences between the constituents. Their spin-polarisation, which results in new spin-orbital electronegativities, is determined by the local difference in the exchange potential, $\Delta v^{\text{xc}}(\mathbf{r})$, in the alloy. This difference is related to the magnetisation $m(\mathbf{r})$ through

$$\Delta v^{\text{xc}}(\mathbf{r}) = c\alpha\rho^{1/3}(\mathbf{r})m(\mathbf{r})/\rho(\mathbf{r}) \quad (1)$$

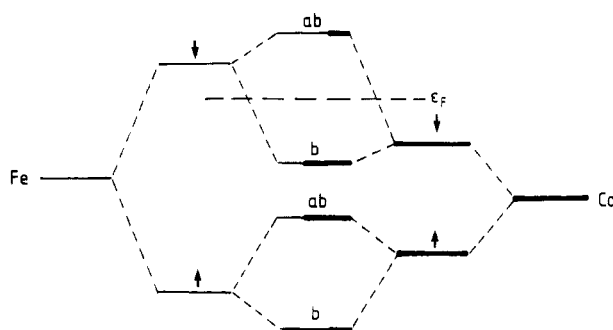


Figure 10. Schematic construction of the spin-polarised MO from non-spin-polarised atomic orbitals representing the LDOS. Bold lines represent Co and fine lines Fe. b, bonding; ab, anti-bonding; ϵ_F , Fermi level.

where α is the $X\alpha$ parameter, $\rho(\mathbf{r})$ is the charge density and c is a constant (Gunnarsson and Lundqvist 1976). The d electron charge density $\rho_A^d(\mathbf{r})$ on atom A is related to the local d electron DOS $N_A(\epsilon)$:

$$N_A(\epsilon) = 2 \sum_{m=1}^5 \sum_{\text{MO}} |\langle d_A^m | \psi_{\text{MO}}^{\text{NSP}} \rangle|^2 \delta(\epsilon - \epsilon_{\text{MO}}). \quad (2)$$

In a muffin-tin approach

$$\rho_A^d(\mathbf{r}) = \int_{-\infty}^{\epsilon_F} d\epsilon \sum_{m=1}^5 \sum_{m'=1}^5 |d_A^m(\mathbf{r})\rangle \sum_{\text{MO}} 2 \langle d_A^m | \psi_{\text{MO}}^{\text{NSP}} \rangle \langle \psi_{\text{MO}}^{\text{NSP}} | d_A^{m'} \rangle \delta(\epsilon - \epsilon_{\text{MO}}) \langle d_A^{m'}(\mathbf{r})|. \quad (3)$$

When the spherical average is taken one obtains:

$$\bar{\rho}_A^d(r) = \frac{1}{4\pi} \int_{-\infty}^{\epsilon_F} d\epsilon \varphi_{d,A}^2(r) N_A(\epsilon) = \varphi_{d,A}^2(r) \frac{n_d}{4\pi} \quad (4)$$

where $\varphi_{d,A}(r)$ is the radial part of the d orbitals on atom A and n_d is the number of d electrons on A. This approximation corresponds to ignoring the inter-sphere charges.

This LDOS is now thought of as being the full DOS of a hypothetical solid, so that electrons can be moved according to this DOS rather than the total DOS of the alloy. The up- and down-spin Fermi levels then depend on the atom.

The spherical average magnetisation density on atom A is then

$$\bar{m}_A(r) = \frac{1}{4\pi} \varphi_{d,A}^2(r) \int_{\epsilon_{F\downarrow}}^{\epsilon_{F\uparrow}} d\epsilon \frac{1}{2} N_A(\epsilon) \quad (5)$$

$$\bar{m}_A(r) = \Delta m_A \varphi_{d,A}^2(r) / 4\pi. \quad (6)$$

As Gunnarsson (1976) has shown, it is reasonable to substitute spherical averages of $m(\mathbf{r})$ and $\rho(\mathbf{r})$ in equation (1). The difference in the local exchange potential is therefore

$$\Delta v_A^{\text{xc}}(r) = \frac{c\alpha_A}{4\pi} \bar{\rho}_A^{1/3}(r) \frac{\varphi_{d,A}^2(r)}{\bar{\rho}_A(r)} \Delta m_A. \quad (7)$$

