Electronic structure of antistructure defects in FeAl

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Abstract. With the aid of the defect-specified supercells used within the framework of the
linear-muffin-tin-orbital (LMTO) method, the familiar difficulties in calculating the anti-
structure (AS) defects in FeAl can be overcome. The calculations are based on the spin-
dependent version of the Hohenberg–Kohn–Sham scheme. It is hence possible to obtain the
electronic structure of the alloy along with the integral properties, e.g. local magnetic
moments of defects. The occurrence and magnitude of the local moment associated with an
AS-Fe defect is in agreement with the experimental findings.

1. Introduction

Transition-metal aluminides (TAl) with a CsCl structure have been extensively studied
during the past 20 years, by using different experimental methods. This applies par-
ticularly to FeAl which is conspicuous due to a wealth of data, for example data on soft-
x-ray emission and absorption (see e.g. Ziesche *et al* 1978, Blau *et al* 1979, Kapoor *et al*
1973) and data on positron annihilation (see e.g. Meurtin and Lesbats 1976, Sob 1982).
A consistent interpretation of these data is only possible within the framework of band
structure calculations. There are some calculations available on ordered metallic binary
compounds (see e.g. Müller *et al* 1979, Podloucky and Neckel 1979, Eibler and Neckel
1980, Pechter *et al* 1981, Koenig and Khan 1983), but only a few of these are self-
consistent. Off-stoichiometric defects, i.e. vacancies and AS defects on both T and Al
sublattices, are a subject of particular interest. It has been well recognized that these
defects play an important role in determining the physical properties of alloys (see e.g.
Caskey *et al* 1973, Wachtel *et al* 1973, Butler *et al* 1969, Sellmyer *et al* 1972, Amamou
and Gautier 1974). Unfortunately, our knowledge of these defects is still far from
complete, which is even more true for the state of the theory.

Recently, there have been two calculational efforts to clarify the electronic defect
structure in TAl alloys. One attempt was made by Koenig *et al* (1986) and Koch *et al*
(1986, 1987, 1988) who used the Green's function formulas within the LMTO scheme
(Andersen 1975) and the atomic sphere approximation (ASA). Another effort was
made by Stefanou *et al* (1986, 1987) who focused on CoAl and CoGa and used the
Korringa–Kohn–Rostoker (KKR) Green's function method. The case of AS defects in

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FeAl has only been treated by Koch and Koenig (1987). However, these authors ran into difficulties by using a single-site-approximation (SSA) for the defect potential. As a consequence of this approximation they failed to arrive at physically meaningful self-consistent results for the AS-Fe defect. Furthermore their result of 0.666 electrons for the charge of an AS-Al atom appears to be rather implausible if this result is compared to the charge of -0.294 electrons of an Al atom in a regular site of a defect-free alloy. An Al atom in an AS position sees a nearest neighbour shell of eight Al atoms, and hence one expects its charge to be close to zero. For CoAl this expectation has been substantiated by Stefanou *et al* (1987) who included these nearest neighbour atoms in determining the associated self-consistent potential within their KKR Green's function scheme.

Apart from above charge problem for the AS-Al atom which has not yet been solved for the FeAl case, there is a similar problem with the occurrence of a local magnetic moment in an AS-Fe defect. This moment is commonly associated with the polarization of the eight nearest-neighbour Fe- atoms of the AS-Fe defect. The existence of a strongly paramagnetic 'CsCl' phase, which is shown by the large γ-value of the electronic specific heat (Kuentzler 1983), is clearly indicative of this kind of local magnetic cluster. Caskey *et al* (1973) conclude from their susceptibility measurements in the paramagnetic state that each AS-Fe contributes an effective moment of approximately 7.8 μ_B, and they relate this large value to the polarization of the eight Fe atoms adjacent to the AS-Fe atom. In later studies by Domke and Thomas (1984) the local moment is estimated to range from 4 μ_B to 5.4 μ_B depending on the concentration of the vacancies in the compound. A thorough understanding of these results can only be expected from a theoretical analysis of such clusters which is still lacking and has therefore been chosen as one of the subjects of the present article.

