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## Isomer shifts and hyperfine fields in iron compounds

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**Abstract.** The  $^{57}\text{Fe}$  isomer shifts and magnetic hyperfine fields in several iron compounds are computed using self-consistent spin-polarised electronic structure calculations within the LMTO formalism. A good account of experimental trends is obtained, and a value for the mean square radius difference between the two nuclear states involved in the  $^{57}\text{Fe}$  isomeric transition of  $\Delta\langle r^2 \rangle = -20 \times 10^{-3} \text{ fm}^2$  is derived. In the compounds considered the hyperfine field is found to scale with the local iron moment except for those cases where the Fe majority band is fully occupied.

### 1. Introduction

Mössbauer spectroscopy using the 14.4 keV isomeric transition in  $^{57}\text{Fe}$  is a very powerful tool for monitoring the local chemical and magnetic properties of metals as well as minerals and biological compounds (Greenwood and Gibb 1971, Shenoy and Wagner 1978). The two most prominent parameters revealed by experiment are the isomer shift and the magnetic hyperfine field. Numerical calculations of these quantities are of considerable interest since they provide valuable insight into the basic electronic properties that cause the observed variations. The present work reports such calculations for a number of metallic compounds containing Fe as a component.

The isomer shift,  $\Delta S$ , is proportional to the total density of electrons at the nucleus  $\rho(0)$  (the contact density):

$$\Delta S = \alpha(\rho(0) - \rho_{\text{ref}}(0)). \quad (1)$$

Here  $\rho_{\text{ref}}(0)$  is the contact density in a reference material and  $\alpha$  is the  $^{57}\text{Fe}$  isomer-shift calibration constant, which depends on the detailed structure of the two nuclear states involved in the Mössbauer transition.

The hyperfine field,  $B_{\text{hf}}$ , can, in the absence of an external field, be separated into three distinct contributions (Greenwood and Gibb 1971): the magnetic dipole term, the orbital momentum term and the Fermi contact term. Of these, the first two are, for the systems studied in this work, generally at least an order of magnitude smaller than the third. Hence, we concentrate in this work on the Fermi contact term, which in the non-relativistic limit is given by

$$B_{\text{hf}} = \frac{8}{3}\pi\mu_{\text{B}}^2(\rho_{\uparrow}(0) - \rho_{\downarrow}(0)) \quad (2)$$

where  $\mu_{\text{B}}$  is the Bohr magneton. In a fully relativistic derivation of the hyperfine field

Blügel *et al* (1987) arrived at a similar expression, except for the fact that the spin density at the origin,  $m(0) = \rho_{\uparrow}(0) - \rho_{\downarrow}(0)$ , should be replaced by the average of this quantity over a region of extension given approximately by the Thomas radius  $r_T = Ze^2/mc^2$ .  $r_T$  gives the distance where the nuclear potential equals the electron rest energy, which in the case of  $^{57}\text{Fe}$  is approximately 16 times the nuclear radius. Thus, the contact hyperfine field is a somewhat more delocalised quantity than the isomer shift. Relativistic effects on calculated hyperfine fields are also discussed by Ebert *et al* (1988).

Numerous theoretical studies have dealt with the computation of electron and spin contact densities. Most of these are based on atomic calculations relying on somewhat crude assertions of the effects of the solid-state environment. Considerably more appropriate for solid-state studies are those calculations that use a proper band-structure approach (Mielczarek and Winfree 1975, Ohnishi *et al* 1983, Svane and Antoncik 1986, Akai *et al* 1986, Dumelow *et al* 1986, Blügel *et al* 1987, Lindgren and Sjöström 1988, Svane 1988, Ebert *et al* 1988, Eriksson *et al* 1988). In the present work equations (1) and (2) are investigated for the case of  $^{57}\text{Fe}$  by computing the electronic structure of several Fe compounds using the first-principles LMTO method (Andersen 1975, Skriver 1984) in the scalar relativistic and local density approximations. The aims of this study are at least threefold. First the linearity between the calculated RHS of (1) and (2) and the measured LHS should be reproduced both as a test of our general understanding of hyperfine interactions and of the accuracy of our computational procedure. Second, a value of the calibration constant  $\alpha$  in (1) may be derived. Third, but not least, the calculations allow the identification of those specific properties that cause the variations in the observed hyperfine interactions.

