Calculations of systematics in B2 structure 3d transition metal aluminides

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Abstract

An all-electron total energy local density functional approach was used to examine features in the electronic structure of B2 structure transition metal aluminides that are possible factors affecting brittleness in these intermetallics. Noting that iron, cobalt and nickel all form stable aluminides with nearly identical lattice parameters, yet manifest different physical properties, we compared calculated results for B2 FeAl, CoAl, NiAl and CuAl, with an eye toward elucidating those features that correlate with the observed physical properties. The first-principles calculations accurately reproduced the formation energies of these compounds. Detailed analyses of the results explicitly demonstrated that factors commonly associated with bonding and brittleness in intermetallics — valency, ionicity and directional bonding — cannot in fact be the critical factors governing the behavior of these materials.

1. Introduction

The B2 compound NiAl is of great technological interest as a promising material for high temperature applications because of its low density (relative to the current generation of superalloys), high melting temperature with strength retention at elevated temperatures, excellent thermal conductivity, and good oxidation resistance. In the past two decades, a great deal of effort, both experimental and theoretical, has been devoted to understanding the nature of the bonding in this intermetallic. Among the factors proposed as important to understanding the nature of the bonding in intermetallics is transition metal valency or *d*-band filling, charge transfer or ionicity, and directional bonding or *p–d* hybridization. Recent work has begun to focus on the most important property in this system from a practical standpoint, the brittleness at room temperature that limits its utility in practical structural applications. Despite great effort, the physical origins of the brittleness at room temperature are poorly understood at best. The purpose of this paper is to investigate in a systematic way, the possible correlation of these factors associated with the bonding with macroscopic behavior in B2 intermetallics.

Nickel's neighbors in the periodic table, iron and cobalt, also form stable aluminides, in the same B2 (CsCl) structure and with similar lattice parameters,

yet manifest different physical properties. This set therefore constitutes an ideal theoretical laboratory to test various hypotheses regarding the origins of the lack of room temperature ductility in NiAL. In this paper, we use a first-principles local density functional method to calculate the electronic structure in stoichiometric B2 FeAl, CoAl, NiAl and "CuAl". Analyses of the results clearly exclude directional bonding, ionicity or charge transfer, or differences in valence, as being the root cause of the brittleness or cleavage. This is not to say that there is no charge transfer or a directional nature to the bonding, in fact our analysis suggests that there is a directional component to the charge density, but rather that the difference in charge transfer or directionality calculated between the various compounds does not follow the observed differences in physical properties.

The paper is organized as follows. First we summarize the observed properties for the B2 aluminides, and review the models that have been proposed in previous work to describe the bonding in these materials. Next, we describe the theoretical method used in the total energy calculations. In the following section, the results of the calculations for B2 FeAl, CoAl, NiAl, and the hypothetical B2 structure "CuAl" intermetallic are presented, followed by a discussion of the nature of the bonding in the various compounds, how the results compare with previous analyses, and what relation the

bonding analyses have to the observed properties of the materials. We close with some brief conclusions.

2. Background: B2 transition metal aluminides

FeAl, CoAl, and NiAl make up a very interesting series of compounds. Elemental Fe, Co, and Ni crystallize in three different structures and are magnetic, yet the aluminides are all paramagnetic [1–3] and crystallize in the same B2 (CsCl) structure depicted in Fig. 1 with nearly the same lattice parameter (2.909 Å [4], 2.862 Å [5], and 2.886 Å [5] respectively). The structures are stable over a wide range of compositions [6] and the crystals are all rather stiff with similar bulk moduli (within 10 GPa of 160 GPa) and elastic constants [7–9]. CoAl and NiAl melt congruently at very high temperatures, 1648 °C and 1638 °C respectively, the peak melting temperature being on stoichiometry, while FeAl melts 400 °C lower [6]. All three remain ordered up to the melting point. More germane to the current investigation are the macroscopic physical properties. FeAl, particularly in the iron-rich regime, is relatively ductile [10], while NiAl and particularly CoAl are brittle at room temperature. NiAl is of particular interest in high-temperature applications, and a major goal of alloy development is to remedy the brittleness at room temperature that precludes its use.

Ductility in polycrystalline materials is frequently correlated with the slip systems available to facilitate deformation. In CoAl and NiAl, $\langle 100 \rangle$ slip predominates, while in FeAl, the $\langle 111 \rangle$ slip systems, just as in
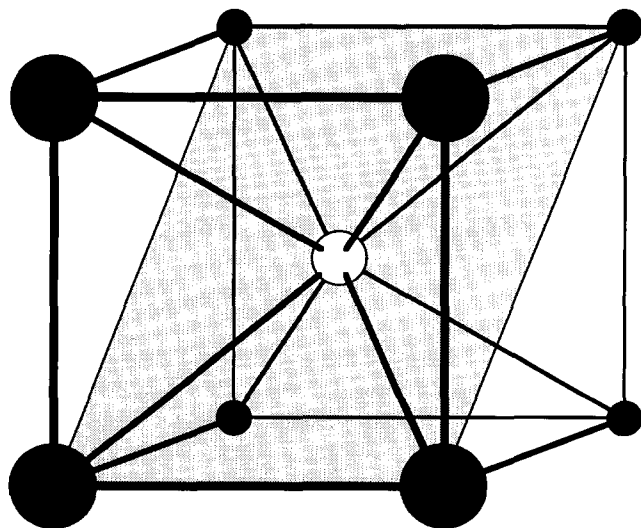

Fig. 1. Schematic representation of the B2 (cesium chloride) crystal structure. The charge densities in later figures or plotted on the section of the [110] plane shaded in the schematic, with the aluminum atom at the center of the plot and the transition metal atoms at the corners.

elemental b.c.c. metals, are operative [11, 12], thereby providing sufficient independent slip systems required for compatible deformation by arbitrary homogeneous strains. Brittleness is also at least somewhat related to cleavage in crystals, and here also there is a distinction between the intermetallics. FeAl, like most elemental b.c.c. metals, cleaves on {100} planes [13]. NiAl and CoAl, however, share a {110} cleavage plane [13]. The goal of this work is to isolate those features in the bonding corresponding to these differences in behavior.

First, it is worthwhile to review past efforts to explore the bonding in these aluminides, and the appropriate place to start is the classical model from which most descriptions derive. According to the classical picture originating from Hume–Rothery [14–16], the structure of a metal is determined by the ratio of the number of valence sp-electrons to the number of atoms. The postulated range of stability for b.c.c.-based structures is for electron-to-atom ratios equal to or slightly less than 3:2. This simple picture is somewhat complicated in transition metals by the presence of d-orbitals, and was generalized to encompass transition metals by treating the d-orbitals as a sink or source of electrons that do not participate directly in determining the structure. While the energetics would be principally determined by the change in occupation of the d-orbitals, the bonding and structure would be determined by the remaining valence sp-electrons, the d-electrons merely acting as observers. This has several notable implications for the B2 transition metal aluminides. In the aluminides, Al contributes three sp-electrons to the valence, and, hence, in order to satisfy the Hume–Rothery criterion, the transition metal atom must be a zero valence atom. For the Fe, Co, and Ni aluminides, this implies a local $d^n s^0$ configuration for the atom, i.e. the s-electrons of the atom collapse into the d-shell in the alloy. This immediately explains why a stoichiometric B2 phase of "CuAl" does not exist, as the d-shell is already full in the Cu atom. That transition metal atoms will substitute on Al sites in Al-poor off-stoichiometry alloys while Al in Al-rich alloys will not substitute on the transition metal site but will introduce vacancies [17–19], is consistent with this picture.

