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Transition-metal aluminide formation: Ti, V, Fe, and Ni aluminides

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The heats of formation for binary and ternary $3d$ transition-metal (Ti, V, Fe, and Ni) aluminides are calculated from first principles within the local density approximation. The calculated heats for Ti and Ni aluminides are typically within ~ 0.02 eV/atom of the experimental values, while the Fe aluminides heats appear to be overestimated by ~ 0.15 eV/atom. This discrepancy appears to be related to the local density underestimation of the on-site magnetic energy in elemental Fe that enters the alloy heat of formation. The stabilities of selected ternary phases are also discussed, and it is shown that sublattice disorder may stabilize some ternary phases. [S0163-1829(98)07134-3]

I. INTRODUCTION

Transition-metal aluminides are a technologically important class of alloys. While there is a significant body of empirical knowledge regarding the properties of these materials, a microscopic understanding of the phase diagrams of these materials is still missing. To answer questions regarding the stability of an alloy and the competition among different phases is a challenging problem that requires detailed and accurate information. A quantity of fundamental interest is the heat of formation, ΔH. Investigations of the heats of transition-metal aluminides provide insight not only into the bonding in these systems, but also allow comparisons with the bonding trends encountered in transition-metal alloys.

The present paper is concerned with theoretical estimates of ΔH for a number of binary and ternary ordered compounds of Al with the $3d$ elements Ti, V, Fe, and Ni. Ti-Al is an important structural material and V is of interest as a ternary addition to that system. The inclusion of Fe and Ni provides a scan of trends across the d row, as well as a test of the consequences of estimating ΔH when one of the alloy components itself is a ferromagnetic metal (only the Fe- and Ni-rich aluminides are magnetic). Comparisons will be made with the available experimental thermodynamic data, and with other calculated estimates for Ni-Al and Ti-Al. In the Ti-, Ni-, and V-based systems, the agreement between theory and experiment is found to be 0.02 eV/atom or better, but for Fe-based systems the agreement is markedly worse, probably related to the local spin density approximation.

One purpose of the present work is to contribute a set of first-principles estimates of ΔH to the thermodynamic data base needed to model ternary (and higher component) aluminide phase diagrams. The observed alloys are found in a diverse group of crystal structures, requiring that the heats of these and other possible competing structures are obtained to a common computational precision. To discuss the stability of ternary alloys, estimates of ΔH for both stable and unstable/metastable binary (and other ternary) alloys must be considered since these alloys may compete in the ternary regime. Because these metastable phases are usually inaccessible experimentally, their heats must be obtained by theory or from fits in a phase diagram construct.

As an example, Ti_3Al forms in the Ni_3Sn structure. The heat for V_3Al has been obtained in the same structure to aid in estimating the extent that this phase intrudes into the region of finite V concentration. Similarly, Ti_3Al and V_3Al have been calculated for in the Cr_3Si ($A15$) structure in which Mo_3Al and Nb_3Al form. The crystallographic data indicating that V_3Al also forms in this structure are not generally accepted; the present calculations indicate that the $A15$ structure is indeed favored, but is likely metastable. Ternary M_2NAl aluminides frequently form in the Heusler BiF_3 structure, in which each constituent occupies its own sublattice. The stability of these ternaries relative to the binaries has been discussed previously.[1] The present paper provides details of the competing binary aluminides and extends the discussion to some partially ordered ternary phases, such as $TiVAl_2$, where the Al atoms are well ordered on one sublattice of the CuAu-I structure and the Ti and V atoms occupy the others in disordered fashion.