To meet these goals, it is desirable to cover classes of Fe systems with as wide a range of chemical and magnetic properties as possible. Therefore, the compounds considered here comprise the ionic FeO, the slightly ionic Fe<sub>2</sub>P, the predominantly metallic FeAl and Fe<sub>3</sub>Al alloys as well as pure  $\alpha$ Fe and finally the YFe<sub>2</sub> inter-metallic compound in which Fe is the more electronegative constituent. In addition, in order to cover the whole Fe–Al composition range, the electronic structure of an isolated substitutional Fe atom in an Al host is also computed.

The technical aspects of our calculations are discussed in § 2. Section 3 presents the electronic structure results and the calculated hyperfine parameters, while § 4 presents the conclusions.

## 2. Details of computations

To compute the electronic structure of the various Fe compounds considered in this work, we use the method of linear muffin-tin orbitals (LMTO) (Anderson 1975, Skriver 1984) in the atomic sphere approximation (ASA) and with the local spin density (LSD) approximation for exchange and correlation (von Barth and Hedin 1972). For the calculation of substitutional Fe in Al, we use the Green-function version of the LMTO method (Gunnarsson *et al* 1983). In ASA the crystal volume is filled with spheres centred on the atomic positions. The spheres are allowed to overlap slightly to cover a volume equal to the actual equilibrium volume and inside each sphere the potential is assumed to be spherically symmetric. A first-order correction for sphere overlap (the 'combined correction term' (Andersen 1975, Skriver 1984)) is employed. The self-consistent crystal charge density is obtained using the tetrahedron method (Jepsen and Andersen 1971) with approximately 100  $k$ -points in the irreducible wedge of the Brillouin zone, the

precise number depending on crystal structure. The spin contact density is read off from our first radial mesh point, which is taken very close to the nuclear radius  $=1.2 A^{1/3}$  fm, with  $A = 57$  the mass number. Explicit tests showed this to be an excellent approximation for comparing *differences* in contact densities, such as are given by (1) and (2). The valence electronic structure is computed including scalar-relativistic effects (i.e. omitting spin-orbit coupling). All electrons are fully included in the self-consistency iterations by applying an unrestricted Dirac-Fock-Slater relativistic atomic program (Ellis and Goodman 1984) to the core states in the presence of the crystal valence charge.

Of the Fe compounds considered here,  $\alpha$ Fe has the BCC structure, while  $\text{Fe}_3\text{Al}$  has the  $\text{DO}_3$  structure, which is obtained from BCC  $\alpha$ Fe by replacing every fourth Fe atom on an FCC sublattice with an Al atom. Similarly, FeAl in the CsCl structure is generated by replacing every second Fe atom in  $\alpha$ Fe by Al. Electronic structure calculations of Fe-Al alloys have been published by Nagel *et al* (1978), Min *et al* (1986), Koch *et al* (1986) and Koch and Koenig (1986, 1987). Experimentally,  $\alpha$ Fe and  $\text{Fe}_3\text{Al}$  are ferromagnets, while FeAl is paramagnetic, although perfectly ordered FeAl is never produced due to formation of vacancies, anti-structure defects and magnetic clusters (see Koch and Koenig (1986) and references therein).

FeO (wüstite) crystallises in the NaCl structure and is found to be paramagnetic above 198 K, while the crystal structure is distorted below 198 K and antiferromagnetic order occurs. This compound is never found with perfect stoichiometry but with 6–10% deficiency of Fe. FeO is believed to be a Mott insulator, where the Fe 3d electrons occupy localised orbitals—a picture clearly in contrast with the itinerant approach used in the present work. The full self-consistent calculation of this state is not possible with the LSD approximation but may be achieved within the self-interaction corrected LSD theory (Svane and Gunnarsson 1988). Such *ab initio* calculations of electronic ground states of Heitler-London type pose great numerical difficulties and are only now becoming possible (Svane and Gunnarsson 1989). Nevertheless, it is interesting to compare contact densities obtained within LSD with experimental hyperfine parameters to see if there is a clear difference. Electronic structure calculations of ideal FeO with the LSD approximation were reported by Anderson *et al* (1979) and Terakura *et al* (1984), while Chou *et al* (1986) have considered defective compounds in a cluster approximation.

