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Cohesive, electronic and magnetic properties of the transition metal aluminides FeAl, CoAl and NiAl

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Abstract. Electronic structure calculations using the tight-binding linear muffin tin orbital (TB-LMTO) method have been performed for three transition metal aluminides, viz. FeAl, CoAl and NiAl. The band structures and density of states (DOS), valence electron charge density contours and Fermi surfaces have been obtained and compared with the available experimental results as well as with existing theoretical calculations. The lattice constants, cohesive energies and heats of formation at equilibrium lattice constants and bulk moduli agree with the experimental values. The calculations show varying degrees of charge transfer from Al site to the transition metal (TM) sites as one goes from FeAl to CoAl to NiAl. The magnetism of pure elements Fe, Co, Ni is mostly quenched in the stoichiometric phases, with only FeAl retaining a magnetic moment of about $0.7 \mu_B$ /atom within the framework of the LMTO.

1. Introduction

Ordered 3d transition metal (TM) aluminides have attracted considerable attention from materials scientists, because of their high corrosion and oxidation resistance, good strength to weight ratio and wide-ranging applications such as high-temperature structural materials, shape memory alloys and soft magnetic materials [1]. In particular, the B2- (or CsCl-) structured intermetallics constituted by one transition and another simple metal atom, display diverse physical phenomena and hence are ideally suited for a systematic study of electronic structure, cohesive properties, charge transfer and chemical bonding. The brittleness of NiAl versus the intrinsic ductility of FeAl, for example, can be understood from the fact that the former has a slip plane along (100) while the latter has (111) slip. A microscopic understanding of this phenomenon can be obtained from electronic structure calculations [2]. All these binary compounds have simple b.c.c. structure with Al at the body centre of the cube formed by eight TM atoms. In this paper, we report the results of our first-principles investigations on electronic structure, cohesive and magnetic properties of FeAl, CoAl and NiAl compounds, using the *tight-binding linear muffin-tin orbital (TB-LMTO) method in the atomic sphere approximation (ASA)*.

One of the earliest calculations on CsCl-type intermetallic compounds was done by Connolly and Johnson [3] using a non-self-consistent LCAO approach. Self-consistent calculations on CoAl and NiAl, reported by Moruzzi *et al* [4] using a KKR method, showed a charge transfer from Al site to TM site. Later Müller *et al* [5, 6] used a modified KKR

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method and analysed the experimental soft x-ray spectra to explain the instability of a homogeneous B2 phase in the aluminides of transition metals other than Fe, Co and Ni and later [6] calculated the density of states (DOS) for all of them. Okochi and Yagisawa [7, 8] compared the results of APW calculations on FeAl and CoAl with the experimental results on electronic specific heat, Knight shift, thermoelectric power and Hall effect. Nagel *et al* [9] presented self-consistent APW calculations with X_α exchange and found that x-ray photoelectron spectra of NiAl have a high-energy shoulder which is absent from FeAl and CoAl. This was mainly because of the position of the d band in NiAl which is well below the Fermi level (E_F), indicating the major contributions of s and p orbitals of Al, in conformity with the work of Connolly and Johnson [3]. Petcher *et al* [10] have done self-consistent calculations on CsCl-type intermetallics using the APW method. Eibler and Neckel [11] also made an extensive study of the electronic and optical properties of these ordered compounds using the APW method supplemented by the hybridized nearly-free-electron-tight-binding (H-NFE-TB) interpolation scheme. They compared their calculated DOS curve for NiAl with the experimental XPS and UPS spectra. They were also able to explain and reproduce the imaginary part of the complex dielectric function. Min *et al* [12] studied NiAl, Ni₃Al, FeAl and Fe₃Al using LMTO and observed that transformation from ferromagnetic to paramagnetic phase for FeAl occurs in a small range of pressure. Domke and Thomas [13] and Koch and Koenig [14] have respectively studied magnetic properties in FeAl and vacancies in B2-structured compounds. Stefanou *et al* [15] have studied point defects in CoAl using the KKR method.

Recently Lui *et al* [16] have measured the valence band structure of NiAl by angle-resolved photoemission with synchrotron radiation and compared with their *full potential linear augmented slater-type orbitals* (FP-LASTO) calculations. They observed better agreement between the theoretical and experimental results than in pure Ni and attributed that to the so-called *self-energy* correction being small in NiAl. Mehl *et al* [17] investigated the high-melting-temperature intermetallic alloys, viz. SbY, CoAl, RuZr and NbIr, using the *full potential linear augmented plane wave* (FLAPW) method. Elastic properties, deformation behaviour and hydrogen-induced embrittlement effects of FeAl and NiAl have been investigated theoretically using FLAPW method by Fu and Yoo [18]. Sluiter *et al* [19] have used a generalized perturbation method to study the NiTi and NiAl alloys and have shown that closely related ordered structures can exist on f.c.c. and b.c.c. lattices during martensitic transformation. Very recently, a pseudopotential calculation for CoAl has been carried out by Ögüt and Rabe [20] in the CsCl structure. They found the relative stability of different Al-rich Co compounds to depend on the full electronic DOS rather than its value at Fermi energy.

In the present work, we report the results of our local-density-approximated (LDA) investigation, using the self-consistent TB-LMTO method. The cohesive properties like equilibrium lattice constants, cohesive energies, formation energies, bulk moduli and magnetic properties for ordered compounds FeAl, CoAl and NiAl are compared with the available experimental results. The purpose of this work is threefold: (a) ordered phase calculations of these compounds would give information which can be used as a starting point for understanding the properties of the corresponding disordered phases, (b) these isostructural compounds offer the possibility of studying the variations of electronic properties as the d band in the 3d TM series is progressively filled and (c) to investigate the effect of Al p and TM d hybridization on magnetic properties. The power of the LMTO method, reduced self-energy errors in these compounds, and expected better insight are the additional driving forces behind these calculations. The plan of the paper is as follows. In section 2, we give the computational details of the TB-LMTO method. In section 3, we

present the results of the our calculations and the final section provides the summary and conclusion.