II. CALCULATIONS

The intent of the present calculations is to calculate ΔH for the various compounds in a number of different structures to a precision of 0.01 eV/atom, given the choice of computational technique and potential construct. The computational approach is similar to that used previously.[1] Briefly, the calculations employ the full-potential linearized augmented Slater-type orbital method[2] (FLASTO). The wave functions are expanded in a set of Slater-type orbitals in the interstitial region, augmented by explicit solutions of the radial wave equations within nonoverlapping spheres at each atomic site for orbital momenta up to $l=8$. Aspherical electron density and potential (“full-potential”) terms are kept throughout space, and the core electrons are treated self-consistently and fully relativistically. Spin-orbit effects are neglected in the self-consistent treatment of the valence states, but are included in a final iteration in most cases.

Sets of special k points were used and were increased in size until details such as the behavior of the energy in the vicinity of an extremum were accurately established. For example, calculations for the CuAu-I structure employed sets of 40, 126, 405, and 550 k points in the irreducible wedge, and the latter three sets were in agreement for the systems reported here. The basis sets ranged up to 39 orbitals per atom. In order to generate meaningful estimates of ΔH, the total energies of both the compound and elemental reference systems were calculated using the same basis sets.

The structural parameters of the crystalline lattices—including lattice volumes, c/a and b/a ratios where appropriate, and internal atomic positions when not determined by symmetry—have been determined by energy optimization. It is well established that local-density-approximation (LDA)-based calculations yield lattice volumes smaller than those observed experimentally. These lattice contractions are of numerical significance to the values of the calculated ΔH and are more important for the $3d$ elements and their compounds than for their $4d$ and $5d$ counterparts. At least for full potentials, the calculated c/a ratios of the hexagonal and tetragonal (and the b/a ratios for the orthorhombic) structures are close to the observed values and the differences are of modest consequence to the energy accuracy aspired to here, although changes from the ideal c/a (e.g., $\sqrt{8/3}$ for hcp or the cubic $c/a=2$ for the $TiAl_3$ structure) *are* of energetic significance. In addition, these values must be determined for those systems where there is no crystallographic data. For a number of the structures considered, a continuous Bain-type distortion can connect bcc- and fcc-like phases. For example, in the CuAu-I ($tP4$) structure, $c/a=1/\sqrt{2}$ corresponds to a bcc lattice and $c/a=1$ to a fcc one. Similarly, the $TiAl_3$ ($tI8$) structure is fcc-like for $c/a=2$ and bcc-like for $c/a=\sqrt{2}$, at which point it is equivalent to the BiF_3 structure.

It is more difficult to compare theory and experiment for the internal atomic coordinates that are not determined by symmetry considerations, except to note that their values are also of energetic significance. The main difficulty is that much of the older crystallographic work determined these coordinates inaccurately, if at all. There is, however, the suggestion that modern crystallographic results and LDA predictions are, like the c/a ratios, in reasonable accord, and that the differences between using the calculated and observed internal coordinates have only a modest effect on the final calculated heats. Unfortunately, this observation is of little computational help since the optimization must be done before an estimate of the error can be made.

The virtual crystal scheme will be used to estimate the heats of two Al-Ti-V phases where Ti and V are disordered on a common sublattice. The scheme, which treats the sites as having the average nuclear charge of the two ($Z=22.5$) is crude, but provides a measure of the energy associated with disorder. In order to estimate ΔH, a similarly treated reference material is also necessary. Noting that V and Ti form a continuous substitutional bcc phase at high temperatures, a $Ti_{0.5}V_{0.5}$ bcc virtual crystal was chosen as the reference. The actual high temperature $Ti_{0.5}V_{0.5}$ phase can be expected to be within ± 0.05 eV/atom of a two-phase mixture of pure V and Ti. Since the alloy occurs at high temperatures, the + sign is expected to prevail and must be accounted for in any estimate of ΔH for a ternary.

III. RESULTS

A. Ti and Ni

The calculated heats of formation for a number of binary and ternary Ti and Ni aluminides in various structures appear in Table I. Experimental calorimetric and electromotive force (emf) heats are included for comparison, as are a number of previously published calculated values. Lattice constants, and other structural parameters where appropriate, are also given in the table. The lattice constants are quoted to one more digit than is significant to the calculated heats; the calculations employed these constants, but the values themselves were not determined to this accuracy.