$\text{YFe}_2$  crystallises in the cubic Laves phase. The electronic structure of this compound has been discussed by Yamada *et al* (1984), Mohn and Schwarz (1985), Dumelow *et al* (1986), Armitage *et al* (1986) and Asano and Ishida (1988). The crystal structure of  $\text{Fe}_2\text{P}$  is complex with a hexagonal unit cell containing three formula units (Carlsson *et al* 1973, Lundgren *et al* 1978, Fujii *et al* 1979). Two crystallographically different Fe sites are found, denoted in the following  $\text{Fe}_2\text{P}(1)$  and  $\text{Fe}_2\text{P}(2)$ .  $\text{Fe}_2\text{P}(1)$  has four nearest-neighbour P atoms, while  $\text{Fe}_2\text{P}(2)$  is surrounded by five P atoms, but at significantly greater separation (about 10%) than for  $\text{Fe}_2\text{P}(1)$ . The two different Fe atoms have clearly different magnetic and hyperfine characteristics, as discussed by Ishida *et al* (1987), Fujii *et al* (1988) and Eriksson *et al* (1988).

Finally, the isolated substitutional Fe impurity in FCC Al was considered by Deutz *et al* (1981), who used the KKR Green-function method.

### 3. Results

Table 1 lists the calculated electron contact densities and hyperfine fields together with experimental information. Also given are the calculated and observed Fe moments and

**Table 1.** Hyperfine parameters for Fe compounds.  $\Delta X$  is the Pauling electronegativity difference between Fe and its ligand,  $\Delta\rho$  the difference in Fe electron contact density with respect to  $\alpha\text{Fe}$  ( $a_0^{-3}$ ) and  $\Delta S$  the experimental isomer shift with respect to  $\alpha\text{Fe}$  ( $\text{mm s}^{-1}$ ).  $B_{\text{hf}}$  is the hyperfine field (T) and  $\mu_{\text{Fe}}$  the Fe magnetic moment ( $\mu_B$ ).

	YFe <sub>2</sub>	$\alpha\text{Fe}$	Fe <sub>3</sub> Al(1)	(2)	FeAl	Al(Fe)	Fe <sub>2</sub> P(1)	(2)	FeO
$\Delta X$	0.5	0	0.2		0.2	0.2	-0.4		-1.7
$\Delta\rho(0)$	+0.35	0	+0.03	-0.81	-0.98	-2.19 <sup>a</sup>	-1.41	-1.52	-4.02 <sup>a</sup>
$\Delta S$	-0.12 <sup>b</sup>	0	+0.06 <sup>c</sup>	+0.20 <sup>c</sup>	+0.25 <sup>c</sup>	+0.42 <sup>d</sup>	+0.27 <sup>e</sup>	+0.54 <sup>e</sup>	+0.88 <sup>e</sup>
$B_{\text{hf}}$ (theor.)	-22.7	-33.9	-31.3	-26.2	-10.4	—	-14.6	-12.3	-23.7
(expt)	-21.3 <sup>b</sup>	-33.8 <sup>f</sup>	-31.8 <sup>g</sup>	-24.2 <sup>g</sup>	0 <sup>c</sup>	0 <sup>d</sup>	-11.4 <sup>e</sup>	-18.0 <sup>e</sup>	-34 <sup>h</sup>
$\mu_{\text{Fe}}$ (theor.)	1.74	2.23	2.21	1.92	0.77	1.73	0.96	2.04	3.73
(expt)	1.45 <sup>i</sup>	2.22	2.16 <sup>j</sup>	1.46 <sup>j</sup>	0 <sup>c</sup>	0 <sup>d</sup>	1.03 <sup>k</sup>	1.91 <sup>k</sup>	—

<sup>a</sup> Paramagnetic.

<sup>b</sup> Guimaraes and Bunbury (1973).

<sup>c</sup> Czjzek and Berger (1970), Jeandey and Peretto (1975).

<sup>d</sup> Preston and Gerlach (1971), Janot *et al* (1974).

<sup>e</sup> Wäppling *et al* (1975).

<sup>f</sup> Greenwood and Gibb (1971).

<sup>g</sup> Johnson *et al* (1963).

<sup>h</sup> Greenwood and Howe (1972).

<sup>i</sup> Half the total moment per formula unit ( $2.90\mu_B$ , Buschow and van Stapele (1970)).

<sup>j</sup> Nathans *et al* (1958).