The exchange splitting of the d orbitals on atom A is given by

$$\Delta \epsilon^A = \langle \varphi_{d,A} | \Delta v_A^{\text{xc}} | \varphi_{d,A} \rangle \quad (8)$$

$$= \Delta m_A I_A \quad (9)$$

where

$$I_A = \frac{c\alpha_A}{4\pi} \int \bar{\rho}_A^{1/3}(r) \frac{\varphi_{d,A}^4(r)}{\bar{\rho}_A(r)} r^2 dr. \quad (10)$$

I_A is the usual Stoner parameter of atom A which is known to be fairly independent of the system (Janak 1977). It can therefore be used (Anderson *et al* 1977) to find the magnetisation Δm_A from the LDOS since the values of $\epsilon_{F\uparrow}^A$ and $\epsilon_{F\downarrow}^A$ have to be chosen in such a way that

$$\left(I_A \int_{\epsilon_{F\downarrow}^A}^{\epsilon_{F\uparrow}^A} d\epsilon \frac{1}{2} N_A(\epsilon) \right) \left(\int_{\epsilon_{F\downarrow}^A}^{\epsilon_{F\uparrow}^A} d\epsilon \right)^{-1} = I_A \bar{N}_A(\epsilon_{F\uparrow}^A, \epsilon_{F\downarrow}^A) = 1. \quad (11)$$

While we have not done this for the clusters (the artificial character of the continuum puts the significance of such a quantitative calculation in doubt) there does seem to be a reasonable (but not perfect) correspondence between the height of the non-magnetic LDOS at ϵ_F for the various atoms and the moments they develop in the spin-polarised calculation (compare parts (c) and (f) of figures 5–8 with the moments of table 3).

As is well known (e.g. Heeger 1969) the local Stoner criterion ($I_A N_A(\epsilon_F) > 1$) has the same form as the Anderson (1961) criterion ($U/\Delta \gg 1$) for the existence of magnetic moments on transition-metal impurities in a host metal. The interpretation of the parameters U and Δ and also the underlying mechanism for the appearance of a local moment are, however, quite different. In the Anderson model, Δ is the width of an impurity resonance state and U is the intra-atomic Coulomb repulsion for the impurity. In our picture Δ would represent the width of the anti-bonding peak in the LDOS since for the cases of interest here, it is this part of the total LDOS which determines the functional $\tilde{N}(\epsilon_{F\uparrow}, \epsilon_{F\downarrow})$ and therefore the energy region that contains the magnetic electrons (figures 5–8). The parameter U is an intra-atomic Coulomb integral. On the other hand, I_A arises originally from intra-atomic exchange, modified (sometimes drastically (Messmer and Birss 1969)) by relaxation and correlation effects. While the detailed balance between the various terms (kinetic, nuclear attraction, electronic repulsion) involved in the energy difference between two spin states is delicate, nevertheless in those cases studied (Colpa 1974) the order of the states based on considerations of exchange alone is correct. Although the Stoner and Anderson criteria are mathematically similar and, once put in parametrised form, may seem identical, the underlying interpretation of the reasons for the presence or absence of magnetic moments is quite different.

Through the local Stoner criterion, the non-magnetic LDOS determines the relative energy positions of the spin-polarised LDOS for atom A and these can be considered to arise from a new set of spin-polarised AO, $d_{A\sigma}$ ($A = \text{Fe, Co}, \sigma = \uparrow, \downarrow$) (the set of levels which would generate the LDOS if atom A were embedded in a crystal of atoms with the same LDOS). The energy positions of the spin-polarised AO (the 'spectral centre' of the LDOS) define spin-dependent orbital electronegativities and in the final step in the construction of the spin-polarised LDOS (figure 10) the atomic spin-orbitals are allowed to interact. The resulting charge transfers are now spin dependent and affect the polarity of the levels and the final values of the local magnetic moments.

It is interesting that (in contrast to the ASW and cluster results) empirical tight-binding calculations by Desjonquères and Lavagna (1979) for the 50 at% FeCo alloy using the method of moments, do not yield any charge transfer effects in the ordered alloy but do show some difference of the LDOS for the minority-spin band in the disordered alloy, which is treated within the coherent potential approximation (CPA). In their method they determine energy positions for 'effective atomic levels' in a way that combines steps 2 and 3 of the above analysis. These energy positions are determined by three parameters that describe the magnetisation on Fe and Co and the charge transfer from Fe to Co. No distinction is made between charge transfers in the minority- and majority-spin manifolds which would be reversed, as in our clusters, for the majority-spin MO since their effective atomic Fe level, $E_{\text{Fe}}^{\uparrow}$, is below the effective Co level $E_{\text{Co}}^{\uparrow}$. We believe this is one of the reasons for the failure of their calculations to yield any difference for the magnetic moments in the ordered and disordered states, in contrast to experiment (figure 1).