The present set of heats for the Ni and Ti binary aluminides, shown in Fig. 1, have the observed phases stable with respect (i) to other possible structures having the same composition and (ii) to competing two-phase mixtures at other compositions. From the results in Fig. 1, Al_3Ni is not predicted to be stable. However, Al_3Ni does occur, not in the structures reported here, but in a structure having 16 atoms per unit cell that is larger than the system sizes being dealt with here. The structures that are calculated are those typical of the light transition-metal aluminides, but lose out badly to a two-phase mixture of Ni_2Al_3 and pure Al.

The spread among the various calculated heats for any one of the Ti-Al systems is small, in part because most are based on full-potential calculations. Given the small spread seen for experiment as well, there is the suggestion that LDA-based calculations overestimate the heats of the compounds of the Ti-Al system by ~ 0.02 eV/atom. The computational and experimental spreads are greater for Ni-Al. In the case of the calculations, this is partially due to a number of them not being full-potential calculations, and partially due to questions of magnetism: a number of the publications do not make clear whether nonmagnetic or ferromagnetic Ni was used as the reference energy when deriving the heat of formation. (The present calculations used ferromagnetic references for both Ni and Fe.) As for experiment, part of the greater spread may be associated with having more data. In any case, the results are not inconsistent with the observation for Ti-Al, i.e., LDA calculations overestimate the Ni-Al heats by ~ 0.02 eV/atom. As discussed later, there is the distinct suggestion in the results for the Fe compounds that the use of the spin-polarized LDA (LSDA) measurably underestimates the elemental magnetic energy, and hence overestimates the alloy ΔH. Applying the Fe observations to Ni suggests that heats in Table I for the nonmagnetic Ni compounds (and for ferromagnetic Ni_3Al, which has a much smaller Ni moment than does elemental Ni) might be reduced in magnitude by ~ 0.01 eV/atom to account for this error.

In order to investigate the relative stability of disordered hexagonal and face-centered phases in the Ti-Al system in the vicinity of $Ti_{0.5}Al_{0.5}$, calculations in two different ordered hexagonal structures are reported in Table I. The WC ($hP2$) structure has alternating close-packed planes of Ti and Al, resulting in six like and six unlike nearest neighbors. The AuCd ($oP4$) structure can be considered a distorted hcp lattice, with each site having four like and eight unlike nearest neighbors. (With $b/a=\sqrt{3}$, the planes remain hexagonal.) The increase in unlike neighbor count is expected to encourage compound formation, as is the case here; the AuCd structure (with the hcp b/a ratio) is more bound than the WC structure. The observed face-centered CuAu-I structure, which has the same number of like (four) and unlike (eight) nearest neighbors as does the AuCd, is only 0.05

TABLE I. Heats of formation ΔH and calculated lattice constants a for compounds of Al, Ti, and Ni. An * indicates a reported structure. Previous experimental (e.g., emf) or calculated (e.g., LMTO) values and techniques are also given; references are given in parentheses. Δh (in eV/atom) in the comments gives the change in heat relative to that for the ideal bcc or fcc c/a ratio.