The fact that the B2 aluminides are strongly ordered, high-strength materials implies strong bonds, and since the transition metal atom has supposedly collapsed its electrons into the non-bonding d-shell, the bonding between the atoms must be accomplished via the aluminum's three electrons, which implies effective transfer of charge to the transition metal atom. The direction of charge transfer suggested in this description is consistent with the Pauling electronegativity of 1.5 for Al, with respect to 1.8 for Fe, Co, and Ni [20]. The brittleness and a {110} cleavage plane would also be consistent with charge transfer. Ionic crystals tend to cleave on

the neutral 50–50 {110} plane rather than the polar {100} because of the large Coulombic energies involved. Furthermore, ionicity would help explain the stability of the *B*2 structure, resulting from the large Madelung energies, and the high ordering energies.

This very simple empirical picture of the bonding in the aluminides has proven surprisingly robust through time. Miedema [21], and others [22], have constructed empirical models derived from, or related to, this picture that have done surprisingly well at describing the energetics of binary alloys based on the filling of the d-bands by sp-valence electrons. This filling of the transition metal d-shell is consistent with many experimental observations, (nuclear magnetic resonance [3], soft X-ray emission [23–28], and photoemission [29–33]), that note that charge transfer from aluminum to the transition metal atom, with concomitant filling of the d-band seen in FeAl and CoAl is complete in NiAl, though a select few photoemission studies dispute specifics of the conclusions [29, 32, 33].

The first calculations of note on these aluminides began with the non-self-consistent augmented plane wave (APW) calculations of Connolly and Johnson for NiAl [34], and while later calculations [24, 26, 27, 34–51] on *B*2 aluminides added greater sophistication such as self-consistency, many essential qualitative features are already described in these early results. The density-of-states (DOS) is characterized by two sharp peaks separated by a "pseudo-gap" [45] resulting from localized d-orbitals on the transition metal, overlaid with a much broader valence sp-band. The Fermi level for NiAl is computed to be above both peaks, indicative of filled d-bands. Subsequent calculations for FeAl, CoAl, and NiAl exhibit a qualitatively similar DOS, suggesting that a rigid band description is approximately valid, with the Fermi levels for FeAl and CoAl below the second DOS peak, indicating unfilled d-levels. This result is in harmony with the classical picture given above. Furthermore, computations of charge transfer, be they obtained by various population analyses [24, 27, 44–46], an Ewald [43] or related [37] construction, have generally concluded that a (small) charge transfer takes place from the aluminum atom to the transition metal atom, generally in the range of 0.2 to 0.6 electrons.

There have been a few discordant notes in what has been a rather broad chorus of consensus on the nature of the bonding in these systems. Cragg and Fletcher concluded charge transfer was minor in a model calculation [48]. Fuggle *et al.*, in photoemission studies on Ni and Pd alloys, assert that the amount of charge transfer is probably small and that d-band filling was caused by hybridization of the d-orbitals with sp-bands [32]. Recent more rigorous calculations by Hong and Freeman led them to conclude that directional bonding and consequent high anti-phase-boundary energies are

at the root of brittleness in NiAl [49]. However, results of full-potential linear-APW calculations for FeAl and NiAl led Fu to conclude that strong directional bonding was the source of FeAl's resistance to cleavage, and NiAl's brittleness was caused by its reduced directional bonding and greater ionicity [50, 51]. A study combining photoemission and the linear-augmented Slater-type-orbital (LASTO) method, on the basis of shifts in core levels, concluded that charge transfer, rather than being from Al to Ni, was from Ni to Al [33]. Diffraction studies on CoAl [52] and NiAl [52, 53] observed buildup of charge consistent with directional bonding, but disputed that charge transfer takes place between the transition metal and the aluminum.

Clearly there exists a great deal of confusion regarding the nature of the bonding in these *B*2 aluminides, and the consequences that that bonding has for observed behavior. The intent of the current calculations is to attempt to resolve some of these questions by studying all three aluminides simultaneously, subjecting each bonding feature to a systemic analysis in all the aluminides, and comparing the results of that analysis to experimental behavior. In addition to the three existing aluminides, it is instructive to compare calculations for "CuAl" as well, even though stoichiometric CuAl does not exist in the CsCl structure in nature.

3. Calculational procedure

The calculations were done using the full-potential form [54] of the linear-augmented Slater-type-orbital (LASTO) method [55]. This is a first-principles method for solving the bulk electronic structure within the local density functional (LDF) approximation. It has been described in detail elsewhere [54–56]; here we only summarize the salient features. Space is partitioned into spheres about atoms or "muffin tins" and interstitial regions. The basis to describe the electronic states consists of Bloch sums-of-tails, or STOs, of the form:

$$\phi_{nlm}(\mathbf{r}) = r^{n-1} \exp(-\zeta r) Y_{lm} \tag{1}$$

in the space between the spheres, matched onto numerical solutions of the spin-orbitless Dirac equation inside the spheres. No "shape approximation" is made to the charge density or potential. Inside the spheres, these quantities are expanded in spherical harmonics up to $l = 8$ while in the interstitial region they are expanded in a Fourier series. The Poisson equation in the interstitial regions is solved using Weinert's method [57] of replacing the charge inside the spheres with a smooth pseudo-charge having the same multipole moments. The core levels within the atomic spheres are calculated self-consistently using the spherical part of the potential inside the sphere. This method enables

very accurate solutions of the LDF equations, dependent on the quality of the chosen STO basis set, and cutoffs in the reciprocal lattice sums. In fact, the method is very similar in philosophy to the full-potential LAPW method [57], except that STOs are used as the basis in the interstitial regions rather than plane waves, and it attains comparable accuracy.

Having atomic spheres of the same size for all atoms simplifies the analyses of charge transfer and ionicity in the alloys. In the calculations which follow, a sphere size of 2.3 bohr (1 bohr ≈ 0.529 Å) was selected. This size, more than ample for the aluminum atoms, was deemed the minimum necessary to be sufficiently accurate for the transition metal atoms (the muffin-tin expansion being more accurate than computationally practical interstitial expansions for calculating total energies using smaller spheres), while remaining small enough that spheres would not overlap in any of the systems being calculated.

The STO basis was of "double-ζ plus polarization" quality. Specifically, this includes 3s, 3p, 4s, 4p, and 3d functions for the aluminum, and 4s, 4p, 3d, 5s, 5p, 4d, and 4f functions for the transition metal atoms (the full argon shell of electrons being treated as core electrons). The ζ's were chosen to minimize the computed energies in small-scale calculations (20 k-points and $g_{cut} = 8\pi/a$ for Fe and $9\pi/a$ otherwise, see below) for the elemental metals. Table 1 lists the optimized ζ's used in the calculations. Additional functions proved to be of little or no value and led on occasion to problems with linear dependence.