3.2.3. Invar-like properties. The compositional dependence of the magnetisation, the lattice constant and the thermal expansion coefficient (figure 1) can be given an essentially similar interpretation to that which we have recently proposed (Kaspar and Salahub 1981)

for the FCC Fe-Ni (Invar) alloys. This explanation depends on the existence of anti-bonding majority-spin levels ($6e_g^\uparrow$ and $7t_{2g}^\uparrow$ in figure 9) at ϵ_F for the iron-rich alloys and their absence at higher Co concentration. The anti-bonding character of these orbitals is apparent from contour diagrams of the wavefunctions (figure 11) and the premise is that occupying these levels will tend to increase interatomic distances. The levels are at ϵ_F for Fe_{15} and CoFe_8Co_6 and hence these clusters may be classified as weak ferromagnets, whereas in FeCo_8Fe_6 and Co_{15} they are above ϵ_F (owing to the smaller exchange splitting) yielding strong ferromagnets.

In our explanation, the increases of the lattice constant (figure 1(a)) and the average magnetic moment (figure 1(b)) observed experimentally on adding Co to pure iron are the consequence of occupying these strongly anti-bonding majority-spin MO. The filling and emptying of the anti-bonding levels in this weak ferromagnetic situation provides a mechanism to change mechanical and magnetic properties. Since temperature (by exciting electrons out of majority-spin anti-bonding MO into minority-spin non-bonding MO near ϵ_F) and pressure (by pushing the anti-bonding MO to higher relative energy) remove electrons from these crucial MO, the thermal expansion coefficient should decrease and the compressibility increase with Co content on the Fe-rich side; the decrease of magnetisation with temperature and pressure should be enhanced in the same region.

The only extended study of the thermal expansion of FeCo alloys which we are aware of provides measurements from room temperature to 850 °C (Fine and Ellis 1948). As expected from our argument, a decrease in the expansion coefficient is found with a broad minimum near the 50 at% ordered FeCo alloy (figure 1(c)). However, since the contribution from lattice vibrations has not been separated, the electronic contribution to the expansion coefficient is unknown. Low-temperature measurements would be helpful in this respect.

We associate the maximum in the lattice constant and the average magnetic moment with the maximum occupation of the anti-bonding states. Additional electrons from a further increase in Co content are put into non-bonding minority-spin levels and the magnetic moment as well as the spin polarisation decreases, causing more minority-spin

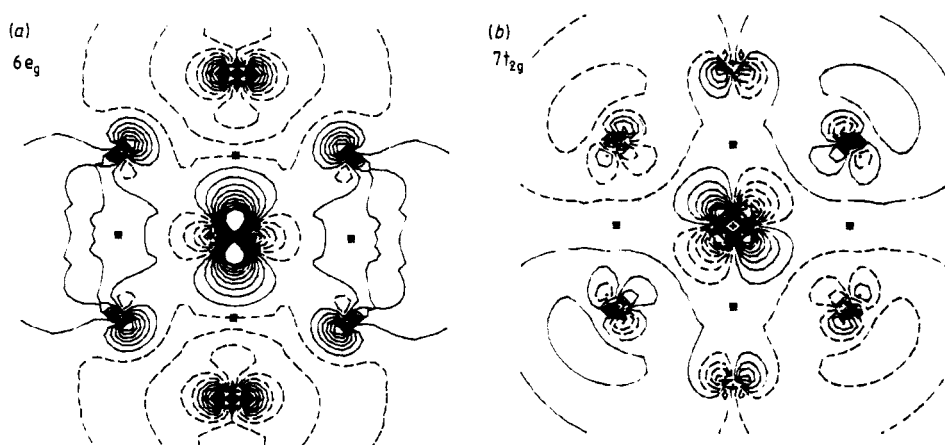


Figure 11. Contour maps of the (a) $6e_g^\uparrow$ and (b) $7t_{2g}^\uparrow$ wavefunctions from the spin-polarised calculation for Fe_{15} . The plane is a $\{110\}$ plane passing through atoms 1, 2 and 3 of figure 2. Broken curves represent negative values of the wavefunction. The lowest contour has the value 0.01 au and adjacent contours differ by 0.02 au.