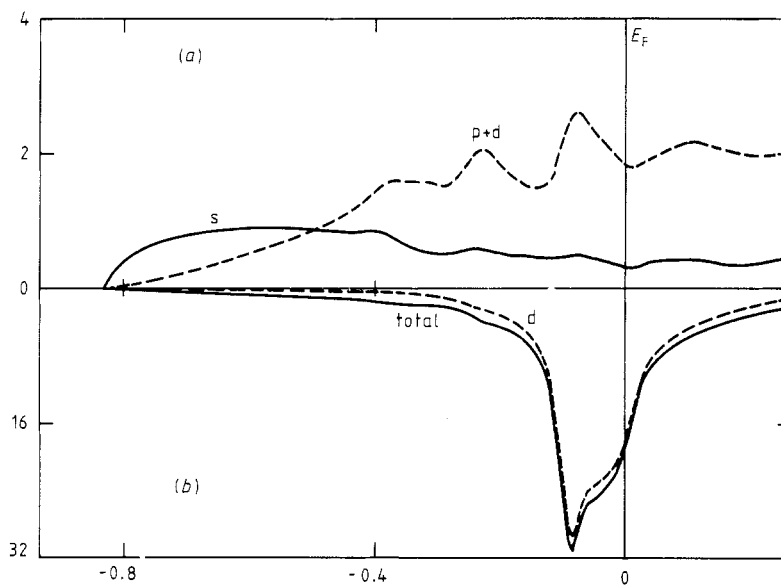
<sup>k</sup> Eriksson *et al* (1988).

the Pauling electronegativity difference between Fe and its ligand:  $\Delta X = X_{\text{Fe}} - X_{\text{L}}$ . Spin polarisation was allowed for in all calculations and in all cases a ferromagnetic minimum of the LSD energy functional was found.

The isolated Fe impurity in Al is experimentally found to be non-magnetic, while the present calculations find a considerable magnetic moment  $\mu_{\text{Fe}} = 1.73\mu_B$  on the Fe atom with the nearest-neighbour Al shell antiferromagnetically aligned;  $\mu_{\text{Al}} = -0.013\mu_B$ . This is in close agreement with the value of  $\mu_{\text{Fe}} = 1.78\mu_B$  found by Deutz *et al* (1981) and, as discussed by these authors, Fe in Al is close to the borderline between magnetic and non-magnetic systems. Therefore, the discrepancy between theory and experiment—though of large qualitative significance—is rather minor. It is most probably due to neglect of the relaxations of the positions of the nearest-neighbour Al atoms in the theoretical calculations. Since the nearest-neighbour distance is approximately 14% greater in Al than in FeAl, one may anticipate that the nearest-neighbour Al shell around the Fe impurity will relax inwards; thus effectively exerting pressure on the Fe impurity with a consequential decreasing moment.

In figure 1 we depict the projected density of states (DOS) of the Fe atomic sphere (paramagnetic case) in comparison with the pure Al DOS. The Fe d states are seen to give rise to a narrow resonance  $\sim 0.1$  Ryd below the host Fermi level with an asymmetrical lineshape due to hybridisation with the Al p states. From the figure it follows that the Fe LDOS at the Fermi level (and hence the Stoner product) is quite sensitive to the final self-consistent position of the Fe d resonance.

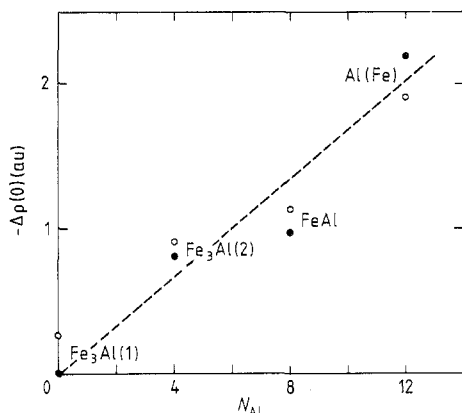
The calculated moment of FeAl is somewhat small and the Stoner product only slightly greater than unity. This indicates that the ferromagnetism of FeAl is only marginally favoured over the paramagnetic ground state. We find a 1.4 mRyd/unit cell total energy difference between these two states (at the experimental equilibrium



**Figure 1.** Partial DOS of (a) FCC Al and (b) substitutional Fe in Al (paramagnetic), in units of electrons per rydberg per atom and per spin. The Al Fermi level is marked and the energy measured in rydberg relative to this.

volume). Similar results were obtained by Min *et al* (1986). The fact that experimentally the paramagnetic state seems to be favoured is, therefore, not very much at variance with theory, especially since samples of FeAl deviate somewhat from pure CsCl structure due to intrinsic defects. We also tried to impose an antiferromagnetic electronic structure in the FeAl alloy, since the occurrence of this ordering has been conjectured (Arrott and Sato 1959), but failed to produce a finite antiferromagnetic moment, i.e., the sublattice moment iterated to a zero value.