2. Computational details

The conventional LMTO-ASA method [21, 22] as well as its transformation to a localized representation (TB-LMTO) [23–26] are well described in the literature. Here we give only the relevant computational details.

We have performed self-consistent scalar relativistic calculations using the ‘frozen core’ approximation and von Barth–Hedin [27] parametrization of the exchange–correlation potential. Spin-polarized as well as unpolarized calculations have been done for the 50:50 stoichiometric compounds FeAl, CoAl and NiAl, using a minimal basis set consisting of s, p and d orbitals for both transition metals and Al. ‘Combined correction’ has been taken into account. 120 k points have been used in the irreducible wedge of the simple cubic Brillouin zone (BZ), for the tetrahedron method of integration [28]; its latest implementation gives proper weighting and corrects errors due to the linear approximation of the bands inside each tetrahedron [29].

In ASA, the crystal is divided into space-filling, and therefore slightly overlapping, spheres centred on each of the atomic sites. We have chosen all spheres to be of the *same* size. The ground state total energies have been calculated self-consistently as a function of unit cell volume and hence the electronic pressure was calculated by numerical differentiation of total energy with respect to volume. The equation of state was fitted by the function [30]

$$P(\Omega) = A_1 + A_2\Omega + A_3/\Omega + A_4/\Omega^3 \quad (1)$$

where P is the pressure and Ω is the volume of the unit cell. The coefficients A_i ($i = 1, 2, 3, 4$) are estimated by a least-squares fit from the equation of state. The theoretical lattice constants are obtained from the condition $P(\Omega) = 0$. The bulk modulus is calculated by using the relation

$$B = -\Omega_0 \left. \frac{dP}{d\Omega} \right|_{\Omega_0} \quad (2)$$

where Ω_0 is the equilibrium volume of the unit cell. The cohesive energy of the compound is calculated by using the expression

$$E_{coh}^{AB} = E_{total}^{AB} - [cE_{atom}^A + (1 - c)E_{atom}^B] \quad (3)$$

where E_{total}^{AB} refers to the total energy per atom of the intermetallic at equilibrium lattice constants and E_{atom}^A and E_{atom}^B are the atomic energies of the pure constituents calculated semirelativistically with a large cut-off ($r_{max} = 30$ au). Here c refers to the fractional concentration of constituent A. In the present work we have used $c = 0.5$. When the ‘frozen core’ approximation is used, the core energies of the free atom cancel.

From the total energy of the compounds and the constituent elemental solids, one can find the formation energies using the relation

$$E_{form}^{AB} = E_{total}^{AB} - [cE_{solid}^A + (1 - c)E_{solid}^B]. \quad (4)$$

The systematic errors in total energy due to the use of ASA are cancelled significantly, leading to a reasonably accurate formation energy.

3. Results and discussions

Having given the procedure for calculating cohesive energy, heat of formation and bulk modulus, we present the result of our calculation in this section.

3.1. Cohesive properties

Self-consistent total energies are calculated for various lattice constants (in steps of 0.1 au) for the ordered B2 compounds FeAl, CoAl and NiAl. The variations of cohesive energies with lattice constant exhibit the expected parabolic behaviour as shown in figure 1. The minima of the energy versus lattice spacing curves give the ground state cohesive energies (within the ASA), whose values are given in table 1. It is to be noted that for FeAl, the total energy reduces as we switch on spin polarization; but for CoAl and NiAl no such magnetic effect is manifested. All the results, in this and the following sections, therefore correspond to spin-polarized FeAl and unpolarized CoAl and NiAl calculations.

Table 1. Cohesive properties of B2-structured FeAl, CoAl, NiAl. The results are shown for spin-polarized calculations.

	FeAl	CoAl	NiAl
No of valence electrons	11	12	13
Lattice constant (au)			
Experiment [36]	5.409	5.408	5.456
Present	5.364	5.317	5.377
FLAPW [16]	—	5.293	
Pseudopotential [19]		5.302	
ASW [30]			5.406
Bulk modulus (Mbar)			
Experiment [2]	—	—	1.89
Present work	2.01	2.11	1.92
FLAPW [16, 17]	—	2.07	2.00
Pseudopotential [19]	—	1.99	
ASW [30]	—	—	2.00
Cohesive energy (eV/atom)	-7.66	-7.57	-7.04
Formation energy (eV/atom)			
Experiment [37]	-0.26	-0.56	-0.64
Experiment [38, 39]	-0.33	-0.44	-0.49
Present work	-0.50	-0.75	-0.77
FP-LASTO [15]			-0.74
FP-LASTO [32]	-0.51	-0.69	-0.67
ASW [31]			-0.74
KKR-CPA [18]			-0.44

The cohesive properties, calculated at equilibrium lattice constants (see table 1), have been compared with the available experimental data. It is evident from table 1 that the computed values of equilibrium lattice constants are consistently underestimated by about 1 to 2%. We observe the same trend in other theoretical calculations using FLAPW [17] and pseudopotential methods for CoAl [20] and using the ASW method for NiAl [31]. This is tolerable within LDA, which is known to overestimate bonding and hence underestimate bond lengths.

The values of bulk moduli calculated from the second derivative of total energy (as discussed in section 2) are about 2 Mbar for all the TM aluminides under consideration.