orbitals to be pulled below the Fermi level. The anti-bonding majority-spin orbitals eventually become unoccupied which, together with the smaller size of Co atoms due to imperfect screening of the larger nuclear charge, leads to a contraction of the lattice. We attribute the fact that the variations of the properties are less pronounced for the BCC Fe–Co alloys than for FCC Fe–Ni to the close-packed structure of the latter. The FCC anti-bonding levels (figure 2 of Kaspar and Salahub 1981) involve anti-bonding interactions with all twelve NN, whereas the BCC structure only has eight NN and $7t_{2g}^{\uparrow}$ and $6e_g^{\uparrow}$ show some weakly bonding interactions as well (figure 11). It should also be noted that BCC Fe–Ni alloys (0 to about 25 at% Ni) show analogous behaviour for a , μ and α (Bozorth 1951) to that of the Fe–Co alloys, so that we may apply our model to those systems as well.

If the broad minimum of the thermal expansion coefficient between 30 and 50 at% Co is entirely an electronic effect of the Invar type, then from our model we must assume that the weak ferromagnetic situation is sustained up to this concentration. This disagrees with the results of the ASW calculation for FeCo which yields a strong ferromagnet having a completely filled majority-spin band. In the band picture, the contraction of the lattice must therefore be explained with the imperfect screening of the Co nucleus alone, and the minimum of the thermal expansion coefficient (if it is an electronic effect) must be explained in some completely different way.

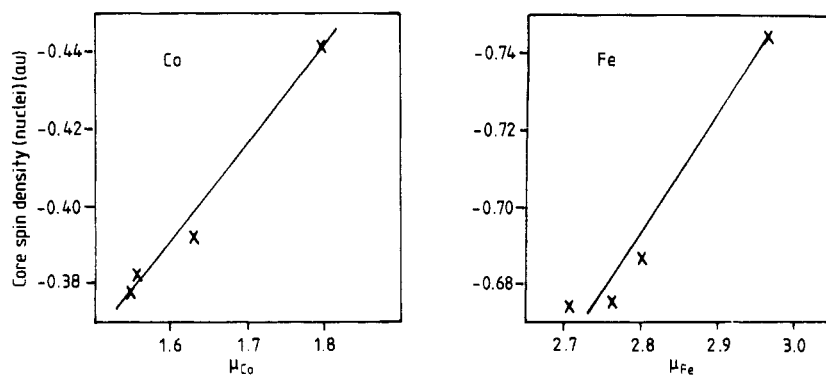
Further details of the cluster MO interpretation of the Invar effects and a discussion of its relationship to other models will be given elsewhere (J Kaspar and D R Salahub 1982, unpublished).

3.2.4. Hyperfine fields. The hyperfine fields (B_{hf}) (spin densities at the nuclei) have been computed for the cluster atoms and analysed in terms of core (1s, 2s, 3s) and valence (4s) contributions (table 5). The extreme sensitivity of this property to the environment of the atoms is apparent. While this precludes a direct quantitative interpretation of hyperfine data for the bulk alloys based on the cluster results, the very fact that the clusters contain several different atomic environments has allowed us to isolate some general systematic trends which are helpful in the interpretation of the bulk data. Several authors (Marshall 1958, De Mayo *et al* 1970, Montano and Seehra 1977) have suggested that $B_{\text{hf}}^{\text{core}}$, the core contribution to B_{hf} , should be proportional to the local magnetic moment on the atom. This is quite closely verified by the cluster calculations (figure 12). In addition we find (figure 13) that the valence hyperfine fields, $B_{\text{hf}}^{\text{val}}$ are proportional to μ_s , the s moment on each atom (table 3, figure 13). It is therefore likely that there is a single underlying mechanism for the variation of μ_s and $B_{\text{hf}}^{\text{val}}$ with composition or with local order. The proportionality of $B_{\text{hf}}^{\text{val}}$ (the 4s spin density at the nucleus) to μ_s (the integrated 4s spin density) indicates that the spatial form of the functions is almost spin independent. What is spin dependent is the degree of hybridisation of the 4s with the 3d functions. Examination of the partial-wave charges for corresponding majority- and minority-spin levels, shows that the main negative contributions to μ_s come from the lower-lying bonding MO. It seems that the stabilisation of the majority-spin d band removes the bonding levels to an energy region where they can mix less effectively with s levels. In most cases the negative s polarisation from the bonding orbitals is larger than the terms of opposite sign from the non-bonding and anti-bonding levels. This change in hybridisation is the source of the negative ‘non-local’ moment of Fe and also the negative value of $B_{\text{hf}}^{\text{val}}$ (see also table 3 of Callaway and Wang 1977).