In  $\text{Fe}_3\text{Al}$  there are two inequivalent Fe sites, denoted (1) and (2) in table 1. The (1) site is surrounded by eight nearest-neighbour Fe(2) atoms, while the (2) site is surrounded by four Fe(1) and four Al atoms in the nearest-neighbour shell. Thus, the near neighbourhood of an Fe(1) atom is very similar to that encountered in  $\alpha\text{Fe}$ , and indeed the electronic configuration of the Fe(1) atom comes out quite close to that of  $\alpha\text{Fe}$ , both in theory and experiment. In contrast, the Fe moment and hyperfine field decrease on the (2) site relative to the (1) site, and the isomer shift with respect to  $\alpha\text{Fe}$  increases due to a smaller contact density for Fe(2). The effect of an increasing number of Al nearest neighbours can be seen in the sequence  $\alpha\text{Fe}$  (or  $\text{Fe}_3\text{Al}(1)$ ),  $\text{Fe}_3\text{Al}(2)$ , FeAl. With increasing Al coordination the Fe magnetic moment is quenched. Experimentally, this quenching is completed between fourfold coordination in  $\text{Fe}_3\text{Al}(2)$  and eightfold coordination in FeAl, while theory predicts its occurrence at more than eightfold coordination. The Fe electron contact density also decreases with increasing Al coordination (figure 2) and from the Fe angular-momentum-decomposed charges this trend is seen to correlate with an increased depletion of s charge from the Fe atom. Thus, from the isomer shift alone, one would conclude that Al is more electronegative than Fe. This contrasts with the Pauling scale of electronegativity, which rates Al as slightly more electropositive than Fe (table 1). However, the Fe d charge (sum of majority and minority occupation) shows no obvious trend with Al coordination (contrary to the

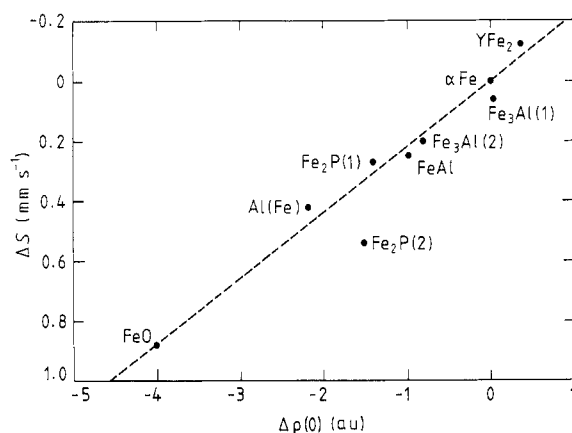


**Figure 2.** Experimental (○) and theoretical (●) electron contact density (relatively to  $\alpha Fe$ ) as a function of nearest-neighbour Al coordination  $N_{Al}$  in Fe–Al systems.

variation of the moment discussed above, which is mainly the *difference* between majority and minority Fe d occupation).

The electronic structure and hyperfine parameters of  $Fe_2P$  have been discussed by Eriksson *et al* (1988). The calculated moments of the two different Fe sites agree well with experiments, although the electron and spin contact densities of the Fe(2) atom are rather badly reproduced, whereas the data for the Fe(1) atom coincide with experimental values within the same accuracy as is found for the other compounds of table 1. In particular, the large experimental isomer shift relative to  $\alpha Fe$ —placing  $Fe_2P(2)$  at approximately 60% of the shift in FeO—is not reproduced in the calculations, which give approximately the same shift for the two inequivalent Fe sites in  $Fe_2P$ , albeit correctly with a more positive shift for the (2) site than for the (1) site. We see no simple explanation for this discrepancy between theory and experiment but note that, among the compounds considered here,  $Fe_2P$  complies worst with the overlapping sphere geometry of the ASA. Apart from the different moments, the most significant difference in electronic structure between the two Fe sites is that the Fe(1) site holds 0.16 more electrons than the Fe(2) site. This charge surplus is an effect of the neighbouring P atoms being closer to the Fe atom at the (1) site than at the (2) site with an increased overlap of charge clouds. The extra electrons at the Fe(1) atom are predominantly of non-s character, but also a 0.04 s electron excess is found. The larger s occupancy enhances the contact density, while the larger non-s charge component screens the s partial wave leading to a smaller contact density. As these two effects roughly balance, the contact densities of the (1) and (2) sites come out approximately equal, with that of the (1) site 0.1 au higher than that of the (2) site. The experimental shifts (table 1) correspond to a 1.2 au higher contact density of the Fe(1) site.