As will become evident from our results, the local, spin-density approximation that our calculation is based upon, runs into difficulties when one is dealing with a perfectly ordered FeAl compound. A spin-polarized starting potential can be smoothly carried to self-consistency yielding a sizeable magnetic moment of 0.55 μ_B for the Fe atom, which is clearly at variance with the experimental observations. On the other hand, the total energy of the ferromagnetic state proves to be slightly above the energy of the paramagnetic state indicating that the latter should be the ground state, in agreement with the experiment. Hence, a study with the objective of the present paper should be based on a calculational method which can readily provide information on the electronic structure of the systems in question as well as on sufficiently accurate total energies. From this point of view, a supercell method, as used in the present article, appears to offer practical advantages over Green's function-based methods which, in fact, describe the same physics when compared with the results of sufficiently large supercells. Moreover, a supercell method is particularly suited to providing an insight into the effect of AS-Fe clustering. As will become obvious from the data obtained on the magnetic moments of these defects, the magnitude of the total defect moments depends, in fact sensibly, on their relative distance.

We have tackled the above problems by carrying out electronic structure calculations within the Hohenberg–Kohn–Sham scheme by using a scalar-relativistic version of the linear-muffin-tin-orbital (LMTO) method. The defect structures were modelled by suitably chosen supercells.

This paper is organized as follows: we first give a brief description of the calculational method (section 2). Results on bulk calculations which are useful in the understanding of defect properties are discussed in section 3. Section 4 is concerned with results that

bear directly on the objective of this paper, that is, the electronic structure of AS defects in FeAl.

2. Calculation method

Andersen's LMTO method (Andersen 1975) in its simplified version of the atomic sphere approximation (ASA) has proved to be a highly effective tool for first-principles calculation of the electronic structure and total energies of crystals (for a detailed review see Skriver 1983). In the present paper we have applied this method along with the local density approximation (LDA) to the exchange–correlation functional $E_{xc}[\rho]$. For spin-symmetric and spin-polarized systems we have used the local spin density (LSD-) expression of von Barth and Hedin (1972). The band structures are calculated within the 'scalar relativistic approximation' (Christensen 1981) where spin–orbit coupling is omitted. All calculations were performed including the 'combined correction terms' (Andersen 1975) which correct for the effect that the expansion of the band states is truncated at the same maximum angular momentum $l_{max} = 2$. Moreover, these terms account for the non-sphericity of the Wigner–Seitz-type shape of the individual atomic cells into which the lattice cell can be partitioned. This extension beyond the ASA is indispensible to ensure the necessary accuracy of the total energy calculation (cf. Skriver 1982, 1985). Apart from the valence states that relate to the $3d^64s^2$ orbitals of Fe and the $3s^23p^1$ orbitals of Al, the core orbitals were kept frozen to their form in their respective isolated atoms.

In order to check the convergence of our calculations with respect to the size of the supercell, the electronic structure, and the total energy was determined for three different supercells that comprised 8, 16 and 32 atomic sites, respectively. The corresponding cell sizes are 4, 8 and 16 times larger than that of the primary cell. We shall, in the following denote these cells by SU8, SU16 and SU32 and treat them as building blocks of a periodic structure whose lattice symmetry is, respectively, body-centred cubic (BCC), simple cubic (SIC) and face-centred cubic (FCC) in the respective order of SU8, SU16 to SU32. In the same order, the distance between nearest defects increases from 9.519, 10.992 to 15.545 au. This is to be compared with the defect-nearest neighbour distance of 4.759 au and the defect–next-nearest-neighbour spacing of 5.496 au. For the largest cell, i.e. for SU32, the order of the Hamiltonian and overlap matrices then becomes as large as 288.