The charge density (and potential) was constructed using wave functions calculated at 110, 70, and 35 special k-points in the irreducible wedges of the Brillouin zones for the f.c.c., b.c.c., and B2 structures respectively (broadening and partially occupying levels very near the Fermi energy). This number is actually greater than that necessary to achieve convergence. In addition, a cutoff g_{cut} needs be chosen for the Fourier expansion of the interstitial terms for each structure [56]. The change densities and computed energies converge rapidly with respect to this cutoff. However, secondary quantities such as lattice parameters and particularly bulk moduli prove much more sensitive and converge

rather less well as a function of g_{cut}, particularly with smaller spheres. The required g_{cut} varies inversely with the transition metal sphere size. Presumably, the effect of the tails of the transition metal d-orbitals in the interstitial regions, with their relatively rapidly varying radial forms, are difficult to treat accurately. In the LAPW method, this problem manifests itself as the need to include very high-energy plane waves in the interstitial basis sets; here the STOs solve the basis set problem, but residues of the problem remain when it comes to constructing the densities and potentials, and evaluating the integrals in the interstitial regions.

4. Results

The first step is to calculate the energies for the elemental metals. The structures and calculation parameters, and the computed total energies, are listed in Table 2. The structure and lattice constant used in each case was the experimental one [58] with the exception of cobalt, where an f.c.c. structure of the same atom density as the ground state h.c.p. structure was used instead (the energy difference between the two close-packed structures is expected to be about 0.1 eV). As is usually the case in LDF calculations, the calculated cohesive energies, particularly for the transition metals, greatly exceed experiment (by more than 2 eV for Fe and Co). (The energies of the atoms includes a spin polarization correction as computed by Wang and Davenport [59].) This is a failure of the LDF approximation. Additionally, the calculations are non-spin-polarized and hence exclude magnetic effects.

TABLE 2. Calculated energies — structure, lattice parameter, number of k-points sampled in the irreducible Brillouin zone (IBZ), and g_{cut} used in the total energy band structure calculations, and the resulting energies per unit cell (uc)

Structure		a (bohr)	k-points (# IBZ)	g_{cut} (in π/a)	Energy (hartree/uc)
Al	atom	–	–	–	– 241.77380
Fe	atom	–	–	–	– 1270.29372
Co	atom	–	–	–	– 1390.85924
Ni	atom	–	–	–	– 1518.13315
Cu	atom	–	–	–	– 1652.27009
Al	f.c.c.	7.65	110	20.2	– 241.92003
Fe	b.c.c.	5.42	70	17.3	– 1270.52842
Co	f.c.c.	6.68	110	20.2	– 1391.10420
Ni	f.c.c.	6.66	110	20.2	– 1518.35156
Cu	f.c.c.	6.81	110	20.2	– 1652.43250
FeAl	B2	5.45	35	15.0	– 1512.49639
		5.50	35	15.0	– 1512.49390
CoAl	B2	5.45	35	15.0	– 1633.07736
		5.41	35	15.0	– 1633.07921
NiAl	B2	5.45	35	15.0	– 1760.32342
CuAl	B2	5.45	35	15.0	– 1894.36375

TABLE 1. Basis sets. The ζ values for the STO functions optimized for each atom (sphere size of 2.3 bohr). Units: bohr^{-1}

Atom	3s	3p	3d	4s	4p	4d	4f	5s	5p
Al	1.0	1.4	1.2	0.8	0.8	–	–	–	–
Fe	–	–	1.9	1.74	1.41	2.43	1.5	2.3	2.0
Co	–	–	1.9	1.85	1.48	2.46	1.3	2.4	2.1
Ni	–	–	1.9	1.94	1.54	2.48	1.1	2.5	2.2
Cu	–	–	1.9	2.00	1.62	2.50	1.0	2.6	2.2

Open shell systems in transition metals using LDF are problematic in any case, particularly for iron [60], and as our current focus is the *B*2 aluminides, all of which are paramagnetic, rather than the elemental metals, we will not dwell on this issue here.

The next step is to calculate the energies of the *B*2 aluminides. Iron, cobalt, and nickel all form *B*2 aluminides with very similar lattice parameters; stoichiometric CuAl does not. To facilitate direct comparisons of the electronic charge density and bonding presented later, all four aluminides were calculated using the NiAl lattice parameter, as it represents a suitable average of the three existing aluminides of interest. However, additional calculations were performed for FeAl and CoAl at their respective experimental lattice parameters. The calculational parameters and computed energies for the *B*2 aluminides are listed in Table 2. Note that the differences for FeAl and CoAl between the total energies at the experimental and NiAl lattice parameters are small (about 0.05 eV), which is not surprising given the less than 1% difference in lattice parameter. This supports the premise that the electronic structure of the common lattice parameter accurately mimics the electronic structure calculated for the true lattice parameter, and therefore that the analyses of the bonding using the results at the common lattice parameter meaningfully compare the bonding in the different systems.

The heats of formation are computed and pictorially summarized in Fig. 2. The Δ*H*s for TAl (T = transition metal atom) are obtained by taking the energy per unit
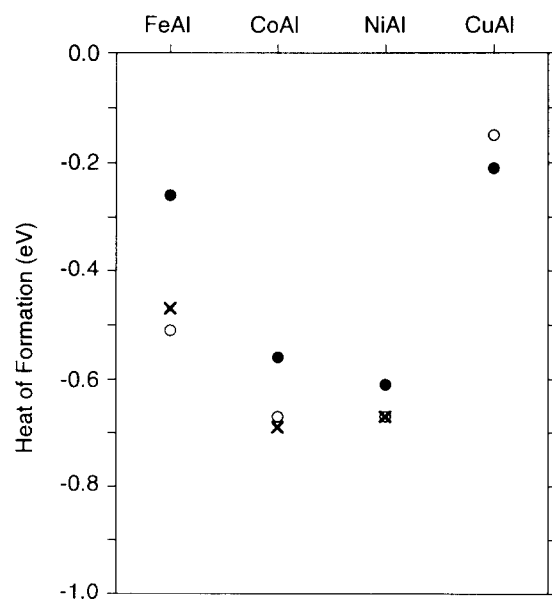

Fig. 2. Computed heats of formation for the *B*2 aluminides. The solid circles represent the experimental heats. The open circles represent the heats of formation computed using the NiAl (5.45 bohr) lattice parameter while the crosses represent the computed value using the experimental lattice parameters.