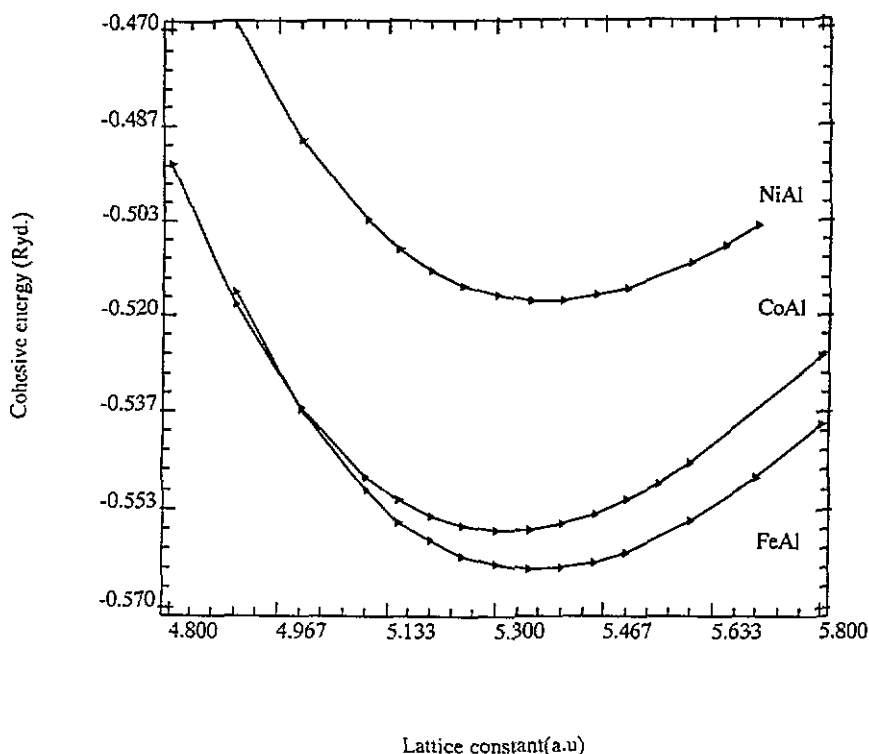


Figure 1. Variation of cohesive energy with lattice constants for FeAl, CoAl and NiAl.

They are given in table 1. For NiAl, our estimate of 1.92 Mbar agrees quite well with the experimental value (1.89 Mbar) as well as with LAPW (2.0 Mbar) [18] and ASW calculation (2.0 Mbar) [31]. On the other hand, in the case of CoAl there is roughly 30% overestimation of the experimental value of the bulk modulus by the present calculations which is not very different from the calculations by Mehl *et al* [17] and Ögüt and Rabe [20].

The heats of formation are displayed in table 1 and the corresponding experimental values are given for comparison. Although our results are in very good agreement with other band calculations [16, 32, 33], they systematically overestimate the thermochemical formation energy data. The discrepancy is typical of LDA. It is to be noted that the experimental heat of formation of FeAl is a *factor of two* smaller than those of CoAl and NiAl which are close in magnitude. On the other hand, the generalized perturbation method within KKR-CPA [19] underestimates the heat of formation for NiAl.

3.2. Electronic structure

The salient features of the electronic structure of the TM aluminides emerge from their DOS (figure 2) and band structures (figure 3), which compare well with the earlier calculations [2, 4, 9]. All the three TM aluminides have similar features with the variation only in the occupation of the d bands as we move from Fe to Ni; the concomitant effects will be illustrated in this section and compared with theoretical and experimental results.

The DOS plots (figure 2) show that the prominent contributions around E_F for each of the three TM aluminides are mainly those from the TM site (dashed line), which form