For FeO both paramagnetic and ferromagnetic band calculations were performed, but the difference in Fe contact density between these two cases is only 0.18 au (highest in the ferromagnetic case). Since experiment refers to the paramagnetic phase above  $T_c = 198$  K, it is the contact density of the unpolarised calculation that is quoted in table 1. The Fe contact density is considerably smaller in FeO than in any of the other compounds considered here. This is due to the ionic character of this compound causing a significant charge transfer to the oxygen atom. Comparing the charge content of a sphere of radius 2.54 au around the Fe atom in  $\alpha Fe$  and in FeO, 0.3 s, 0.2 p and 0.1 d electrons are lacking in the latter case. This leads to the drastic 4.0 au decrease in contact



**Figure 3.** Experimental isomer shift  $\Delta S$  ( $\text{mm s}^{-1}$ ) plotted against theoretical contact density  $\Delta\rho(0)$  ( $a_0^{-3}$ ) of  $^{57}\text{Fe}$  in Fe compounds. Both quantities are given relative to  $\alpha\text{Fe}$ .

density, which is more than 50% of the total valence electron contact density in  $\alpha\text{Fe}$  (approximately  $7.5 \text{ au}$ ). The Stoner product is, however, quite high, approximately 3.7, in the paramagnetic state of FeO and, consequently, ferromagnetism is energetically very much favoured in our zero-temperature calculations. In the ferromagnetic calculation of FeO, the whole majority d band is occupied, leading to a total spin moment of  $\mu_{\text{tot}} = 4.00\mu_{\text{B}}$ /unit cell. The Fe moment is  $3.73\mu_{\text{B}}$ . In the LMTO calculations of FeO reported by Andersen *et al* (1979), the spin polarisation was not complete and  $\mu_{\text{tot}} = 3.44\mu_{\text{B}}$ . We ascribe the difference to our use of the combined correction term in the present calculations. Like Skriver *et al* (1978), we interpret the strong spin polarisation as a hint that the system strives towards localisation of the Fe d states. It is noteworthy that the contact density obtained in the present band approach agrees well with the experimental isomer shift, while the hyperfine field is less accurately calculated.

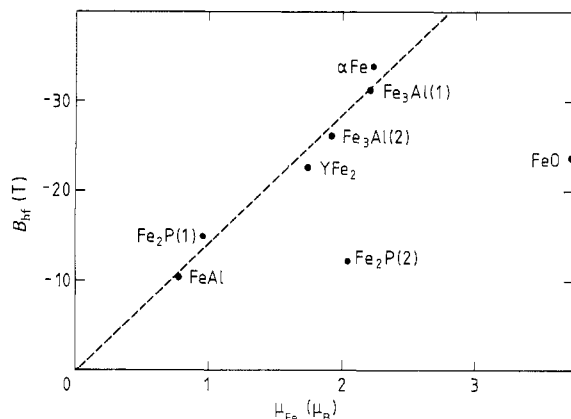
In the cubic Laves phase compound  $\text{YFe}_2$ , Fe is clearly the more electronegative constituent. Therefore, charge is transferred to the Fe atom and the increased s charge, in comparison with  $\alpha\text{Fe}$ , leads to a larger electron contact density, in agreement with experiment. The experimental Fe magnetic moment quoted in table 1 is obtained as half the total moment per formula unit, i.e. assuming no net moment on the Y atom. This definitely underestimates the experimental value for the Fe moment, since our calculation reveals a significant antiparallel moment on the Y atom ( $\mu_{\text{Y}} = -0.38\mu_{\text{B}}$ ). An NMR investigation (Oppelt and Buschow 1976) indeed gave a hyperfine field of  $-22.2 \text{ T}$  on the Y site in  $\text{YFe}_2$ . The computed total moment per formula unit ( $3.1\mu_{\text{B}}$ ) and the Fe hyperfine field agree excellently with experiment. In this and other respects, our results for  $\text{YFe}_2$  resemble those of Mohn and Schwarz (1985) and Asano and Ishida (1988).