Compound	Structure	ΔH (eV/atom)	a (a_B)	Comments
Ti_3Al	Ni_3Sn*	−0.28	10.608	$c/a=0.831$, $\delta=-0.005$
		−0.28, −0.29, −0.30		FLAPW, FLMTO (Refs. 14,15)
		−0.26, −0.25		calorimetry (Refs. 8,7)
		−0.29		emf (Ref. 16)
	Cu_3Au	−0.28	7.568	
		−0.29, −0.27		FLMTO, FLAPW (Refs. 15,14)
	Cr_3Si	−0.22	9.525	
	BiF_3	−0.14	12.006	
TiAl	CuAu-I*	−0.41	7.505	$c/a=1.020$, $\Delta h=-0.002$
		−0.44		LMTO (Ref. 15)
		−0.39, −0.38, −0.37		calorimetry (Refs. 17,7)
		−0.38		emf (Ref. 16)
	CsCl	−0.26	5.958	
	WC	−0.25	5.372	$c/a=1.623$
	AuCd	−0.36	5.364	$c/a=1.630$ (hcp $b/a=\sqrt{3}$)
$TiAl_2$	Ga_2Hf*	−0.44	7.423	$c/a=6.127$
	Cu_2Mg	−0.28	13.65	
$TiAl_3$	$TiAl_3$*	−0.41	7.179	$c/a=2.242$, $\Delta h=-0.08$
		−0.43, −0.43		FLAPW, FLMTO (Refs. 18,15)
		−0.39, −0.37		calorimetry (Refs. 6,16)
	Cu_3Au	−0.38	7.435	
		−0.41, −0.40		FLMTO, FLAPW (Refs. 15,18)
Ni_3Al	Cu_3Au*	−0.46	6.566	$\mu_{\mathrm{Ni}}=0.20\mu_B$
		−0.50		LMTO (Ref. 19)
		−0.40, −0.43, −0.42		calorimetry (Refs. 17,20,21)
		−0.49		emf (Ref. 22)
	BiF_3	−0.38	10.412	nonmagnetic
		−0.48		LMTO (Ref. 19)
Ni_5Al_3	Ga_3Pt_5*	−0.58	6.95	$c/a=1.765$, $b/a=2.002$
NiAl	CsCl*	−0.70	5.354	
		−0.78, −0.83, −0.82		LMTO, FLAPW (Refs. 19,23)
		−0.65, −0.74		FLASTO, LMTO (Refs. 24,25)
		−0.60, −0.74, −0.69		calorimetry (Refs. 6,17,7)
		−0.68, −0.68		calorimetry (Refs. 26,27)
		−0.70, −0.64		emf (Refs. 22,28)
	CuAu-I	−0.54	6.746	locally unstable ($c/a=1$)
		−0.58		LMTO (Ref. 19)
Ni_2Al_3	$Ni_2Al_3^*$	−0.65	7.484	$c/a=1.229$
		−0.64		LMTO (Ref. 19)
		−0.61		calorimetry (Ref. 17)
		−0.79±0.04		emf (Ref. 22)
$NiAl_2$	CaF_2	−0.47	10.527	
$NiAl_3$	Cu_3Au	−0.21	7.137	
		−0.23		LMTO (Ref. 19)
	$TiAl_3$	−0.22	7.137	$c/a=2.0005$
		−0.24		LMTO (Ref. 19)
Ni_2TiAl	BiF_3^*	−0.64	10.906	
		−0.78, −0.76		LMTO, FLAPW (Ref. 23)
		−0.58		calorimetry (Ref. 29)
NiTi	CsCl*	−0.35	5.523	
		−0.42, −0.47, −0.45		LMTO, FLAPW (Refs. 30,23)
		−0.35		calorimetry (Refs. 8,31)