The s–d hybridisation is a subtle feature of the electronic structure and is highly dependent on the environment. Its complete understanding represents a very difficult

Table 5. Calculated hyperfine fields (kG) for the calculations^a.

	Fe ₁₅	CoFe ₈ Co ₆	FeCo ₈ Fe ₆	Co ₁₅
Central atom	Fe	Co	Fe	Co
1s	-11	0	-3	-2
2s	-292	+1	-87	-53
3s	+171	+6	+52	+35
Valence	-415	-445	-300	-273
Total	-548	-438	-337	-293
Experiment	-339 ^b	-265 ^c	-340 ^e	-219 ^g
1st NN	Fe	Fe	Co	Co
1s	-25	-24	-17	-16
2s	-664	-649	-403	-409
3s	+335	+318	+222	+220
Valence	-56	+81	-59	-41
Total	-409	-273	-257	-246
Experiment	-339 ^b	-343 ^d	-260 ^f	-219 ^g
2nd NN	Fe	Co	Fe	Co
1s	-26	-19	-27	-20
2s	-675	-407	-720	-462
3s	+341	+226	+358	+251
Valence	+74	-324	-37	-129
Total	-286	-524	-427	-360
Experiment	-339 ^b	-265 ^c	-340 ^e	-219 ^g

^a 1 au = 523.6 kG.^b Budnick *et al* (1961).^c For the 47 at% FeCo alloy (Arp *et al* 1959).^d For the 47 at% FeCo alloy (Johnson *et al* 1963).^e For the 53 at% FeCo alloy (Johnson *et al* 1963).^f For the 53 at% FeCo alloy (Arp *et al* 1959).^g For HCP Co (Arp *et al* 1959).**Figure 12.** Core contribution to the spin density at the nuclei (au) against local magnetic moment for first and second NN atoms in the clusters Fe₁₅, CoFe₈Co₆, FeCo₈Fe₆ and Co₁₅.

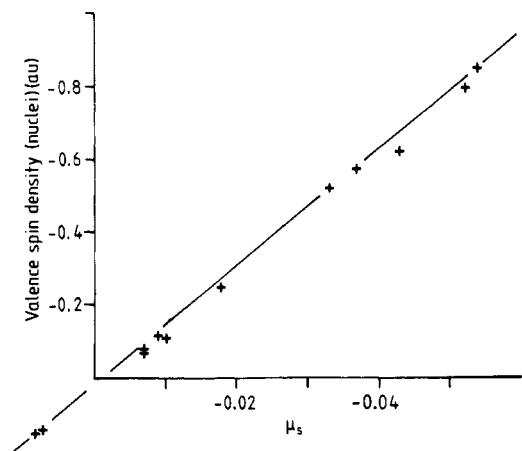


Figure 13. Valence contribution to the spin density at the nuclei (au) against magnetic moment due to valence s electrons (μ_s).

problem. While we do not pretend to have solved this problem, the following, admittedly oversimplified, analysis does shed some light on what we feel are the main contributing factors to the changes in the hybridisation and hence of μ_s and $B_{\text{hf}}^{\text{val}}$ upon changes in the local environments of the Fe and Co atoms.

Reasoning qualitatively that the maximum in the 4s radial density is far from the nucleus, it will feel the NN potentials quite strongly. In figure 14 we have plotted μ_s for each of the atoms in the cluster against the sum of the NN d moments. While the correlation is far from perfect, there is a definite tendency for a given atom to have a large s moment if it is surrounded by atoms having large d moments and *vice versa*. Considering that in the FeCo alloys the Fe d moments are always larger than those of Co, then increasing the Co concentration should lead to less negative values of μ_s and also less negative values for $B_{\text{hf}}^{\text{val}}$.