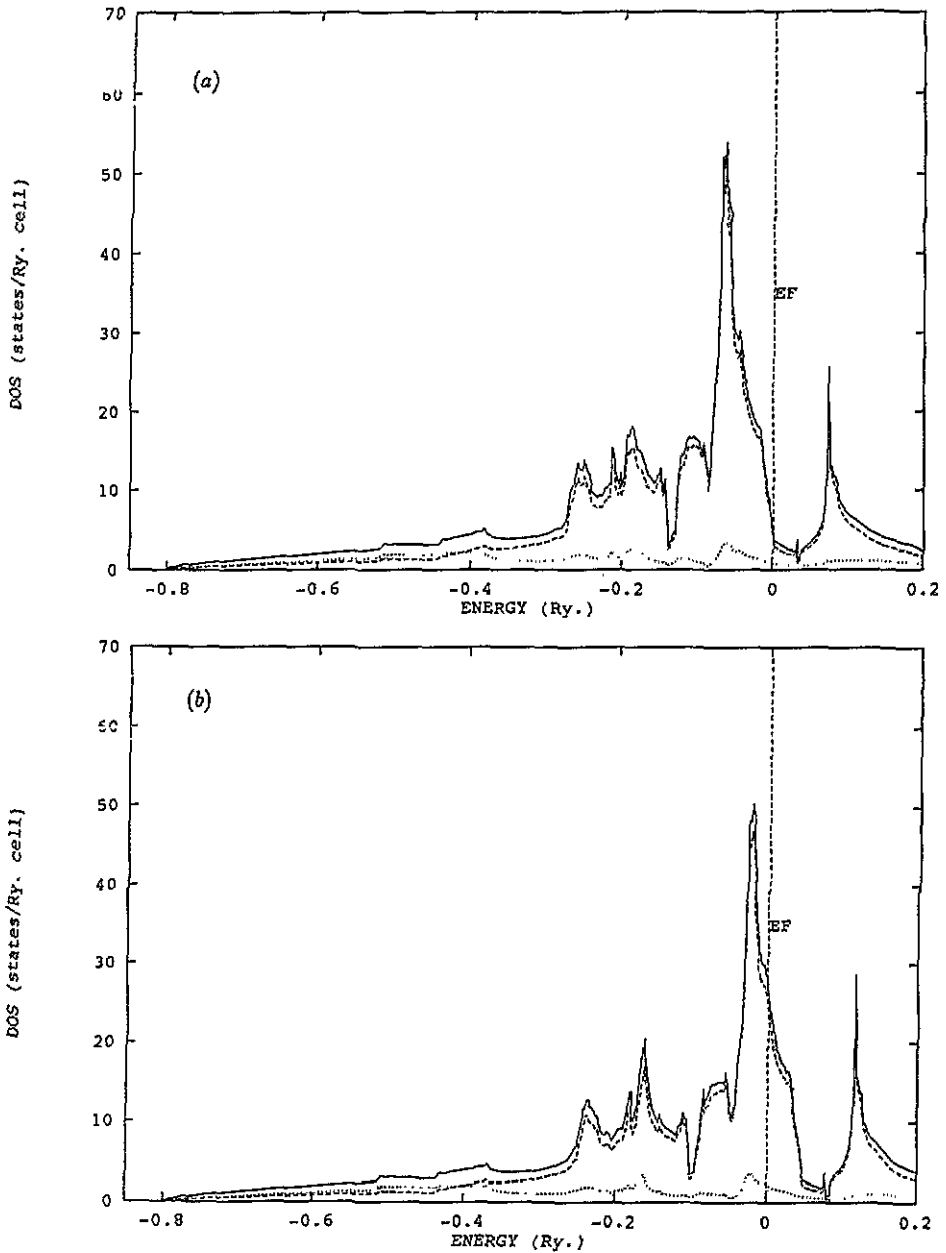


Figure 2. Density of states for (a) FeAl up spin, (b) FeAl down spin, (c) CoAl and (d) NiAl. The continuous curve gives the total DOS whereas the contributions from Al and the TM are respectively given by dotted and dashed curves.

a pseudogap between the bonding and the antibonding peaks. The s and p contributions from Al yield a relatively flat DOS (dotted line), with hardly any feature around E_F . In the case of FeAl, E_F appears on the steeply falling edge of the bonding (t_{2g}) peak, while for CoAl, E_F appears on the rising edge of the antibonding peak. In the case of NiAl, the d band being nearly full (sixth-band Fermi surface in figure 4(d)), the antibonding state

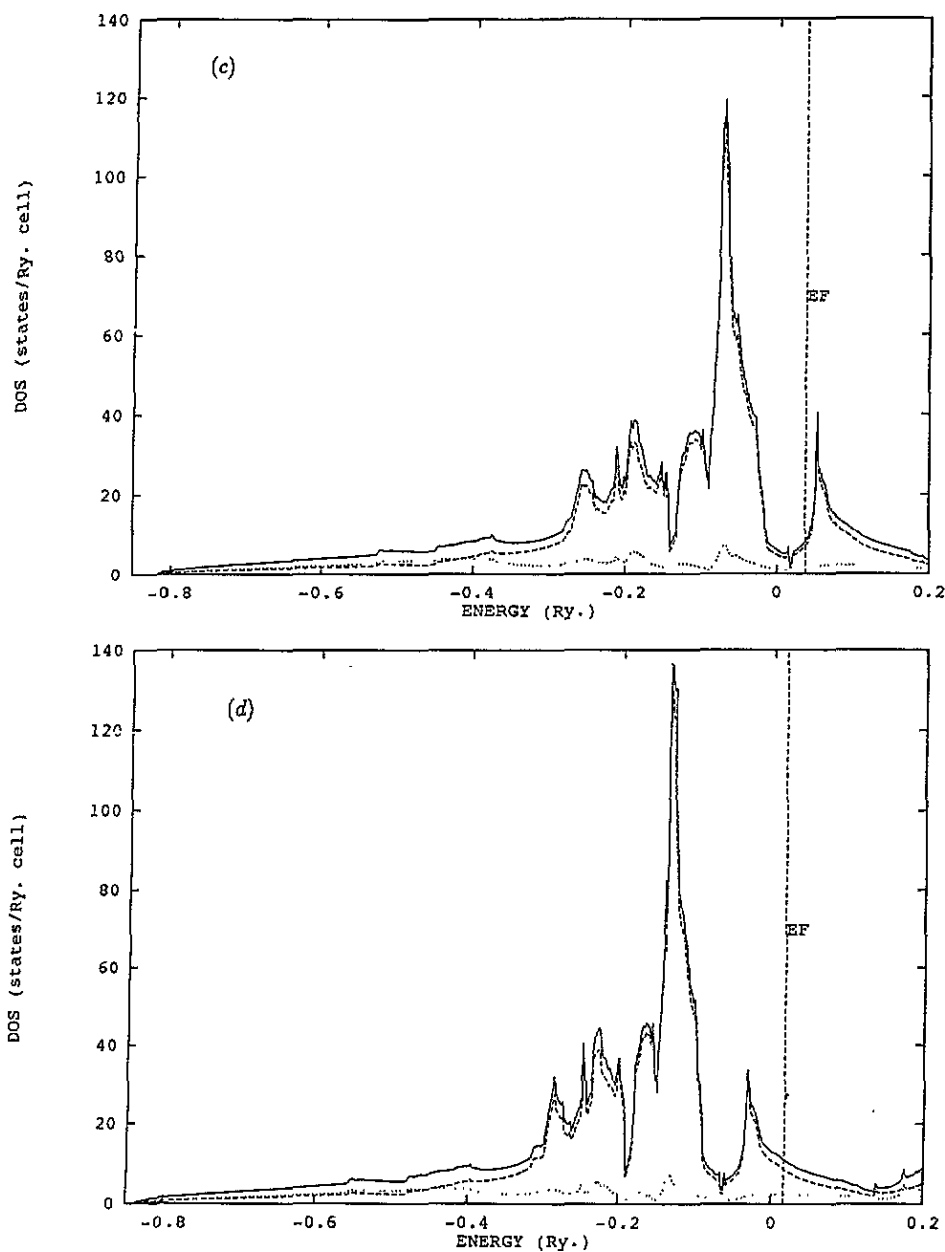


Figure 2. (Continued)