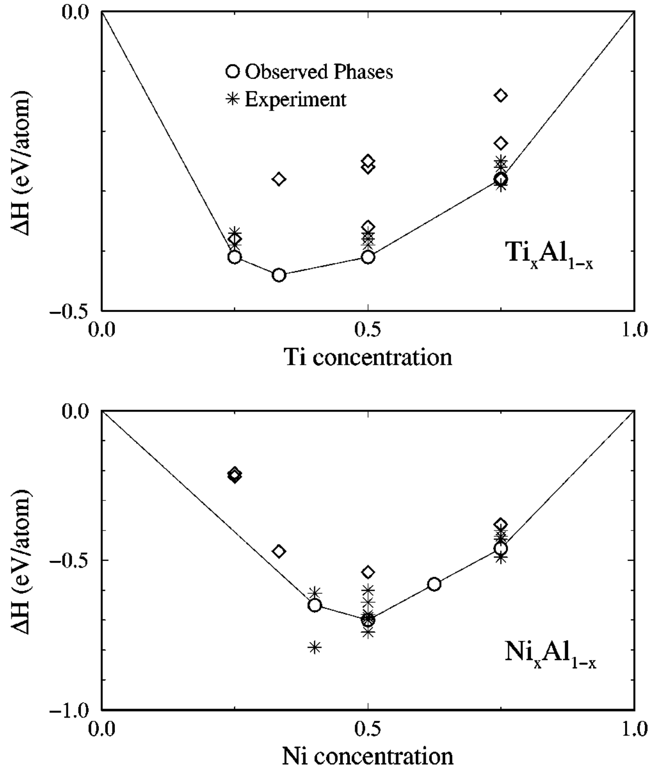

FIG. 1. Calculated and experimental heats of formation for Ti_xAl_{1-x} and Ni_xAl_{1-x} alloys as a function of Ti or Ni concentration. Lines are drawn connecting the calculated values for the observed phases.

eV/atom more bound, suggesting that near $Ti_{0.5}Al_{0.5}$ the hexagonal structure is nearly—but not quite—degenerate with the fcc.

In Table I the heat for the ternary Ni_2TiAl in the BiF_3 structure is also given. As discussed previously,[1] this phase is calculated (and observed) to be stable relative to two- and three-phase mixtures of the binaries. The heat for this system is substantial, significantly larger than the heats of the Ti-Al or Ti-Ni alloys. Thus, even though the heat of NiAl is somewhat larger than that of the ternary, the two- and three-phase mixtures are less bound by ~ 0.11 eV/atom than the ternary. In fact, the ternary is so strongly bound that the ternary and all the binaries with aluminum concentration less than or equal to 50% that we have considered are connected by two-phase lines in the ternary phase diagram. Ni_2TiAl is the one ternary aluminide, to our knowledge, for which an experimental ΔH has been obtained. This value is old, and the disagreement between theory and experiment is greater than that encountered for the binary phases.

B. V and Fe

The calculated and experimental values of ΔH for V and Fe binary compounds are given in in Table II. (The moments of alloys that are calculated to be magnetic are also given in the table.) At high temperatures, Al is soluble in V up to 50%. The dominant ordered phase is V_5Al_8, whose unit cell of 26 atoms exceeds the scope of this paper. There are experimental data for only one V-Al system considered in Table II, namely, VAl_3, and agreement between calculation and experiment is fortuitously exact. Despite the observation concerning vanadium solubility, V_3Al has been reported[3] to occur in the Cr_3Si structure. This assignment is plausible granted that Nb_3Al occurs in this structure, but implausible from size considerations: The majority (minority) atomic site is 14-fold (12-fold) coordinated, suggesting that the majority atom should be the larger, contrary to the relationship between V and Al. While such Frank-Kasper phases are favored both in transition-metal alloys[4] and in transition-metal aluminides[5] by such size differences, they sometimes do occur with the ''wrong'' size mismatch. Among the structures considered for V_3Al, Cr_3Si is the most stable, and is stable against two-phase mixtures of VAl_3 and pure V, and of VAl and V. The situation is different when experimental data at other compositions[6,7] are considered, as is seen in Fig. 2. There are three widely scattered experimental values[6,8,9] for V_5Al_8 and two scattered values[7,8] for disordered V-rich alloys. A line connecting probably the most reliable[6] of the V_5Al_8 values and elemental V yields a two-phase ΔH that lies below the diamond corresponding to the Cr_3Si structure, indicating that the ordered V_3Al phase is unstable to the two-phase mixture or, in turn, to a disordered bcc V-based phase. Granted the experimental scatter, the issue cannot be resolved easily. It would appear, however, that the Cr_3Si structure is the most stable among several plausible ordered structures for V_3Al, and that its binding is sufficiently close that it is possible that it is experimentally accessible as a metastable state, with or without benefit of impurities.