In calculating the bulk properties, 286 non-equivalent k-points were used in the irreducible wedge (1/48) of the Brillouin zone (BZ). The partial and total local density of states (LDOS) on different atomic sites was obtained by employing the proven tetrahedron method (Jepsen and Andersen 1971, Rath and Freeman 1975). Calculations on the perfect bulk material were performed by partitioning the irreducible wedge of the BZ into 1000 tetrahedra. The width of the energy grid was chosen to be 1 mRyd. Since the BZ shrinks in size on forming the supercells, the number of k-points and tetrahedra can gradually be reduced as the supercell increases. Tests on the convergence of the number of electrons on the defect sites and the total energies show that the accuracies of 0.01 electrons and 1 mRyd can only be ensured if one chooses 91 k-points and 250 tetrahedra for the SU8 supercell. Correspondingly, 84 k-points and 216 tetrahedra are required for the SU16 case, 22 k-points and 32 tetrahedra for the largest cell, SU32. In the latter case, the total energies change slightly with increasing number of k-points. For example, the total energy of the SU32 supercells increases by about 0.6 eV if one enlarges the number
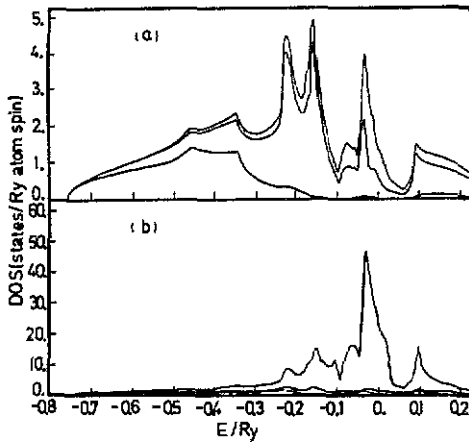
Figure 1. Partial and total LDOS for the Al and Fe atom in a FeAl alloy. Curves from bottom to top: contribution of s electrons, (s+p) electrons, (s+p+d) electrons. The graphs (a) and (b) refer to Al and Fe atoms, respectively. The Fermi level E_F has been chosen as the energy zero in all LDOS plots.

Table 1. Partial densities of states (n) at the Fermi level and number of electrons (N) from integrated LDOS up to the Fermi level for the Fe and Al atomic sites, respectively, decomposed with respect to angular momentum. The density in units of Ryd^{-1} is referenced to the respective atom.

	$n_s(E_F)$	$n_p(E_F)$	$n_d(E_F)$	$\sum_a n_a(E_F)$
Fe	0.208	1.440	37.016	38.764
Al	0.028	0.842	1.678	2.548

	N_s	N_p	N_d	$\sum_a N_a$
Fe	0.604	0.788	6.890	8.282
Al	0.922	1.376	0.420	2.718

of k-points from 10 to 22. This is different from the electronic structure which remains practically unaffected. We have checked the accuracy of our supercell calculations for the SU32 case by dividing the total energy by 16 and comparing the result with the total energy of the unit cell obtained from an analogous calculation. The relative error amounts to only 1.2% as compared with the cohesive energy of the unit cell. An energy grid of 1 mRyd was used throughout the calculations of the present paper.

3. Bulk properties

To our knowledge, first-principles calculations on the cohesive properties of FeAl have not yet been reported in the literature. For that reason we shall first discuss some properties of the perfect bulk material in connection with our calculations on the electronic structure.

Figure 1 shows the partial and total local density of states (LDOS) for the Fe and Al sites. The associated numbers of electrons (obtained by integrating the LDOSs up to the Fermi level) are listed in table 1. Three points deserve particular interest and bear much

Table 2. Calculated structural properties of FeAl. The experimental lattice constant is also listed for comparison.

	Present work	Experiment (Müller *et al* 1983)
S (au)	2.682	2.706
B (Mbar)	1.97	
H (eV per atom)	0.49	

resemblance to results on related Al alloys (Koenig and Khan 1983, Koch and Koenig 1986).

(i) The LDOS of a Fe site displays two d-peaks of different heights which are mainly related to the band states of $d_{t_{2g}}$ and d_{e_g} character, with the latter referring to states of the lower peak. These peaks are separated by a deep minimum near the Fermi level which is, however, closer to the higher peak and hence gives rise to quite a large value of the total LDOS, $n(E_F)$, at the Fermi level. This pecularity is also reflected in the concomitant electronic properties of FeAl as, for example, its electric resistivity, its thermopower, and its electronic specific-heat coefficient (Caskey *et al* 1973) all of which are conspicuously different compared with those of other TAl alloys.

(ii) As can be seen from the comparable magnitude of the (s+p) LDOS on the Al atom and the d LDOS on both atoms, there is a strong hybridization between the Al p states and the Fe d states. Conversely, almost no hybridization exists between the Al s states and Fe d states.

(iii) In accordance with the empirical observation that Fe is more electro-negative than Al, we see from table 1 that on forming the alloy there is, in fact, a charge transfer of 0.282 electrons from the Al to the Fe site.