becomes occupied as is clearly seen in its E_F sitting above the last peak. This effect of band filling on the formation of compound was demonstrated through exhaustive XPS studies by Fuggle *et al* [34]. The DOS at E_F in the present calculations for FeAl are found to be 26.22 states Ryd⁻¹/cell for minority spin and 4.05 states Ryd⁻¹/cell for majority spin, for CoAl 8.36 states Ryd⁻¹/cell and for NiAl 11.08 states Ryd⁻¹/cell. Eibler and Neckel [11] estimated the $N(E_F)$ from low-temperature specific heat measurements for FeAl and NiAl to be 31.3 states Ryd⁻¹/cell and 7.25 states Ryd⁻¹/cell by setting the electron-phonon

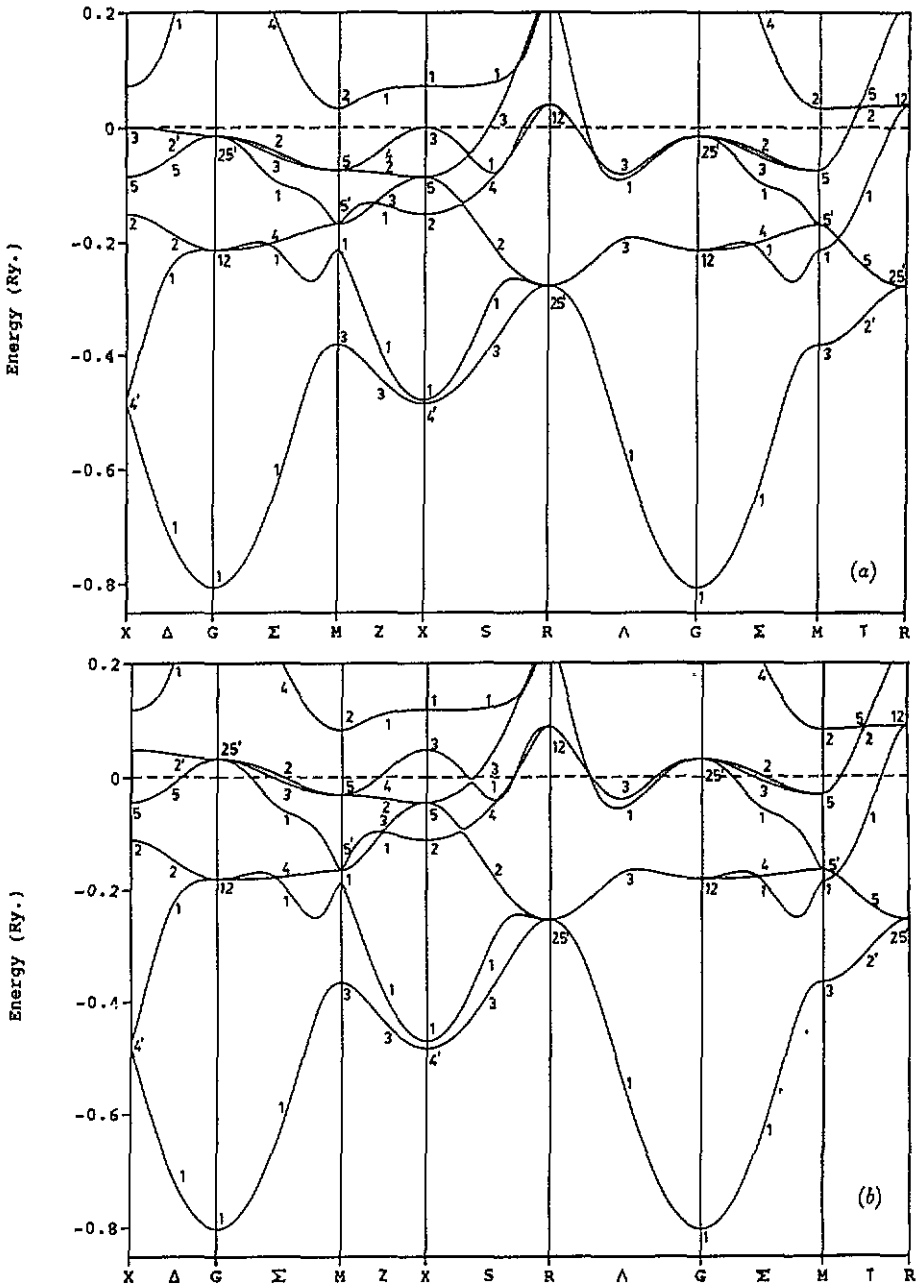


Figure 3. Band structures for (a) FeAl up spin, (b) FeAl down spin, (c) CoAl and (d) NiAl along certain symmetry directions.

coupling constant to zero. Their unpolarized calculated values are 32.05 states $\text{Ryd}^{-1}/\text{cell}$, 8.67 states $\text{Ryd}^{-1}/\text{cell}$ and 7.25 states $\text{Ryd}^{-1}/\text{cell}$ respectively for FeAl, CoAl and NiAl. For CoAl, Mehl *et al* [17] obtained $N(E_F)$ as 8.1 states $\text{Ryd}^{-1}/\text{cell}$ which is in very good agreement with the present result. There is a fair agreement with 9.1 states $\text{Ryd}^{-1}/\text{cell}$ obtained by Ögüt and Rabe [20], for CoAl.