Fe-Al offers a different set of problems: three significant observed phases—Al_5Fe_2, Al_2Fe, and Al_3Fe—have not been calculated in their observed structures because the first is a defect structure, the second is triclinic with 18 atoms in the cell, and the last has a 51 atom unit cell. Further, the reported occurrence of Fe_2Al in the $MgCu_2$ structure is generally not accepted, despite the fact that the criterion[4] that the minority atom (with the greater coordination number) is the larger atom is satisfied. The Fe_2Al results in Table II indicate that the calculated ΔH of the more plausible $MoSi_2$ structure is better bound, and is calculated to be just bound with respect to a two-phase mixture of FeAl and Fe_3Al. The two observed structures for which ΔH have been calculated are stable with respect to the other calculated phases. The situation is even worse for experiment, where the reported ΔH for $FeAl_3$ and Fe_3Al are of such a magnitude that two-phase mixtures of them should suppress the observed phases between them.

C. Magnetism and ΔH

The most serious problem associated with the calculations for the Fe compounds is that the calculated heats of FeTi, FeV, $FeAl_2$, and FeAl are larger than experiment by 0.15 ± 0.1 eV/atom (cf. Table II). These systems are calculated to be nonmagnetic (FeTi) or to have significantly reduced Fe moments. On the other hand, for Fe_3Al, where the calculated Fe moments are comparable to those in elemental Fe, the calculated ΔH is apparently an underestimate. The problem appears to be related to the local spin density approximation (LSDA) used here. Bagno, Jepsen, and Gunnarsson[10] reported linear muffin-tin orbital atomic sphere approximation calculations for paramagnetic and spin-polarized ferromagnetic Fe with various exchange-correlation potentials, includ-

TABLE II. Calculated heats of formation ΔH and lattice constants a for binary compounds of Al, V, and Fe, and for ternary compounds including also Ti and Ni. An * indicates a reported structure. Δh (in eV/atom) in the comments gives the change in heat relative to that for the ideal bcc or fcc c/a ratio. For systems calculated to be magnetic, the site-specific moments are given in the comments.