We now turn to the cohesive properties, i.e. the lattice constant, the bulk modulus and the heat of formation. The lattice constant is related to the Wigner–Seitz radius S used in our ASA approximation and has been determined by locating the minimum of the total energy as a function of S. The bulk modulus B has been obtained by calculating the second derivative of the total energy with respect to S. In accordance with Williams and Kübler (1979) and Hackenbracht and Kübler (1980), we have determined the heat of formation, H, by forming the difference between the total energy of the compound and the total energies of the constituent metals weighted by their concentration in the compound and by dividing this expression by the number of basis atoms. All calculational results on the bulk cohesive properties are compiled in table 2 where the experimental lattice constant has also been inserted for comparison.

It should be pointed out that there is no experimental evidence of a magnetic moment in the perfectly ordered alloy of FeAl, in contrast to the result at which spin-polarized LDA calculations generally arrive. However, we have calculated the total energies both for the para- and ferromagnetic state. It turns out that the total energy per unit cell is 1.5×10^{-3} eV higher for the ferromagnetically-ordered perfect compound compared with the paramagnetic case. Although one can hardly attach much importance to such a minute difference, the result indicates that FeAl obviously represents a borderline case for which an LDA calculation cannot provide a sufficiently definite criterion as to whether or not spin ordering occurs. By contrast, the situation for AS-Fe defects will

Table 3. AS-Al defect. Angular decomposition of the number of occupied states in the defect cell. The notation SU8, SU16 and SU32 refers to supercells containing 8, 16 and 32 atomic sites, repectively. Results obtained by Koch and Koenig (1987) are also compiled for comparison.

		s	p	d	Total
FeAl (present work)	SU8	0.982	1.448	0.382	2.822
	SU16	1.004	1.488	0.386	2.878
	SU32	0.986	1.504	0.380	2.870
FeAl (Koch and Koenig 1987)		1.152	2.013	0.501	3.666

Table 4. AS-Fe defect (notation as in table 3). The local magnetic moments in the defect cell and in the cluster which comprises the defect cell and its nearest neighbours are given in units of Bohr magnetons, μ_B, and are denoted by M_{imp} and M_{Cl}, respectively. The spin-symmetric and spin-polarized calculations are characterized by (S–S) and (S–P) in the table.

		s	p	d	Total	M_{imp}	M_{Cl}
FeAl (S–S)	SU8	0.650	0.842	6.564	8.056		
	SU16	0.640	0.834	6.534	8.008		
	SU32	0.644	0.836	6.544	8.024		
FeAl (S–P)		↑0.336	0.434	4.484	5.254		
	SU8					2.51	4.88
		↓0.323	0.406	2.011	2.740		
		↑0.335	0.425	4.520	5.280		
	SU16					2.60	7.30
		↓0.319	0.403	1.961	2.683		
		↑0.334	0.427	4.486	5.247		
	SU32					2.51	7.77
		↓0.321	0.410	2.005	2.736		

turn out to be completely clear-cut. In this case the respective total energy differences are three orders of magnitude larger in favour of the occurrence of local moments.

4. Results and discussion

In table 3, we have listed the integrated LDOSs up to the Fermi level for the AS-Al atom on the Fe sublattice (Al_{Fe}). The various results on the total number of valence electrons shown have been obtained from calculations on different supercells and from a summation over both spin directions. The respective numbers for the AS-Fe atom on the Al sublattice (Fe_{Al}) are given in table 4 both for the spin-symmetric and the spin-polarized calculations. We have also listed the local magnetic moments in the defect cell (M_{imp}) and in the cluster (M_{Cl}) which comprises the defect cell and its nearest neighbours. As is obvious from the data given in tables 3 and 4, the electronic structure of the defects is

not sensitive to the size of the supercell. Hence, one is justified in considering the SU8-type calculations as ensuring a sufficient convergence of the electronic structure data. (Note that the supercell SU8 is four times larger than the primary cell.) Another interesting feature that evolves from these tables is that the AS-Al and AS-Fe defects are less charged compared with the respective bulk atoms of the ordered alloy. This has to be expected because the electro-negativity of the nearest neighbours is the same in that situation. Moreover, our results are substantiated by the KKR Green's function calculations of Stefanou *et al* (1987) on CoAl which also yield the charge of the AS-Al and AS-Co defect close to neutrality. This contrasts with the work of Koch and Koenig (1987) who arrive at the result that the AS-Al defect in FeAl carries more charge than the same atom in the ordered alloy. This contradictory and not very plausible result might be connected to the authors' particular use of the Green's function formula within the LMTO scheme and with the single-site approximation (SSA) for the defect potential. Moreover, the authors fail to obtain convergent results on the AS-Fe defect. It appears that the deficiencies of these calculations must be blamed on the inadequacy of the assumed SSA defect potential. As follows from the work of Stefanou *et al* and from our experience, AS defect potentials can realistically be described only if one consistently includes the effect of nearest neighbours.