cell for TAl using the experimental lattice parameters, and subtracting the energies for elemental T and f.c.c. Al. As Fe, Co, and Ni are magnetic, these raw values need to be corrected to account for the fact that the elemental calculations were not spin-polarized. The LDF magnetization energies have been given in ref. 61, and the displayed results reflect the magnetization energy-adjustment per transition metal atom of 0.29, 0.11, 0.08 and 0.00 eV for Fe, Co, Ni, and Cu respectively. The resulting heats of formation are then compared to the available experimental values [62]. The experimental Δ*H* for CuAl, as no stoichiometric *B*2 structure exists in nature, is taken to be the Δ*H* for the existing CuAl intermetallic [62]. All the computed formation energies are in good agreement with experiment, the largest discrepancy being -0.21 eV for FeAl, and the error changing monotically to $+0.06$ eV for CuAl, and are in line with previous calculations of formation energies for these *B*2 aluminides. The latter observation merely reaffirms that a variety of approaches that employ the LDF approximation converge to essentially the same results. The minor differences in the results between this work and a previous study [33] using the same method for NiAl (*e.g.* Δ*H* = -0.74 eV atom^{-1} *vs.* -0.67 eV atom^{-1} here) are caused by slight differences in calculational details—basis set, atom sphere size, and g_{cut}—and, for the most part, are insignificant. The first observation testifies to the cancellation of errors that must be taking place in the formation energies where purely bulk calculations are compared, as opposed to cohesive energies where atomic results are compared to bulk and the ensuing computed values are quite poor. The results for "CuAl" need to be regarded with some caution as its equilibrium lattice parameter will differ from the other aluminides (it will be significantly larger) and hence its heat of formation is likely to be underestimated. Furthermore, its equilibrium structure is not *B*2. It is interesting to note that the remaining discrepancy between the computed and experimental heats of formation roughly equals the magnetization correction.

Lattice parameters and bulk moduli were not computed; the LDF equilibrium lattice sizes for the calculations, with the exceptions of f.c.c. Al and B2 "CuAl", are smaller than that allowed by overlapping spheres. Limited calculations using smaller spheres (2.1 bohr) yielded qualitatively reasonable results—lattice parameters 3–5% smaller than experiment, reproducing the observed minimum in lattice parameter in CoAl—but would have required computationally impractically large g_{cut}'s to achieve acceptable precision. Our intent here, however, is to identify those differences in bonding among the *B*2 aluminides critical in understanding the physical behavior, rather than to calculate equations of state.

One of the features we wish to address is the question of the importance of charge transfer in the bonding of the B2 aluminides. To do this requires that some scheme for characterizing the charge distribution be adopted. There exist a variety of ways to calculate and analyze charge distributions, such as Mulliken populations, but most are somewhat arbitrary. To some extent, this merely reflects the reality that charge transfer in metallic systems, where electrons are delocalized and shared among many atoms, is a poorly defined quantity at best, and, as will be demonstrated later, is of doubtful relevance for these intermetallics in any case. The approach we use is to integrate the full valence charge within the atomic spheres we have used in the calculation. The references are all bulk systems rather than atoms; for the elemental metals, this by definition implies a system with no charge transfer. All sphere sizes are the same in every calculation so that:

(1) a particular atom in the metal and intermetallic can be compared equally

(2) the transition metal atoms in the aluminides can be compared one to another, along with the common aluminum atom

(3) transition metal and aluminum atoms are compared on an equal footing in the B2 structure.

This provides a reasonable scheme for partitioning the charge and estimating charge transfer and, more meaningfully, *differences* in charge transfer between different intermetallics. The absolute value of the amount of valence charge within a certain radius of an atom is not so meaningful (though, in principle, this is a measurable quantity) because one could just as easily have chosen spheres of different sizes, but the trends should be instructive. Keeping these caveats in mind, Table 3 presents a breakdown of the valence charge distributions in each of the systems calculated. The charge within the spheres can be broken down as a function of the angular momentum, so in addition to the total charge, the table lists the sp-charge and, for the transition metal, the d-charge within the atomic spheres. Again, the computed values accord with previous theoretical calculations.

Another feature from which conclusions regarding charge transfer are frequently made is shifts of core-level binding energies. Figure 3 summarizes the results for the B2 aluminides. To facilitate comparison to experiment and other theory, all, except "CuAl", use the experimental lattice parameter, though the results are nearly identical using the NiAl lattice parameter throughout (charges within 0.04 electrons, shifts within 0.1 eV). The shifts with respect to E_f in the LDF eigenvalues, ΔE_B, of the core levels from the elemental metal to the intermetallic proved nearly identical within a particular shell and, within approximately 0.1 eV, the same for all shells on a given atom. The rectangles in the figure represent the range of computed core-level shifts for each aluminide. In the same figure, the calculated change in electron charge within the muffin tins is also shown. For reference for future calculations and experiments, Table 4 provides calculated core levels for both atoms in the B2 structure. These values, of course, have no physical meaning in LDF, as unlike Hartree-Fock, there is no Koopmans' Theorem interpretation of the eigenvalues. In addition, they take no account of final-state-relaxation effects. For the Ni $2p_{1/2}$ level for example, the difference in E_B between experiment and theory is approximately 23 eV [30, 33]. The results for NiAl again agree well with those of a previous study [33].

5. Analysis and discussion

In this section we will attempt to bridge the gap between the first principles calculations, results of which have been presented above, and the physical properties of technical interest, particularly brittleness. For the most part, the results we have presented have appeared before, if only in disjoint pieces and perhaps with less rigor. The aim of this work is to identify characteristic trends across this series and systematically isolate (or eliminate) those features of the bonding that correlate with (or alternatively, do not have anything to do with) properties of interest. In particular, the break in behavior

TABLE 3. Charge analysis: breakdown for the calculated valence electron charge (in *e*) present inside atomic spheres for the elemental metals and the intermetallics

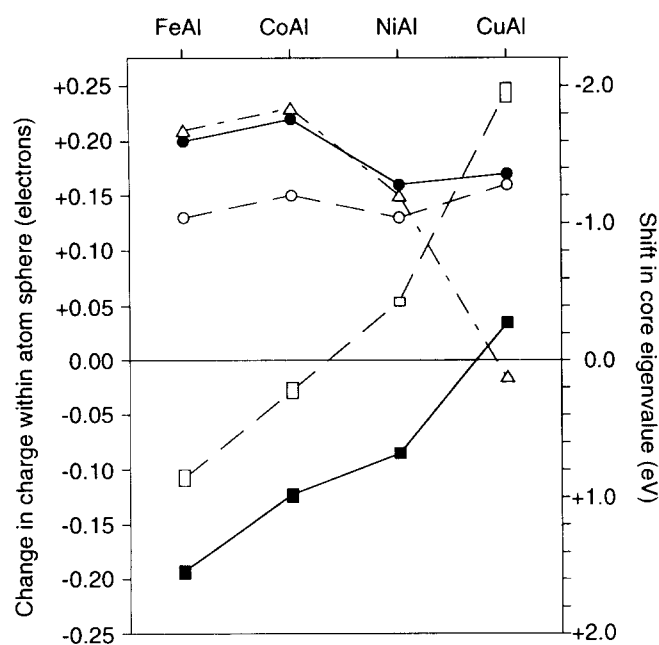|		Al	Fe	FeAl	Co	CoAl	Ni	NiAl	Cu	CuAl
Al	sp	1.30	–	1.44	–	1.39	–	1.38	–	1.39
	Total	1.42	–	1.66	–	1.61	–	1.58	–	1.59
T	sp	–	0.77	0.74	0.86	0.79	0.87	0.87	0.86	1.08
	d	–	6.12	6.35	7.20	7.41	8.26	8.41	9.22	9.20
	Total	–	6.92	7.09	8.09	8.21	9.16	9.29	10.11	10.29
Intestitial		1.59	1.10	2.27	0.92	2.20	0.84	2.14	0.90	2.13

Fig. 3. Core-level shift *vs.* charge transfer analysis. Open symbols represent the results for the transition metal atoms and the solid symbols represent the results for the aluminum atom. The rectangles represent the range of computed core-level binding energy shifts from the elemental metal to the $B2$ aluminide (with respect to E_f) using the scale at right. Using the scale on the left, the circles represent the change in total density within the muffin-tin spheres (radius equals 2.3 bohr) and the triangles the change in d-electron population within the transition metal spheres.

between FeAl an CoAl, and the extremity of behavior of CoAl in the $B2$ series is the pattern to be unearthed.