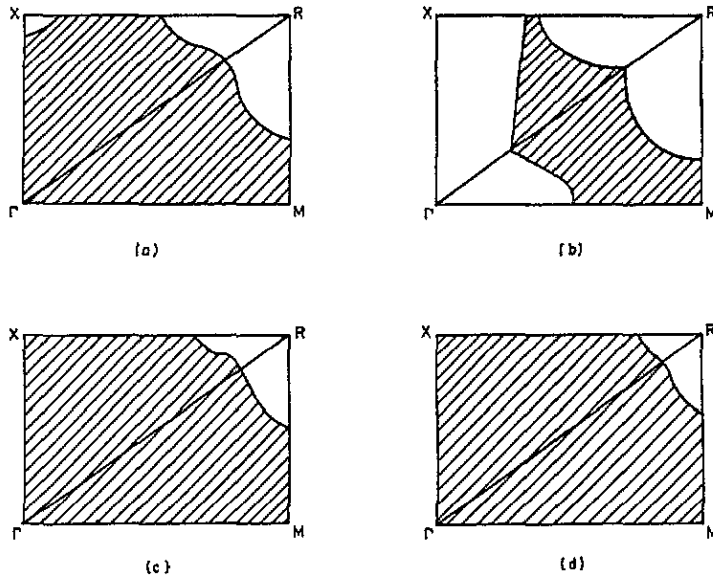


Figure 4. Sixth-band Fermi surface cross-sections for (a) FeAl up spin, (b) FeAl down spin, (c) CoAl, and (d) NiAl in the (110) plane.

Table 2. Band energies at high-symmetry points with respect to Fermi level in eV.

Symmetry points	FeAl			NiAl			
	Up	Down	Unpolarized	CoAl	LASTO [10]	Expt [10]	Present
Γ_1	10.97	10.92	10.87	11.69	10.74	11.00	11.69
Γ_{12}	2.91	2.47	2.76	3.39	3.02	2.72	3.62
$\Gamma_{25'}$	0.2	—	—	0.87	1.49	1.44	1.58
$\Gamma_{12}-\Gamma_{25'}$	2.7	—	—	2.52	1.5	—	2.04
R_{12}	-0.53	-1.19	—	0.21	0.97	0.91 ± 0.10	1.05
$R_{25'}$	3.78	3.40	—	4.23	3.88	3.50 ± 0.15	4.32
$R_{12}-R_{25'}$	—	—	—	4.02	2.91	2.59 ± 0.25	3.27

[16]. This discrepancy may be attributed to the 'frozen core approximation' as well as to the use of ASA in our calculation. Relaxation of the core would certainly help in the further narrowing of the d bands. For CoAl, we get a value of 4.02 eV for the d band width. In the case of FeAl, R_{12} for both majority and minority spins lies above the Fermi energy. Hence the estimation of d band width is taken as the difference between E_F and $R_{25'}$. Another plausible way to define the d band width is to take the difference between Γ_{12} and $\Gamma_{25'}$ levels. These numbers, for FeAl (up spin), CoAl and NiAl respectively, come out from our calculations as 2.7 eV, 2.52 eV and 2.04 eV, which may be compared with the corresponding values of 2.33, 2.16 and 1.78 eV obtained by Nagel *et al* [9] from their APW calculations. The difference could be attributed to the fact that they used X_α exchange in their calculations. For CoAl, Mehl *et al* [17] and Ögüt and Rabe [20] obtained the d band widths as 2.4 eV and 2.0 eV respectively which agree with our results. On comparison, the qualitative features of the band structure in the present work agree well with their results. The energy of $\Gamma_{25'}$ for minority spin in the case of FeAl lies above E_F . In all these

compounds, d bands get narrowed compared to the pure transition metals viz. Fe, Co, and Ni, as observed by Moruzzi *et al* [4].

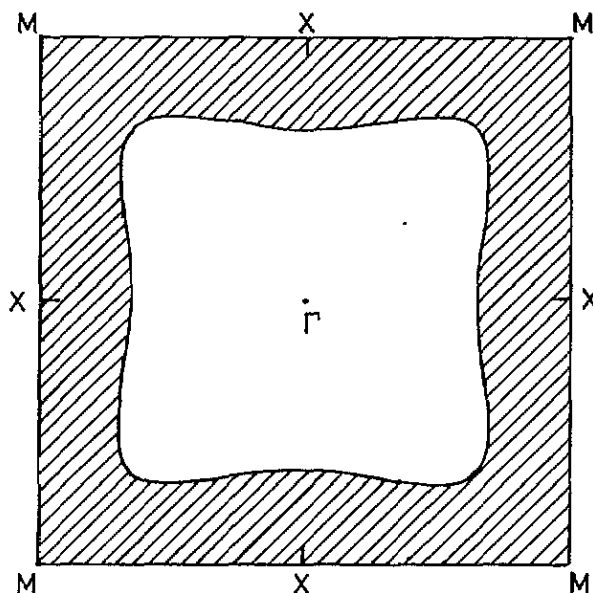


Figure 5. Seventh-band Fermi surface cross-section for NiAl.

We have also estimated the Fermi surface cross-sections for FeAl, CoAl and NiAl. For the sixth band, these are plotted in the (110) plane, as shown in figure 4. There is a hole pocket at R for all three, but the size of that pocket decreases as one goes from FeAl towards NiAl. In addition to this, there is a small hole pocket just appearing at X for FeAl (up spin), whereas in the case of FeAl (down spin) there is an appreciable difference with the occupied region shrinking. On comparison of the seventh-band FS for NiAl with that of Lui *et al* [16] (figure 8 in their paper) we observe an excellent agreement. Our result (figure 5) shows a hole pocket at Γ . For the case of CoAl, we observe a similar feature (figure not shown) with the size of the hole pocket much larger than that for NiAl.