Compound	Structure	ΔH (eV/atom)	a (a_B)	Comments
V_3Al	$Cr_3Si^{*(?)}$	-0.12	8.976	
	Ni_3Sn	-0.04	10.209	$c/a=0.785$, $\delta=.006$
	Cu_3Au	-0.05	7.124	
	BiF_3	-0.08	11.285	
VAl	CsCl	0.05	5.710	reported disordered bcc
	CuAu-I	-0.20	7.033	$c/a=1.067$, $\Delta h=-0.02$
VAl_3	$TiAl_3^*$	-0.29	7.029	$c/a=2.202$, $\Delta h=-0.06$
		-0.29		calorimetry (Ref. 6)
	Cu_3Au	-0.14	7.272	
Fe_3Al	BiF_3^*	-0.23	10.586	$\mu_{4b}=2.21$, $\mu_{8c}=1.59\mu_B$
		-0.32 ± 0.09		calorimetry (Ref. 17)
	Cu_3Au	-0.04	6.591	nonmagnetic
Fe_2Al	$MoSi_2$	-0.30	4.788	$\mu_{Fe}=0.32$ $c/a=3.918$, $z_{Fe}=0.322$
	Cu_2Mg	-0.06	12.278	reported, but unlikely
FeAl	CsCl*	-0.42	5.330	$\mu_{Fe}=0.65\mu_B$
		-0.25, -0.26, -0.28		calorimetry (Refs. 8,17,16)
		-0.42 ± 0.07, -0.32		calorimetry (Refs. 17,27)
	CuAu-I	-0.17	6.715	locally unstable ($c/a=1$)
$FeAl_2$	$MoSi_2$	-0.42	5.516	$c/a=2.98$, $z_{Al}=0.350$
	$FeAl_2$*	-0.27		calorimetry (Ref. 8)
$FeAl_3$	$TiAl_3$	-0.22	7.031	$c/a=2.03$, $\Delta h=-0.0005$
	Cu_3Au	-0.15	7.066	
	$FeAl_3$*	-0.29		calorimetry (Ref. 17)
TiV_2Al	BiF_3	-0.00_4	11.497	reported disordered bcc
	CuAu-I	-0.12	6.974	$c/a=1.13$, $\Delta h=-0.03$
$TiVAl_2$	CuAu-I*	-0.30	7.182	$c/a=1.067$, $\Delta h=-0.01$
$Ti_3V_3Al_2$	Ni_3Sn	-0.12	10.423	$c/a=0.807$, $\delta_{Ti}=-\delta_V\approx0$; alternating $(V,Ti)_3Al$ planes
Fe_2TiAl	BiF_3*	-0.54	10.799	$\mu_{Fe}=0.52$, $\mu_{Ti}=-0.14\mu_B$
	CuAu-I	-0.24	6.884	locally unstable ($c/a=1$)
$FeTiAl_2$	CuAu-I	-0.34	6.990	$c/a=1.069$, $\Delta h=-0.02$
	$TiAl_3$	-0.26	7.702	$c/a=1.598$, $\Delta h(\text{fcc, bcc})=-0.04$, -0.006
Fe_2VAl	BiF_3*	-0.53	10.571	
FeV_2Al	BiF_3	-0.02	11.034	$\mu_{Fe}=1.15$, $\mu_V=-0.19\mu_B$, reported disordered bcc
Ni_2VAl	BiF_3*	-0.41	10.729	reported a too large
Fe_2NiAl	BiF_3*	-0.11	10.590	$\mu_{Fe}=1.81$, $\mu_{Ni}=0.64\mu_B$
$FeNiAl_2$	BiF_3	-0.57	10.614	reported CsCl
VTi	CsCl	-0.02	5.808	reported disordered bcc
FeTi	CsCl*	-0.52	5.505	
		-0.21, -0.32		calorimetry (Refs. 8,31)
FeV	CsCl*	-0.22	5.499	$\mu_{Fe}=1.06$, $\mu_V=-0.20\mu_B$, reported metastable phase
		-0.06		calorimetry+assessment (Ref. 7)
NiV	CsCl	0.01	5.405	reported disordered bcc

ing the LSDA and several gradient corrected (GGA) ones. The energy difference between paramagnetic and ferromagnetic bcc Fe ranged from 0.22 eV/atom for the LSDA to 0.46 eV/atom for one of the gradient corrections; the magnitude of this difference between the LSDA and the GGA is consistent, albeit somewhat smaller (~0.05 eV/atom) than more recent full-potential results.[11–13] Even with the significant difference in magnetization energy, the behavior of the calculated moments using the LSDA and the GGA are in general agreement[13] with each other, suggesting that the

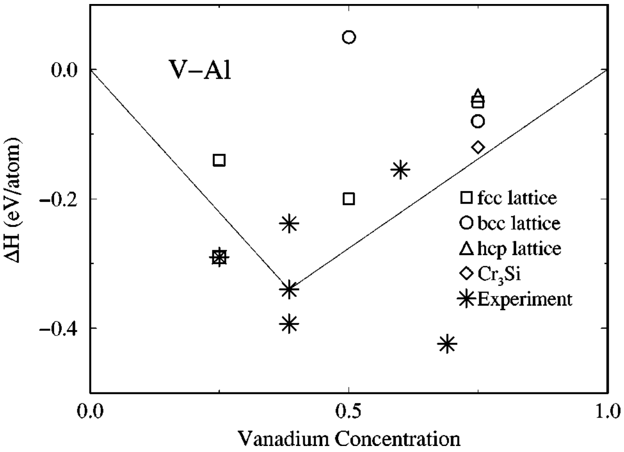

FIG. 2. Calculated and experimental heats of formation of V-Al systems as a function of composition. The different open symbols denote compounds on different underlying lattices. The tie lines represent competing two-phase heats using the presumably most reliable (Ref. 6) experimental heat for V_5Al_8.