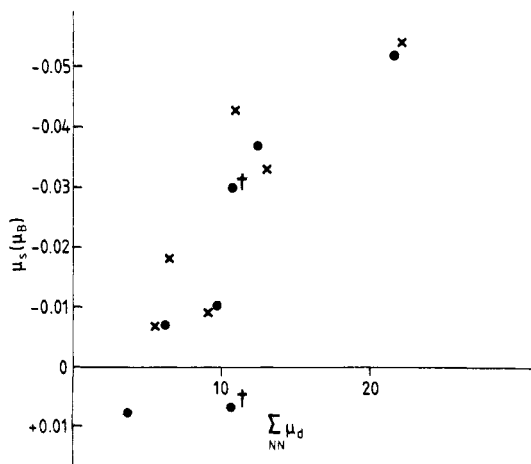


Figure 14. Magnetic moments due to valence s electrons (μ_B) for the various atoms of the clusters against the sum of NN d moments (μ_B). ●, Fe; ×, Co; ●†, values for Fe₁₅; the higher value corresponds to transferring the single electron in $6e_g^\uparrow$ to the $4t_{2g}^\uparrow$ level which is at the same energy.

for both Fe and Co. Indeed, these are the trends of $B_{\text{hf}}^{\text{val}}$ which are required to interpret the experimental variation of $B_{\text{hf}}(\text{Fe})$ and $B_{\text{hf}}(\text{Co})$, given the values of the local moments from the neutron experiments and the proportionality between these and $B_{\text{hf}}^{\text{core}}$.

A quantitative analysis is fraught with difficulties owing to the high sensitivity of the fields to both theoretical (e.g. the exchange-correlation potential) and experimental (e.g. sample preparation and history) factors. Nevertheless, if we are willing to allow some reasonable assumptions, some progress can be made.

We first examine the dependence of the core contact field for Fe on the local magnetic moment. The calculated slope of figure 12 is $-163 \text{ kG } \mu_{\text{B}}^{-1}$. An experimental estimate of this quantity can be made from the difference (-10 kG) in the hyperfine fields of De Mayo *et al* (1970) for the disordered and ordered 50 at% alloy if the following assumptions are made: (i) that the first NN of Fe in the ordered alloy are Co atoms whereas in the disordered alloy the ratio is 4 Fe to 4 Co; (ii) that only the first NN are important for the difference in the valence field in these alloys; (iii) that, because of the approximate constancy of the Co moment, change in the Co hyperfine field is entirely due to the 4s valence field changes coming from the different environment and corresponds to a linear change of 54 kG over a 50 at% Co concentration range (Arp *et al* 1959); (iv) that the same value, 54 kG for a 50 at% change in Co concentration, is appropriate for Fe (figure 14 does not show any marked difference for Fe and Co); (v) that the difference in the local magnetic moment on Fe for the ordered and disordered alloy is $0.26 \mu_{\text{B}}$ (Spooner *et al* 1971). Then the difference in the hyperfine field of the disordered and ordered 50 at% FeCo alloy can be written as

$$\begin{aligned} \Delta B_{\text{Fe}}^{\text{tot}}(\text{disordered} - \text{ordered}) \\ = \Delta B^{\text{val}}(50 \text{ at\% change in Co concentration}) + a \Delta \mu (\text{disordered} - \text{ordered}) \end{aligned} \quad (12)$$

or $-10 \text{ kG} = -54 \text{ kG} + a(-0.26 \mu_{\text{B}})$ from which it follows that $a = -169 \text{ kG } \mu_{\text{B}}^{-1}$, a value surprisingly close to our computed value. Given the uncertainties in our assumptions this close agreement must be regarded as fortuitous; however, it does show that the computed value is not unreasonable. An important consequence is that the small difference of only about -20 kG between the experimental fields on Fe in the 50 at% FeCo alloys and in pure Fe (Johnson *et al* 1963, De Mayo 1970) requires a large positive change in the 4s contact field in going from Fe to the 50 at% alloys; with our computed value, the experimental increase in the local Fe moment by $0.8 \mu_{\text{B}}$ would change the core contact field by -130 kG and consequently the iron 4s field should change by $+110 \text{ kG}$. Since this change is about twice as large as the value implied from the changes in the neighbours (54 kG), the change in the valence field must involve local chemical effects for the concentration range 0–50 at% Co and does not change just linearly with the Co concentration. Since the value of the 4s contact field for pure iron from band calculations (Callaway and Wang 1977) is found to be about -100 kG , the 4s field for the 50 at% alloy may actually change sign as has been suggested by De Mayo *et al* (1970). Again it should be emphasised that this analysis is very sensitive to the assumptions although the qualitative conclusions are not dependent on a precise value of a . Analysis of band calculations for the alloys would be of interest.