3.3. Charge transfer and magnetic properties

The valence electron charge densities can be calculated from the self-consistent ASA potentials from our electronic structure calculations. Furthermore, within ASA, it is possible to get the *intersphere* charge transfer from Al site to the TM site, and we find its magnitude increasing as we go from FeAl to NiAl. Table 3 summarizes the values of charges projected onto each site and angular momentum, for all three compounds. In general, there is depletion of s like and p like charges which in turn populate the d levels. We attribute this to the energy level difference between atomic levels of Al and those of TM, i.e. the 3p level of Al lies above the 4s levels of TM, while the 3s level of Al lies above the 3d level of TM. This naturally leads to charge transfer.

As discussed by Schultz and Davenport [33], in order to understand the B2 structure of the compounds under study, we apply the modified Hume-Rothery rule in which the d-electrons are passive and act as a source or a sink. The sp electrons of Al and those of TM form the conduction band. They however, hybridize with the d band as well. Now in the process, if the Hume-Rothery rule is to be satisfied then the electron to atom ratio

should be around 1.5. This necessitates the charge transfer to a relatively narrow d band largely from Al. As far as FeAl is concerned, we notice from our spin-polarized calculation that the d electron up-spin density in FeAl is around 3.8, whereas it is 4.36 in elemental Fe. On the other hand the down-spin density has gone up from 2.2 in elemental Fe to 3.1 in FeAl. This indicates that there is a charge transfer in both ways as far as FeAl is concerned. However, there is net charge transfer from Al to Fe site of around 0.27 electrons.

Schultz and Davenport [33] have calculated the charge transfer by using the LASTO method under the muffin tin approximation for FeAl. In order to compare with the present results, we distributed their values of charges in the interstitial equally among Al and TM regions and find a very good agreement, with just 2% deviation.

Figure 6 shows the charge density differences in the three compounds, defined by the expression,

$$\delta\rho(\mathbf{r}) = \rho_{solid}(\mathbf{r}) - \rho_{superposed}(\mathbf{r}) \quad (5)$$

Where ρ_{solid} is the self-consistent *solid state* charge density obtained at our calculated equilibrium lattice constant, and $\rho_{superposed}$ is the *superposed* atomic charge densities at the same lattice constant. We plotted these contours using the results of the unpolarized calculations in the cases of CoAl and NiAl, and using the sum of the up- and the down-spin contributions in the case of FeAl. The resulting figures (6(a)–(c)) clearly show a bonding charge density between the Al site and the TM site. We would like to note that this definition does not indicate the charge transfer as conventionally understood [33] but, gives an insight into the charge readjustment that takes place after zeroth-order charge density calculations have been performed by superposing the atomic charge densities. A similar procedure has been followed by Fu and Yoo [18]. Although in all cases the bonding charge density shows anisotropy, it is more pronounced in FeAl and CoAl. These observations are consistent with Fu and Yoo. It is to be noted that there is a gain of charge along the Al–TM direction around the TM site and a depletion along TM–TM directions. In the case of FeAl, the charge readjustment is such that the total magnetic moment of the system is reduced as compared to pure Fe (table 3, 4), by depletion of the up-spin charges from Fe region and gain of down-spin charges in the same region.

Table 3. Charges on TM and Al sites for both spin-polarized and unpolarized cases. In the spin-polarized case, the first and second rows correspond to up spin and down spin respectively.

	Transition metal				Aluminium			
	s	p	d	Total	s	p	d	Total
Unpol.								
FeAl	0.597	0.793	6.878	8.268	0.904	1.386	0.440	2.723
CoAl	0.620	0.843	7.892	9.356	0.877	1.326	0.441	2.644
NiAl	0.686	0.883	8.847	10.416	0.870	1.314	0.400	2.583
Spin pol.								
FeAl	0.298	0.402	3.798	4.497	0.448	0.679	0.223	1.351
	0.300	0.394	3.076	3.771	0.458	0.708	0.215	1.381

The d level population increases in these compounds and the d-band biasing of the majority spin over minority spin electrons decreases, thereby quenching the magnetism. The magnetic moments of pure Fe, Co and Ni as well as for FeAl compound are given in table 4. The magnetic moments of the pure Fe, Co and Ni agree very well with the available experimental and theoretical results. In the present study, ordered CoAl and NiAl