In figure 3 the experimental isomer shifts are plotted against the calculated contact densities for the Fe compounds considered. The linearity of (1) is well reproduced, except for the discrepancy for  $\text{Fe}_2\text{P}(2)$ . Leaving out this point of the analysis, the best straight line provides a value for the isomer shift calibration constant:

$$\alpha(^{57}\text{Fe}) = -0.22 \text{ a}_0^3 \text{ mm s}^{-1}. \quad (3)$$

Parametrising  $\alpha$  in terms of the mean square nuclear radius difference between the





**Figure 4.** Theoretical magnetic hyperfine field (T) plotted against theoretical Fe moment ( $\mu_B$ ) in Fe compounds.

excited isomer level and the ground state:  $\alpha = \beta \Delta \langle r^2 \rangle$  with  $\beta = 11.0 a_0^3 \text{ fm}^{-2} \text{ mm s}^{-1}$  (Shenoy and Dunlap 1978), we obtain

$$\Delta \langle r^2 \rangle (^{57}\text{Fe}) = -20 \times 10^{-3} \text{ fm}^2.$$

This calibration falls within the range of previous values (Ingalls *et al* 1978).

In figure 4 are shown the calculated hyperfine fields against calculated Fe magnetic moments. While most of the points fall on a straight line (predicting  $B_{\text{hf}} = -14.2 \mu \text{ T}/\mu_B$ ),  $\text{Fe}_2\text{P}(2)$  and  $\text{FeO}$  are clearly away from this line; in both cases there is too small a ratio between  $|B_{\text{hf}}|$  and the Fe moment. There is no firm theoretical basis for expecting a linear relationship between  $B_{\text{hf}}$  and  $\mu$ —only for the core contribution to  $B_{\text{hf}}$  does this hold (Freeman and Watson 1965). Nevertheless, figure 4 indicates that the valence contribution to  $B_{\text{hf}}$  in most cases scales with the core contribution to give the linear relationship. This explains why magnetic moments, derived from Mössbauer experiments, often agree with other experimental values from, e.g., neutron scattering. It is, however, important to understand the cases that do not obey this rule. The hyperfine fields of  $\text{Fe}_2\text{P}$  were discussed recently by Eriksson *et al* (1988). In particular, the anomalous behaviour of  $\text{Fe}_2\text{P}(2)$  was found to originate from the Fe 4s valence electrons polarising parallel rather than antiparallel to the Fe d moment, leading to a large positive valence hyperfine field. The ‘normal’ antiparallel 4s alignment (found in  $\alpha\text{Fe}$ ,  $\text{Fe}_3\text{Al}$ ,  $\text{FeAl}$ ,  $\text{YFe}_2$  and  $\text{Fe}_2\text{P}(1)$ ) can be understood in terms of the 4s–3d hybridisation, which pushes majority (minority) 4s weight *above* (*below*) the Fermi level and thereby leads to less majority (more minority) 4s occupation (Anderson and Clogston 1961, Herring 1966). For the Fe(2) site in  $\text{Fe}_2\text{P}$ , the same effect is at work, but here essentially the whole majority Fe(2) d band is below the Fermi level, and the direct ferromagnetic 4s mixing into the majority band dominates over the above antiferromagnetic effect. Hence, a positive 4s moment follows. The same mechanism is responsible for  $\text{FeO}$  failing to fit to the common line of figure 4, since in this compound also the whole Fe majority band is occupied. The Fe 4s local moment is parallel to the 3d moment and accordingly there is a large *positive* valence electron contribution to the hyperfine field of Fe in  $\text{FeO}$ .

Comparing calculated and measured hyperfine fields in table 1, significant discrepancies are found only for these two cases of  $\text{Fe}_2\text{P}(2)$  and  $\text{FeO}$ . The difference in the latter case may be due to the rather complex experimental situation in comparison with

our simplified assumptions of an ideal (rather than a distorted and Fe-deficient) rock-salt structure as well as ferromagnetic and itinerant (rather than antiferromagnetically localised) Fe  $d$  states. Since the orbital contribution to the hyperfine field for Fe is positive, an unexpectedly large value of this term cannot explain the discrepancy in  $\text{Fe}_2\text{P}(2)$  and  $\text{FeO}$ . On the other hand, our present procedure for obtaining the Fermi contact density term by just reading off the magnetisation density in the first radial mesh point may be too crude in these cases, where the large positive valence electron contribution originates from a somewhat localised peak around the origin (Eriksson *et al* 1988). Further efforts are needed to clarify this point. We note that for these two cases the hyperfine field is composed of a large negative core term plus a large positive valence term, while in the other systems considered in the present study the valence term is small.