5.1. Charge transfer

Charge transfer between the transition metal atom and the aluminum atom is a feature, for all its ambiguity, commonly investigated in examinations of the bonding. The Hume-Rothery-based arguments and differences in electronegativity, rationalize a description of the bonding that includes a polarization of charge from the aluminum to the transition metal atom, and the interpretation of most subsequent experiments and theory concurs with this view.

An examination of Fig. 3 reveals that the total charge within the transition metal spheres does indeed increase upon formation of the $B2$ compound with respect to the elemental metal, and that the d-shell, with the exception of "CuAl", is the principal source of this increase. This supports the view that the d-band is filled as a consequence of alloying with aluminum. The increase in total charge within the transition metal sphere across the series varies from 0.12 to 0.18 electrons, 0.15 to 0.24 electrons being gained in the d-shell (a loss of 0.02 d-electrons for Cu, however). While the transition metal atom has gained charge in the alloy, so has the aluminum. In fact, with respect to the elemental metal, the aluminum gains more charge in the intermetallic, 0.16 to 0.24 electrons, than the transition metal atoms. Hence, both atoms in the $B2$ structure have more electrons than they do in the elemental form, the charge coming at the expense of charge in interstitial regions.

The Al sphere has roughly twice the departure from neutrality as the T sphere, *i.e.* is missing twice as many electrons. Rather than being indicative of transfer, though, this is merely a natural consequence of having more than twice as many sp-valence electrons. While the d-orbitals are mostly localized within the muffin tins and therefore are counted in the analysis, the sp-orbitals extend well outside the spheres and their occupation is not well represented in the count. The number of d-electrons on T is increased, and this would possibly explain the results of soft X-ray experiments [23–28]. However, this increase in d-charge is at least partially compensated by a concomitant *decrease* in sp-valence charge, in support of a conjecture made some years back regarding the aluminides [48]. So while the transition metal atom has more charge, focusing on only the localized ds overemphasizes this effect. Compensating transfer for transition metal alloys had first

TABLE 4. Computed core-level binding energies: binding energies, in eV, with respect to the Fermi level

Level	Al	Fe	FeAl	Co	CoAl	Ni	NiAl	Cu	CuAl
Al1s	1499.2		1497.6		1498.1		1498.4		1499.4
Al2s	102.7		101.2		101.7		102.0		103.0
Al2p$_{1/2}$	65.2		63.7		64.2		64.5		65.5
Al2p$_{3/2}$	64.7		63.2		3.8		64.1		65.1
T1s		6974.6	6973.8	7567.3	7567.2	8184.8	8185.2	8828.8	8830.6
T2s		810.6	809.7	889.3	889.0	971.2	971.6	1058.2	1060.3
T2p$_{1/2}$		699.1	698.2	771.5	771.3	847.2	847.6	927.9	930.0
T2p$_{3/2}$		686.6	685.7	756.8	756.5	829.8	830.2	907.5	909.5
T3s		86.3	85.4	94.2	94.0	102.2	102.6	111.9	113.8
T3p$_{1/2}$		53.8	53.0	59.1	58.9	64.5	64.9	71.4	73.4
T3p$_{3/2}$		52.2	51.4	57.3	57.1	62.3	62.7	68.8	70.8

been noted for gold alloys [63]; here we see that the same picture applies in d-aluminides.

The redistribution of charge in the B2 aluminides is poorly characterized as charge transfer, if any charge transfer can be said to have occurred at all. The single notable trend appears to be the incremental addition of a d-electron as one goes across from FeAl to CuAl, all atoms having greater charge in the B2 intermetallic than in the elemental metals. That the transition metals have slightly more charge might be explained by having tri-valent nearest-neighbor atoms, and the aluminum atoms because of their much nearer neighbors. Regardless of how one measures the charge transfer, however, it is unambiguous that *charge transfer is nearly constant in going across the B2 series* and therefore cannot be a critical factor in describing the differences in behavior of the B2 aluminides. Furthermore, the fact that the FeAl crystal has a {100} cleavage plane rather than the {110} plane preferred by ionic crystals further argues that whatever charge transfer there is must be small for FeAl, and hence all these aluminides. A common transfer would be consistent with the observation that the four transition metals share nearly identical electronegativities [20].

5.2. Directional bonding

Directional bonding or p–d hybridization has been identified as a possible culprit in the brittleness of B2 aluminides [49–51], in analogy to, for example, diamond, which has highly directional bonds and is the hardest material known, yet is very brittle. The rationale is that highly directional bonding leads to poor energetics in the deformation necessary for plastic behavior. For titanium aluminides, directional bonding has been claimed to be a critical factor in explaining the brittleness of the materials [64, 65] and has been proposed as a factor in describing the behavior of the B2 aluminides. Directional bonding however, is very difficult to quantify, and, while easy to recognize, is mostly a subjective judgment. In semiconductors, the directional nature of the bonding is unmistakable; in intermetallics, the issue is clouded by the large number of semi-core-like d-electrons that mask the behavior of the sp-valence electrons.

Figure 4 shows contour maps of the calculated valence charge densities for each of the B2 aluminides using the NiAl lattice parameter, using a common set of contours specially selected to highlight features in the density. The panels depict the valence density in the {110} plane of the B2 structure in the geometry shown in Fig. 1, with the transition metal atoms at the corners and the aluminum atom at the center of the plot. Directionality cannot be explicitly excluded, but the total valence density in each case does not exhibit obvious directional character. Instead, it has the distinct
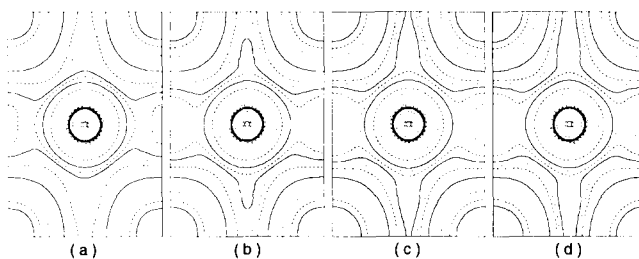