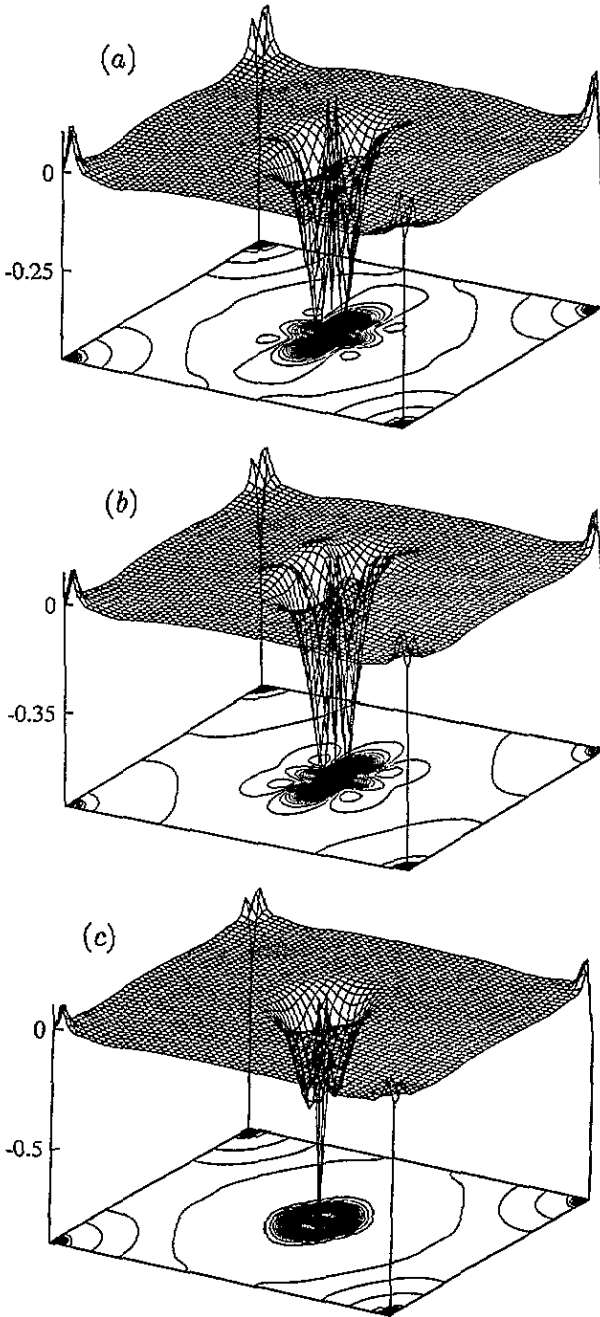


Figure 6. Bonding charge densities for (a) FeAl, (b) CoAl and (c) NiAl in (110) plane. The TM atom is at the centre and the Al atoms at the corners.

do not show any magnetic moment, whereas FeAl has a magnetic moment of about 0.7 Bohr magnetons per atom. Since the magnetic and paramagnetic ground states are just 0.63 mRyd away we also performed calculations using Ceperley–Alder [35] exchange–correlation potentials which yield a difference of 0.99 mRyd. Hence, both the von Barth–Hedin and

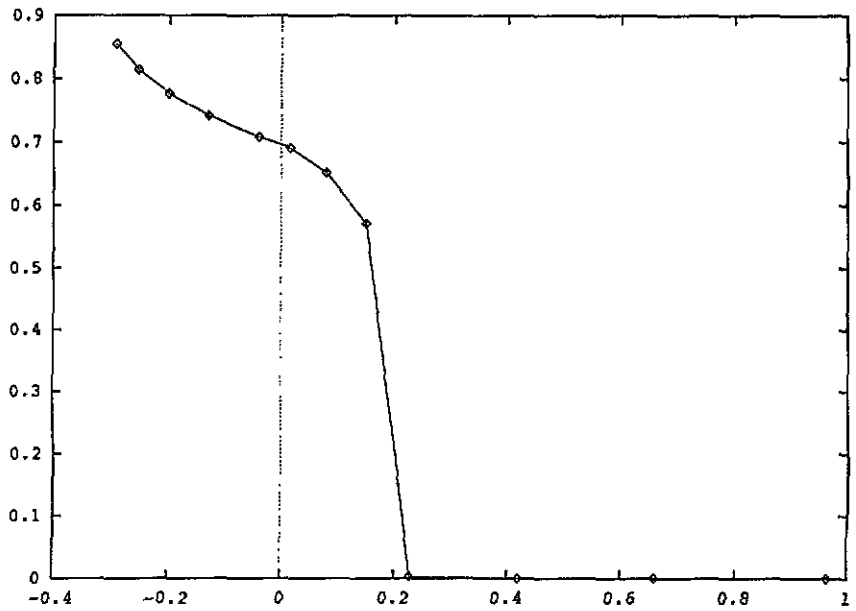


Figure 7. Hydrostatic pressure variation of the magnetic moment in FeAl.

Table 4. Magnetic moments of pure Fe, Co and Ni and FeAl in units of Bohr magnetons (μ_B) per atom.

	Moruzzi <i>et al</i> [40]	Experimental [41]	Present calculation
Fe	2.15	2.22	2.13
Co	1.56	1.72	1.55
Ni	0.59	0.606	0.56
FeAl	—	—	0.69

Ceperley–Alder potentials yield consistently the same result. This is also consistent with the earlier LMTO calculations by Min *et al* [12]. Since the energy difference is very small it is very difficult to conclude whether FeAl is magnetic or not. The apparently small magnetic order could be an artifact of the approximations involved in the model used. It may be noted that there is no experimental evidence for magnetic moment in ordered FeAl alloys. Spin-polarized calculations show zero magnetic moment for CoAl and NiAl for the range of lattice parameters used by us. This is in support of the ASW calculations by Hackenbracht and Kubler [31], where they find very little spin splitting even for the Ni_3Al compound and magnetic moment is quenched at a critical pressure value of 0.046 Mbar. For FeAl, the pressure variation of the magnetic moment obtained by us is shown in figure 7. We find the rate of variation of magnetic moment with pressure to be $-0.36 \mu_B \text{ Mbar}^{-1}$ at zero pressure and the magnetic moment at equilibrium volume to be $0.695 \mu_B/\text{atom}$. It can be seen from figure 7 that the magnetism is quenched beyond 0.22 Mbar.

4. Summary

We have performed *ab initio* TB-LMTO calculations on the FeAl, CoAl and NiAl compounds and obtained their cohesive, electronic and magnetic properties. We find very good agreement between our results of band structure and earlier theoretical and experimental results. We observe a charge transfer from the Al site to the TM site which are quantitatively obtained from the ASA. The FeAl compound retains a magnetic moment of $0.7 \mu_B/\text{atom}$, whereas in CoAl and NiAl it is totally quenched due to d band population. The d band widths of these compounds are found to decrease compared to the pure TM cases. The cross-sections of the Fermi surface compare very well with the experimental results of Lui *et al* [16] for the case of NiAl.

Acknowledgments

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