We have carried out spin-polarized calculations for different supercells and obtained the self-consistent local magnetic moments which are listed in table 4. We find that the local moment of the defect site is not sensitive to the size of the supercell. The value of 2.5 μ_B seems to be well converged. Not surprisingly, the eight nearest neighbours of the AS-Fe defect prove to play an important role in determining its magnetic moment and contribute by about 0.6 μ_B per atom within the cluster. In accordance with this approximate value we obtain, for the nine-atom clusters SU16 and SU32, magnetic moments of 7.30 and 7.77 μ_B, respectively, which is in good agreement with the experiment of Caskey *et al* (1973). The small value obtained for SU8 is connected with the insufficient size of that cell in containing only four nearest-neighbour Fe atoms. The calculation of Stefanou *et al* (1987) on the AS-Co defect in CoAl suffers from the shortcoming that the total magnetic moment is underestimated by 50%. This may be due to some artificiality in including the influence of the nearest neighbours. As may be concluded from the favourable agreement of our results with the experiments, the supercell approach obviously guarantees a sufficiently realistic treatment of the crucial nearest-neighbour influence. In contrast to the perfect bulk calculation, a non-spin-symmetric calculation on the AS-Fe defect yields a total energy of the supercell which is 1.3 eV lower than for the same system in its paramagnetic state. A total energy difference of this magnitude is certainly not fortuitous and also lends considerable credibility to the obtained magnetic moment.

Figure 2 shows the LDOS of AS-Al atoms for various sizes of the supercell. The two lower curves in each of the plots refer to an angular momentum decomposition of the LDOS as in figure 1. The characteristic structures in these curves are obviously shifted to lower energies compared with the respective structures in figure 1(*a*) which refer to the ordered alloy. A striking feature of s-type LDOS is that a peak at the low energy edge starts splitting off as the size of the supercell is increased from SU8 to SU32. This can be explained by the fact that the potential of the AS-Al atom is lowered by the presence of positively charged Al neighbours, and hence the 3s level shifts to the lower energies where the host band structure displays a gap. Consequently, the 3s level becomes localized. The finite width of the associated structure in the s-type LDOS is obviously connected to the finite size of the supercell as follows from the development of the peak
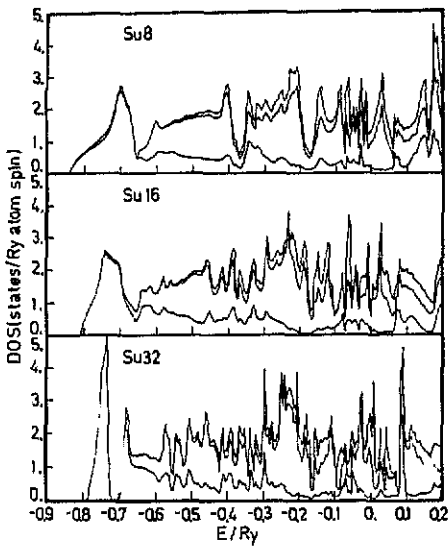
Figure 2. Partial and total LDOS for the AS-Al defect. Curves from bottom to top: contribution of s electrons, (s+p) electrons, (s+p+d) electrons. The notation SU8, SU16 and SU32 refers to supercells containing 8, 16 and 32 atomic sites, respectively.
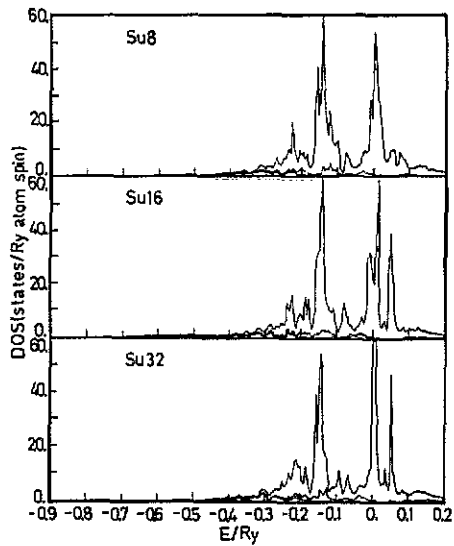
Figure 3. Partial and total LDOS for the AS-Fe defect from an artificially spin-symmetric calculation. Curves from bottom to top: contribution of s electrons, (s+p) electrons, (s+p+d) electrons. As in figure 2 the notation SU8, SU16 and SU32 refers to supercells containing 8, 16 and 32 atomic sites, respectively.