In summary, the overall picture of the hyperfine fields that emerges from the calculations and experiments is that $B_{\text{hf}}^{\text{core}}$ is proportional to the local moment on a given atom whereas changes in $B_{\text{hf}}^{\text{val}}$ depend primarily on the moments of the nearby surrounding atoms.

3.2.5. Some comments on order-disorder effects. The results in the previous sections have yielded some insight into the dependence of magnetic moments and hyperfine fields of a given atom on its environment. The chemical (electronegativity) effects on the local moments discussed in § 3.2.1 depend primarily on the type of NN as do the valence hyperfine fields. The core hyperfine fields also depend on the neighbours in an indirect fashion through their dependence on the local moments. Since the major effect of an order-disorder transition is to change the local arrangement of atoms, we believe the following comments may be helpful in understanding the observed magnetic effects of the order-disorder transition of the Fe-Co alloys.

The number of FeCo interactions (which lead, according to the analysis of § 3.2.1, to the large value of μ_{Fe}) is a maximum for the ordered alloys and is reduced in the disordered ones. The analysis of polarised neutron experiments by Spooner *et al* (1971) gives, in accordance with our view, larger moments for Fe and smaller moments for Co in the ordered 50 at% Co alloy compared with the disordered one. Since the core hyperfine fields are proportional to the local moments, $B_{hf}^{core}(Fe)$ should become more negative and $B_{hf}^{core}(Co)$ more positive upon ordering. On the other hand, the arguments of the last section would indicate that $B_{hf}^{val}(Fe)$ should become less negative and $B_{hf}^{val}(Co)$ more negative upon ordering. To our knowledge, no measurements have been made for Co. There have been conflicting data for $B_{hf}(Fe)$ (Johnson *et al* 1961, De Mayo *et al* 1970, Montano and Seehra 1977), the later experiments showing that $B_{hf}(Fe)$ becomes less negative on ordering, indicating that the change in B_{hf}^{val} is larger than that in B_{hf}^{core} .

As in the discussion in § 3.2.3 we do not attribute the increase in the average magnetisation with ordering (figure 1(b)) simply to an increase in the Fe magnetic moments by a minority-spin charge transfer from Fe to Co since this increase would be counteracted by the corresponding decrease in the Co moments. The increase in the average magnetisation can be rationalised if, recalling the Invar mechanism, we assume that some of the anti-bonding majority-spin MO of the disordered system (which we identify with the $6e_g^\uparrow$ and $7t_{2g}^\uparrow$ MO of the clusters) are partially unoccupied and become filled in the ordering process. This would also lead to an increase of the lattice constant upon ordering, in agreement with experiment (figure 1(a)). We would also predict from this reasoning that the thermal expansion coefficient should be smaller for the ordered alloy. Fine and Ellis (1948) have indeed found a slightly smaller thermal expansion coefficient for the slowly cooled (presumably ordered) 50 at% FeCo alloy than for a quenched sample. This mechanism requires at least the disordered alloys to be weak itinerant ferromagnets.

We hope that this analysis will provoke a more comprehensive experimental study of these properties.

4. Summary

The present study shows that the basic features of the BCC FeCo alloys are already present in small, 15-atom mixed FeCo clusters. Examination of the LDOS in conjunction with a local Stoner criterion and simple spin-dependent orbital-electronegativity arguments has led to an explanation for the concentration dependence of the local moments. The average magnetisation, volume and thermal expansion coefficient behave in a similar (though less dramatic) fashion to those of the Invar alloys and we interpret their behaviour as being due to the presence of localised majority-spin anti-bonding orbitals near the Fermi level for a limited range of concentration. The changes observed experimentally in the hyperfine fields

at Fe and Co are interpreted as the result of changes in the core contact field which are found, from the clusters, to be roughly proportional to the local magnetic moment, and changes in the valence contributions which depend primarily on the moments of the nearby surrounding atoms. Finally, the calculations have led to a rationalisation of the effects of the order-disorder transition on the magnetic and mechanical properties of the alloys.

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