Fig. 4. Contour plots of total valence charge densities for (a) FeAl, (b) CoAl, (c) NiAl, and (d) CuAl in the B2 structure using $a = 5.45$ bohr. The contours have been chosen to highlight variations of the density in the interstitial regions: 0.008, 0.016, 0.024, 0.030, 0.032, 0.034, 0.036, 0.038, 0.040, 0.05, 0.1, 0.2 e bohr^{-3}. The contour values increase cyclically from dotted lines to dashed to solid to dotted again.
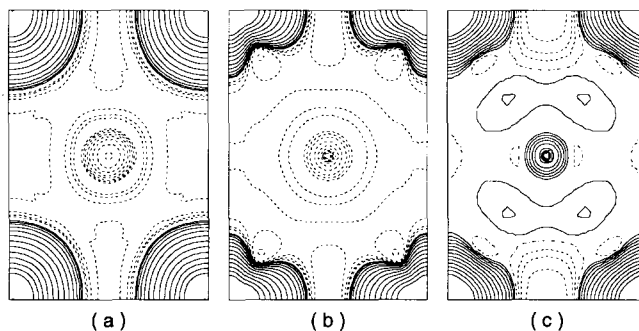

Fig. 5. Contour plots of the valence density differences going from (a) FeAl to CoAl, (b) CoAl to NiAl, and (c) NiAl to CuAl. Thirteen contours proceed logarithmically from 0.0001 to 0.1 e bohr^{-3}. Solid contours denote addition of charge while dashed contours denote loss of charge. In addition, for (c) a dot–dash contour denotes zero change.

appearance of overlapping spherical atoms. The only clear trend from FeAl to CuAl, consistent with the charge analysis above, is the very slight withdrawal of charge from the interstitial region, but other than that very little is evident.

While the total valence density does not have recognizable features, the changes in the density from FeAl to CuAl are much more revealing. Figure 5 depicts the changes in the valence density in going from FeAl to CoAl (Fig. 5(a)), CoAl to NiAl (Fig. 5(b)), and NiAl to CuAl (Fig. 5(c)). The valence density differences are plotted in the same geometry as in Fig. 4, and share a common set of logarithmically spaced contours that are, of course, more diffuse than the ones used in Fig. 4. In Fig. 5(a), the added electron is concentrated in a compact spherical region about the cobalt atom, accompanied by a mild (remembering the logarithmic nature of the contours) loss of charge about the aluminum atom, and in the interstices. Clearly, consistent with the charge analysis above, the extra electron of CoAl with respect to FeAl resides predominantly in d-orbitals about the cobalt and, furthermore, does so symmetrically. Of course, the tendency of all cobalt

orbitals to contract in response to the greater core charge will overaccentuate the spherical nature of any change, but the change about neither atom exhibits any significant asphericity.

The change in valence density in going from CoAl to NiAl, shown in Fig. 5(b), has more distinct features. As in the previous plot, the added electron is concentrated in what must evidently be d-orbitals about the transition metal atom, along with a slightly smaller loss of charge about the aluminum and the interstitial regions. However, the added density about the nickel is not isotropic, but rather has a very directional nature. The density change is predominantly of e_g (d_{z^2} and $d_{x^2-y^2}$) character directed along the [100] directions toward the second nearest-neighbors in the $B2$ lattice, *i.e.* the other nickel atoms. This is accompanied by reduced charge along the Ni–Al nearest-neighbor direction. Considering that overlaid on this change is an isotropic contraction of the charge about the nickel resulting from the increased core attraction, this directional change is quite dramatic.

From NiAl to "CuAl", the change in valence density is intermediate between the previous two examples. The added charge about the copper is still compact (d-like) and somewhat directional, but not nearly to the degree that was the case for the nickel. In addition, charge continues to be lost between transition metal atoms, but, by contrast, the aluminum atom gains instead of loses a modest amount of charge.

The change in density described above is fully consistent with the breakdown of the charge density given in Table 3, *i.e.* the difference going from Fe to Cu is the incremental filling of d-orbitals about the transition metals. However, the character of those changes is not consistent with the hypothesis that directional bonding is at the root of the brittleness of the $B2$ aluminides. If directional bonding were the critical factor in describing the brittleness in the $B2$ aluminides, the break in behavior should occur between CoAl and NiAl where the change in bonding density shows a clear directional nature, yet the change in cleavage behavior, ordering energies, and brittleness occurs between FeAl and CoAl. This does *not* say that there is no directional bonding in these intermetallics, in fact it almost certainly exists, it only shows that directional bonding does not correlate with the observed behavior of interest. In fact, this perhaps explains how two different pieces of work [49, 51] can yield entirely different conclusions regarding the importance of directional bonding, and underscores the hazards inherent in performing only a limited set of calculations on one material rather than a systematic investigation of trends between different materials. One can find directional bonding in a single material, but unless it is compared to another material with different

properties, it is possible that directional bonding is totally irrelevant for those properties.

5.3. Filling d-bands

For the Hume-Rothery rules to be valid, the only sp-valence electrons in TAl must be three, from the Al, and the s-electrons of the transition metal atoms must collapse into the d-shell. This implies a sequential filling of the d-shell in TAl from FeAl to NiAl, which achieves a filled d^{10} configuration. Numerous band structure calculations have demonstrated filling of the d-bands in TAl, up to NiAl at which point the d-bands are filled. Fuggle *et al.* [32] injected a cautionary note, however, making the important distinction between the observation that the d-bands are filled, and the conclusion that the d-orbitals on Ni are completely filled. The argument is that while the so-called d-bands are predominantly of T d-character, they also contain T and Al valence sp-character as well, *i.e.* the bands are hybridized.

The charge breakdown presented in Table 3 indeed supports the idea that the d-orbitals on the transition metal atom are sequentially filled by an additional electron going from FeAl to NiAl. Within the T muffin tins, the number of electrons of $l = 2$ increases by 1.06 electrons from FeAl to CoAl, and 1.00 electrons from CoAl to NiAl. However, the d-electron count for NiAl is much less than the ten postulated in the Hume-Rothery picture, and while some of this could be attributed to the fact that the computed number of electrons of $l = 2$ within the muffin-tin spheres is not the same thing as the number of d-electrons (for one thing the d-orbitals are not entirely contained within the muffin tin causing the d-electron count to be underestimated), the 1.59 electrons missing is rather large. Furthermore, "CuAl" exhibits an additional 0.79 electrons in the d-shell, demonstrating that indeed the d-orbitals on Ni in NiAl are not filled. The valence density difference plot of Fig. 5(c) graphically illustrates this point, showing that the additional electron of "CuAl" with respect to NiAl is contained in the d-shell of Cu rather than distributed as delocalized sp-electrons.