with increasing cell size. As long as this size is finite, there will be a 3s 'impurity band' whose width is essentially determined by the overlap of the 3s orbitals of neighbouring supercells.

The LDOS of the AS-Fe atom shows a distinctly different behaviour as a function of the cell size as can be seen from figure 3. The curves (analogous to those of figure 2) refer to 'paramagnetic' calculations where the spin polarization has artificially been kept at zero. Obviously, the dependence of the electronic structure on the cell size is quite small suggesting that the electronic structure of the AS-Fe defect is mainly determined by the large overlap between the d orbitals of the AS-Fe atom and its chemically identical eight nearest neighbours. The substantial difference in these orbital overlaps compared with the situation in the ordered alloy gives rise to distinct changes in the LDOS. The peak that appears at -0.15 Ryd in the LDOS of the ordered alloy and may be considered as the binding-type counterpart of the anti-bonding 3d peak structure at E_F, becomes strongly enhanced. Moreover, a sharp additional peak develops at 0.06 Ryd. Not surprisingly, the distinct features of the LDOS bear much resemblance to the DOS of BCC Fe metal, which has the same local symmetry as the AS-Fe defect. (For the DOS of BCC Fe see e.g. Moruzzi *et al* 1978.) The total number of electrons on the AS-Fe turns out to be smaller than that of any of the host Fe atoms. (See table 1.) This is due to the negative charge of the nearest neighbour atoms and the associated repulsive potential that pushes some d states above the Fermi level. The relatively large LDOS at the Fermi level, connected with band states of an anti-bonding 3d character, introduces an instability that drives an electronic transition into a state with a finite local moment. In their Green's function calculation, Stefanou *et al* (1987) find a similar behaviour of the AS-Co defects
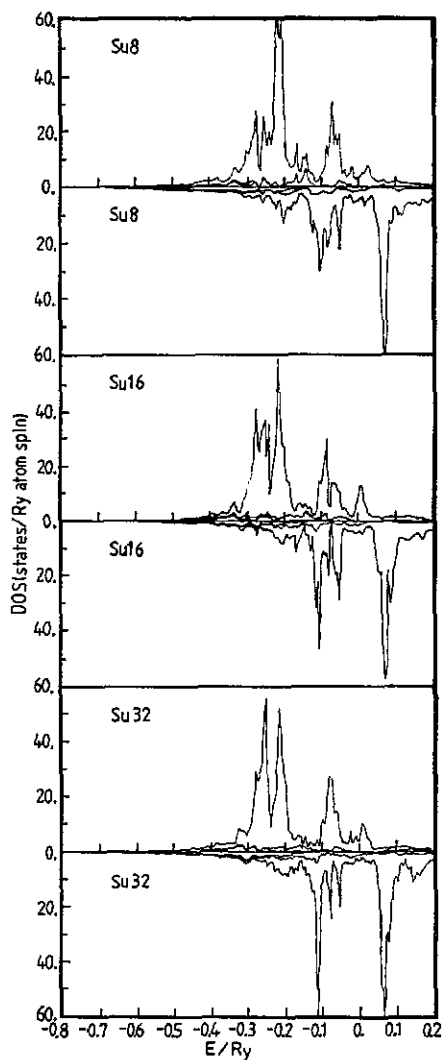
Figure 4. Partial and total LDOS for the AS-Fe defect from a spin-polarized calculation. Curves from bottom to top: the contribution of s electrons, (s+p) electrons, (s+p+d) electrons. The SU8, SU16 and SU32 refer to supercells containing 8, 16 and 32 atoms. The curves below the zero-line refer to the minority spin.

in CoAl and CoGa. Figure 4 shows the results of our calculation on the spin-polarized LDOS of the AS-Fe atom for the various supercells. There is now a dramatic difference in the LDOSS of the majority and minority spins, and the spin-averaged LDOS at E_f is considerably lower than in the paramagnetic state. It can also be seen from figure 4 that the LDOS of the AS-Fe atom is not very sensitive to the cell size. The LDOS, even of the smallest supercell, still reflects these generic structures.