#### 4. Conclusion

From first-principles calculations we have obtained the linear correlations between the isomer shift and the contact density as well as those between the hyperfine field and the spin density at the nucleus. The proportionality constant for the isomer shift is in agreement with previous determinations (Ingalls *et al* 1978). For the hyperfine field both theoretical and experimental proportionality constants have been reported yielding values of  $-13 \text{ T}/\mu_{\text{B}}$  (Ohnishi *et al* 1984),  $-15$  to  $-17 \text{ T}/\mu_{\text{B}}$  (Lindgren and Sjöström 1988) and  $-10 \text{ T}/\mu_{\text{B}}$  (Wäppling *et al* 1975), respectively. These numbers agree well with our finding of a proportionality constant of  $-14 \text{ T}/\mu_{\text{B}}$ .

In the present study we felt it desirable to investigate the trend of isomer shifts and hyperfine fields for as wide a class of systems (metallic to ionic) as possible. However, the  $\alpha\text{Fe}$ ,  $\text{Fe}_3\text{Al}$ ,  $\text{FeAl}$  and  $\text{Al}(\text{Fe})$  systems form a group of their own, with the same iron-ligand (Al) electronegativity difference and approximately the same bond length. Therefore, intuitively, one would expect the contact density, and accordingly the isomer shift, to correlate with the number of nearest-neighbour ligand atoms. Both experimentally and theoretically, a fairly linear relationship between these properties is found, indicating that the local chemical environment in these systems is of major importance concerning the isomer shifts. Both the experimental and our theoretical magnetic moments also suggest such a dependence, since in  $\text{Fe}_3\text{Al}$ , where the Fe(1) atom has eight nearest Fe neighbours, similar to  $\alpha\text{Fe}$ , the Fe(1) moment is the same as in  $\alpha\text{Fe}$ . Also, experimental studies of anti-structure Fe atoms in the  $\text{FeAl}$  compound (Parthasarathi and Beck 1976) give similar results with an Fe moment approximately the same as in  $\alpha\text{Fe}$ .

Since it has been suggested that there is a direct connection between the isomer shift and the  $4s$  orbital population (Menil 1985) we have also investigated this possibility. However, no simple relation was discovered. This is perhaps not too surprising since the relation suggested was for ionic bonds and in the compounds studied here the chemical bonding is of varying nature (metallic to ionic).

Both the all-electron calculations of the magnetic moments and other ground-state properties (pressure, occupation numbers, band masses etc) are in fair or excellent agreement with experiment (where a comparison was possible) and with calculations using the frozen-core approximation. This we have already noted elsewhere (Eriksson *et al* 1988). It can be explained by the fact that the deep-lying core orbitals are relatively insensitive to changes in the valence charge density. The property most sensitive to

relaxing the core orbitals is the isomer shift, since the charge density is dependent on the total potential. The hyperfine field, on the other hand, is mainly an effect of the exchange potential and therefore this quantity is less sensitive to the use of the frozen-core approximation. The only apparent disagreement between theory and experiment is the fact that we find a ferromagnetic ground state in FeAl. Experimentally, there have been reports of FeAl being paramagnetic or antiferromagnetic (Arrott and Sato 1959, Miyattani and Iida 1968). However, anti-structure defects and vacancies (Koch and Koenig 1986) play an important role for the magnetism in 3d aluminide systems, making a comparison rather difficult. In connection with the magnetic properties of an Fe impurity in Al, we have noticed the difference between our theoretical ferromagnetic ground state (in agreement with the calculation by Deutz *et al* (1981)) and the experimental paramagnetic ground state. Possibly, this reflects the non-negligible relaxations of the nearest neighbours. Alternatively, it indicates that the magnetic properties of 3d impurities in an Al host might in some cases be of metamagnetic character.

According to figure 4, with the exception of Fe<sub>2</sub>P(2) and FeO, the hyperfine field is proportional to the magnetic moment. For these systems the valence contribution to the hyperfine field is relatively small. Since the core contribution is indeed proportional to the Fe moment (Freeman and Watson 1965), it follows that an approximately linear behaviour is expected even if the 4s contribution to the hyperfine field would not correlate with the magnetic moment. There are, however, cases where the valence contribution is of appreciable magnitude (Fe<sub>2</sub>P(2) and FeO), and an estimate of the magnetic moments using only hyperfine fields will, therefore, be less reliable.

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