According to the LDF calculations, the $B2$ aluminides are *not* Hume-Rothery electron compounds. In each aluminide, the number of sp-electrons exceeds the number permitted for the $B2$ structure by roughly one (presuming that "CuAl" corresponds to a full d-shell and that any electron not in the d-shell is in the valence). Furthermore the valence across the series is nearly the same. Implicit in these results is the conclusion that the d-orbitals are direct participants in the bonding. If they were not, the valence electron-to-atom ratio of roughly two would preclude stability of the $B2$ structure, *i.e.* it must be the action of the d-orbitals to stabilize this structure, for if only sp-electron bonding was pres-

ent, the Hume-Rothery rules would dictate a different structure. The interaction of the d and sp-electrons could already be inferred from the observation that FeAl and CoAl are paramagnetic despite having unfilled d-shells; the above bonding argument provides more indirect support for this interpretation. Furthermore, this line of reasoning suggests that the resulting bonding is directional so as to stabilize the B2 structure against the Hume-Rothery instability. So while the arguments in the previous section demonstrate that directional bonding is not the key element in understanding the brittleness of B2 aluminides, the nature of the d-band filling suggests that directional bonding is indeed present. The d–sp hybridization had already been illustrated in a previous LASTO study on NiAl [33] in the marked effect on the calculated bands of artificially setting the coupling between the d-states and the sp-states to zero.

5.4. Core-level shifts

Core-level shifts are frequently interpreted in terms of charge transfer, usually associated with lower core-level binding energies on the atom that has gained electrons, and higher core-level binding energies on the atom that has lost electrons. From Table 3 it can be seen that the net charge in the atomic spheres is greater in the compounds than in the elemental metals for each of the constituent atoms (by charge we mean electrons, so that charge transfer is positive when the number of electrons increases). Glancing at Fig. 3, the calculated shifts for FeAl and CoAl are consistent with this naïve picture. For NiAl, however, although the calculations show *both* atoms have *more* charge than in the elemental metals, the core-level shifts suggest a transfer of charge from Ni to Al [33], and the computed shifts for *both* sites in "CuAl" are incompatible with the increase in valence electron charge. The core electrons are almost entirely (within 0.01 total electrons) contained inside the muffin tins within which the valence charge is computed, and hence a hypothetical initial-state screening effect should follow that value. Though the computed charge transfers are nearly identical for each case, the core-level shifts vary greatly, the shifts going to higher binding energies in the sequence from FeAl to "CuAl".

What went wrong? First, the simple rule discounts the effect of the large amount of charge outside the spheres, and furthermore neglects its character. It has been suggested by Watson *et al.* [63], that there will be compensating flow in the d and sp systems. In the charge analysis, while the change in d-occupation will be accurately represented because of the compactness of the d-shell, the sp counter-flow will be underestimated, and the degree of compensation is difficult to quantify. In addition, this simple analysis of initial state effects on core levels neglects a Coulombic Madelung

term that tends to oppose the screening term effects on the core levels. For example, Okochi and Yagisawa [43] estimated that the Madelung term amounted to 0.82 eV for CoAl using their estimated transfer of 0.28 electrons. Second, final state relaxation, especially for core levels, can be very large – an order of magnitude or more than the shift of interest – and the expectation that relaxation effects cancel this will not be perfectly realized. Third, the Fermi level is not the appropriate reference to calibrate core levels against charge transfer, even neglecting the above issues. It is merely the most convenient reference to compare computed values and experiment. These factors all argue that great care be taken in interpreting core level data in terms of charge transfer, especially when shifts of such small magnitude are involved. For the LDF calculation, in addition, there is the problem that the eigenvalues cannot be interpreted as removal energies, as they can in Hartree-Fock theory (in the limit of no relaxation), because of self-energy terms. Again, the hope that these terms cancel out may not be well realized. For the Ni 2p levels, for example, the discrepancy between the LDF eigenvalues and the measured core levels is rather large, approximately 23 eV, and testifies to the magnitude of the above terms. Given that the shifts of interests are of the order of less than 1 eV, it should not be surprising that initial-state screening effects might be washed out. The difficulty in analyzing core level results in terms of charge transfer has been commented on before [63]. This work reiterates this caution for the B2 aluminides.

5.5. Comparison to previous work

Most previous calculations are in substantive agreement with the current results, even though the current calculations are usually more rigorous, using a state-of-the-art full-potential method. Calculated heats of formation agree with one another [33, 38, 40], and with experiment [62]. The determination that the d-orbitals on the transition metal atoms are more filled in the compound than in the pure metal is almost universally shared. The conclusion that greater d-band filling is caused by charge transfer, however, is not supported in the current work. First, the degree of increased d-occupation is not that large and, second, as Cragg and Fletcher noted [48], increased T d-occupation can lead to a concomitant loss in T sp-charge resulting from repulsion between the electrons, and out results show evidence for this effect. Because the d-orbitals are much more compact than the valence sp-orbitals, however, this tradeoff can be easily mistaken for charge transfer when actually very little net transfer has occurred. This phenomenon reconciles the results of our calculations where little charge transfer is found, to the results from early soft X-ray studies from which charge transfer to the transition metal atoms was inferred but probably

merely reflected increased d-occupation. As we had noted above, the distribution of electrons in the *B*2 aluminides is not well described as charge transfer, and the results that show *both* atoms gaining electrons highlight this fact.

The best experimental information regarding the charge density distribution in these systems comes from a 1963 X-ray diffraction study on CoAl and FeAl by Cooper [52], and a recent high-energy electron diffraction study on NiAl by Fox and Tabbernor [53]. They observed a buildup of charge between nearest neighbor T–Al atoms with a corresponding depletion of charge between second nearest neighbor Al–Al and Ni–Ni atoms, and loss of charge on both atomic sites. The bonding was described as "essentially covalent with some metallic character and no ionic component" [53]. A direct comparison of the experimental analysis with the LASTO results is difficult, in part because the references used for the charge distribution in the experiments consisted of Hartree-Fock atoms while the charge analyses were all referenced to bulk LDF calculations; nevertheless, it is possible.

The most notable feature in the experiments was the buildup of charge along the $\langle 111 \rangle$ axis between the nearest neighbor aluminum and transition metal atoms. Any departure from sphericity in the total valence density plots of Fig. 4 that would correspond to this directional buildup is not noticeable because of the masking effect of the large number of d-electrons on the transition metal atoms. However, it is possible to deduce directional character from the density difference plots of Fig. 5 in the following manner. The shape of the density is going to be dominated by the electrons in the d-shell on the transition metal because of their compactness and great number with respect to the sp-valence electrons. Ideally, a completely filled d-shell is spherical. The d-shell is filled in "CuAl" (near enough for our purpose), the valence density differences working backward to NiAl, CoAl, and FeAl remove charge from a sphere, so that the complement of the difference density determines where the electrons in the d-shell are directed in the sphere. The difference density from "CuAl" to NiAl, and NiAl to CoAl, is directed toward second-nearest neighbor atoms and away from first-nearest neighbor atoms, and hence the occupied d-charge in CoAl and NiAl is deformed from a sphere in the opposite sense, with charge directed along the $\langle 111 \rangle$ nearest neighbor axes and away from $\langle 100 \rangle$ second-nearest bond directions. Hence the directional nature of the valence density revealed in the experiments is reproduced in the calculation. Further, since the density difference from CoAl to FeAl is roughly spherical, this directional character exists in that intermetallic as well.