Charge-induced perturbations, i.e. the Friedel oscillations around the defects, can be found both in the spin-symmetric and non-spin-symmetric SU32 calculations. The excess charge runs through at least two zeros as one moves from the impurity to the sixth order of neighbouring shells. In the case of the AS-Al defect, for example, the excess charge of 0.403 electrons on the impurity is almost totally screened by the charge of -0.375 electrons of the first shell, but the second shell still carries a charge of -0.223 electrons. Any trustworthy calculation on charge defects should always yield oscillations of this kind.

Acknowledgment

References

Amamou A and Gautier F 1974 *J. Phys. F: Met. Phys.* **4** 563
Andersen O K 1975 *Phys. Rev.* B **12** 3060
Blau W, Weissbach J, Merz G and Kleinstuck K H 1979 *Phys. Status Solidi* b 93 713
Butler S R, Hanlon J E and Wasilewski R J 1969 *J. Phys. Chem. Solids* **30** 1929
Caskey G R, Franz J M and Sellmyer D J 1973 *J. Phys. Chem. Solids* **34** 1179
Christensen N E 1981 *Phys. Rev.* B **30** 5753
Domke H and Thomas L K 1984 *J. Magn. Magn. Mater.* **45** 305
Eibler R and Neckel A 1980 *J. Phys. F: Met. Phys.* **10** 2179
Jepsen O. and Andersen O. K. 1971 *Solid State Commun.* **9** 1763
Hackenbracht D and Kübler J 1980 *J. Phys. F: Met. Phys.* **10** 427
Kapoor Q S, Watson L M and Fabian D J 1973 *Band Structure Spectroscopy of Metals and Alloys* ed D J Fabian
     and L M Watson (London: Academic) p 215
Koch J M, Stefanou N and Koenig C 1986 *Phys. Rev.* B **33** 5319
Koch J M and Koenig C 1986 *Phil. Mag.* **54** 177
—— 1987 *Phil. Mag.* **55** 359
—— 1988 *Phil. Mag.* **57** 557
Koenig C and Khan M A 1983 *Phys. Rev.* B **27** 6129
Koenig C, Stefanou N and Koch J M 1986 *Phys. Rev.* B **33** 5307
Kuentzler R 1983 *J. Phys.* **44** 1167
Meurtin M and Lesbats P 1976 *Fourth Int. Conf. Positron Annihilation (Helsingor, Denmark)* unpublished
Moruzzi V L, Janak J F and Williams A R 1978 *Calculated Electronic Properties of Metals* (New York:
     Pergamon) p 85
Müller Ch, Wonn H, Blau W, Ziesche P and Krivitskii V P 1979 *Phys. Status Solidi* b 95 215
Müller Ch, Blau W and Ziesche P 1983 *Phys. Status Solidi* b 116 561
Pechter K, Rastl P, Neckel A, Eibler R and Schwarz K 1981 *Monatsh. Chem.* **112** 317
Podloucky R and Neckel A 1979 *Phys. Status Solidi* b 95 541
Rath J and Freeman A J 1975 *Phys. Rev.* B **11** 2109
Sellmyer D J, Caskey G R and Franz J 1972 *J. Phys. Chem. Solids* **33** 561
Skriver H L 1982 *Phys. Rev. Lett.* **49** 1768
—— 1983 *The LMTO Method* (New York: Springer)
—— 1985 *Phys. Rev.* B **31** 1909
Sob M 1982 *J. Phys. F: Met. Phys.* **12** 571
Stefanou N, Zeller R and Dederichs P H 1986 *Solid State Commun.* **59** 429
—— 1987 *Phys. Rev.* B **35** 2705
von Barth U and Hedin L 1972 *J. Phys. C: Solid State Phys.* **5** 1629
Wachtel E, Linse V and Gerold V 1973 *J. Phys. Chem. Solids* **34** 1461
Williams A R and Kübler J 1979 *Phys. Rev.* B **19** 6094
Ziesche P, Wonn H, Müller Ch, Nemoshkalenko V V and Krivitskii V P 1978 *Phys. Status Solidi* b 87 129