It is worth noting Fu's calculations for FeAl also describe similar features [50]. The full potential LAPW calculations show a buildup of charge along the Fe–Al nearest bonds with depletion of charge in d electrons of e_g symmetry on the transition metal. Our calculations show that the same directionality also exists in CoAl, and, though reduced in magnitude, also for NiAl. Furthermore, the sequence described by the density difference plots of Fig. 5 is consistent with the calculations of Eibler and Neckel [41], who in a hybridized nearly free electron tight binding calculation, further broke down the d-charge into e_g and t_{2g} components.

The calculations and the bonding analyses presented above concur with the conclusion derived from the diffraction experiments [52, 53] that there is no ionic component to the bonding. However, there is an apparent disagreement as to whether the constituent atoms of NiAl gain or lose charge. Two points are important to keep in mind. First, the experiment references spherical Hartree-Fock atoms in making this determination, while the calculations use bulk elemental metal calculations as a reference; the electronic configurations of an isolated Hartree-Fock atom and an LDF bulk atom will be different. Second, the spheres within which the electron charges are integrated encompass the $\langle 111 \rangle$ bond charge at issue as they very nearly touch at the midpoint, as illustrated in Fig. 6. The "atomic" charge of the *B*2 calculation incorporates the "$\langle 111 \rangle$bond" charge of the experiment and the "atomic" charges of experiment and theory do not represent the same quantity. However, the $\langle 100 \rangle$ second-nearest neighbor bond midpoints of the experiments are roughly equivalent to the interstitial regions of the calculations, and can be directly compared. There is agreement that there is loss of charge in these regions. Hence there
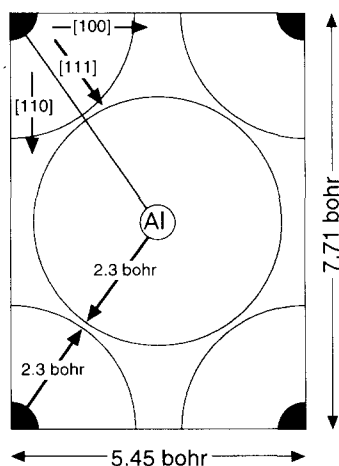

Fig. 6. A schematic representation of the space-filling nature of the muffin-tin spheres used in the full-potential calculations. Note that the $\langle 111 \rangle$ nearest neighbor bond area is almost totally contained within the spheres.

is substantive agreement between the results of the experiments and its conclusions, and the results of the current calculations.

6. Summary and conclusions

In this work we systematically examined the late three-d transition metal B2 aluminides using a first-principles method to analyze the nature of bonding, emphasizing those features in the bonding that could play a role in the observed behavior, in particular brittleness. The results of the calculations for FeAl, CoAl and NiAl are in good agreement with available experiment where comparison is possible, indicating that the calculations are providing a good description of the bonding in these systems. While there have been many studies of these aluminides, only recently have they begun to focus on brittleness and cleavage [49–51], and most of those have isolated on a narrow aspect of a single material. This has frequently led to quite divergent interpretations of the bonding and the implications of that bonding on observed behavior. Noting the similarity in lattice parameter, it was hoped that it would be possible to take advantage of this ideal theoretical laboratory to make more definitive conclusions regarding the nature of the bonding and the role of the bonding in brittle behavior. The results of the current calculations bear out this expectation and the following conclusions regarding the electronic structure of the B2 aluminides emerge:

(1) Charge transfer or ionicity is not a critical factor in these intermetallics. Regardless of whether charge transfer exists at all, the magnitude of transfer is the same for each aluminide, despite their different properties.

(2) The results do not support the interpretation of any significant ionic component to the bonding. The charge breakdown of Table 3 disagrees with the notion that charge has been transferred from one atom to another and, while the {110} cleavage planes and high ordering energies of CoAl are consistent with ionic bonding, the {100} cleavage plane of FeAl is not, and yet the degree of charge transfer in all three compounds is calculated to be the same.

(3) The velency of the B2 aluminide is constant across the series, i.e. the number of sp-electrons is the same, and, hence the amount of d-shell electrons is not a distinguishing characteristic that can be associated with the change of behavior in the series.

(4) The B2 aluminides are not Hume-Rothery electron compounds. While the d-bands of NiAl are filled, the d-orbital shell is not, and the valence electron-to-atom ratio permitted for a B2 structure is exceeded.

(5) Simple directional bonding does not correlate with brittleness and cleavage planes of the aluminides. The abrupt change in directionality, looking at differences in valence density, takes place between CoAl and NiAl, yet the break in behavior takes place between FeAl and CoAl, CoAl and NiAl being much more similar to one another than either is to FeAl.

(6) While directional bonding does not determine brittleness, its presence can be inferred, for all the B2's, from the observations that: (a) FeAl and CoAl are non-magnetic; (b) the B2 structure is stable despite violating the Hume-Rothery valence electron count for the B2 structure, and (c) the charge difference analysis. In other words, d–sp hybridization is implicit in the results.

The calculations suggest that CoAl should be intermediate in its behavior between FeAl and NiAl, in contrast to experiment where CoAl represents the extremity in behavior, with a significant break between FeAl and CoAl. The standard culprits proposed in electronic structure calculations for explaining brittle behavior can therefore be excluded for B2 aluminides. Other work has examined other possible contributing factors. Fu's work on surface energies of FeAl and NiAl [51] shows that, though the gap is narrower in FeAl, the [110] surface is more stable in both cases than the [100]. Anti-phase-boundary energies are computable quntities proposed [49] as being relevant as they are related to the energetics of dislocation behavior, the rationale being that if a second slip system besides the ⟨100⟩ present in NiAl could be activated, the von Mises criterion for ductile behavior could be satisfied. However, recent experiments have enabled additional slip systems in NiAl via alloying without resulting in a ductile material [66]. Taken together, these results paint a rather bleak picture for the ability of first-principle theory to contribute to the alloy development process of B2 aluminides. Ideally the goal of theory in this enterprise is to obtain a better fundamental understanding of the microscopic properties that lead to the macroscopic behavior, and yet none of the quantities accessible to theory appear to correlate with the observed behavior of technological interest. Clearly the process of crack formation and propagation in these materials is a dynamic phenomenon dependent on the energetics of deformation whose characterization goes well beyond the description of the bonding evident in the few single-point geometries accessible to first principles calculations.

In order to understand brittleness in B2 aluminides, it appears finite temperature simulations involving thousands of particles are indicated. As it will be a long road before first principle Car-Parrinello methods [67] become thinkable on the scale necessary, especially for systems with transition metal atoms, this dictates semi-

empirical schemes, such as the embedded atom method [68]. However, data for developing semi-empirical potentials for bulk metals are scant and, although they may not have direct bearing on many physical properties, first-principles calculations are well suited to generate data necessary to refine these potentials, particularly in those cases where the experimental data are absent. For example, the full elastic constants of CoAl have been calculated [69], but only the bulk and shear modulus are available experimentally [8]. Structural energies, elastic constants, lattice parameters, equation of state, some phonon eigenmodes — all these are quantities accessible to calculation with reasonable accuracy and useful in potential refinement, and are frequently more expensive, more difficult, or not possible at all to measure experimentally.

Acknowledgments

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