LSDA may correctly predict the magnetic properties while underestimating the magnetization energies. To set the scale, the LSDA magnetization energy is typically less than 0.01 eV/atom for the magnetic alloys considered in Table II, except for those with large Fe moments such as FeV_2Al (−0.015 eV/atom), FeV (–0.034 eV/atom), Fe_2NiAl (–0.035 eV/atom), and Fe_3Al (–0.13 eV/atom). That these energies are smaller than expected from simply comparing the moments in the alloys and bulk Fe is due to the fact that the increase in magnetization energy comes at the expense of interatomic bonding, i.e., more antibonding majority and fewer bonding minority orbitals on the Fe atoms in the alloy are occupied.

A larger site magnetic energy for the reference energy of ferromagnetic Fe results in a reduced calculated $|\Delta H|$ for a nonmagnetic compound. The results of the preceding section would appear to indicate that the present full-potential LDA estimate of this spin-polarization energy is a substantial underestimate. (Note that a 0.1 eV error for elemental Fe translates into a 0.05 eV/atom error in ΔH for a 1:1 nonmagnetic compound.) Granted the spread in the experimental heats, the present results imply that the error in the LDA estimate of the spin-polarization energy is even greater than suggested by the results of Bagno, Jepsen, and Gunnarsson[10] and others,[11–13] i.e., the GGA results are also underestimates.

Since the site magnetic exchange energy is expected to vary roughly as the square of the site moment, these errors are expected to be an order of magnitude smaller, or ~ 0.01 eV/atom, for the Ni compounds. Recent comparisons[13] between GGA and LSDA calculations for fcc Ni give differences of this order. The scatter in the reported experimental Ni-Al heats is such that any consequences of the magnetic energy error are not detectable, but the calculated heats of the Ni compounds (including ferromagnetic Ni_3Al) given in Table I might be reduced by such an amount.

Fe_3Al in its ground state BiF_3 structure is ferromagnetic. (Spin-polarized calculations in the Cu_3Au structure find a nonmagnetic ground state.) Because the calculated moments are similar to elemental Fe, the error per Fe should be reduced significantly in magnitude compared to the other compounds. Even taking into account the fact that the minority site moment is larger than the moment of bcc Fe at its calculated lattice constant ($2.01\mu_B$ compared to $2.21\mu_B$ at the experimental volume), the errors in ΔH for Fe_3Al due to the magnetism are expected to be of the same sign as the other Fe compounds. This expectation, however, is not borne out by the Fe_3Al results reported in Table II; these values indicate that the error is of the opposite sign if the experimental number is taken seriously.

The other magnetic systems listed in Table II are the ternaries Fe_2TiAl, FeV_2Al, and Fe_2NiAl. As expected for elements from the left-hand end of the transition-metal row, the small Ti and V moments in Fe_2TiAl and FeV_2Al are coupled antiferromagnetically to the Fe moments. (Fe_2VAl is nonmagnetic because the Fermi level falls in a pseudogap in the density of states, and thus the Stoner criterion is not satisfied.) The reasonably large Fe moment ($1.15\mu_B$) calculated for FeV_2Al is due in part to the increased site volume in this compound compared to other systems where Fe is the minority constituent. Of the magnetic ternaries, both Fe_2TiAl and Fe_2NiAl have been reported to occur, but no experimental heats are available to compare with. The calculations are consistent with Fe_2TiAl existing, but Fe_2NiAl is predicted[1] to be unstable to various two- and three-phase mixtures. This disagreement between theory and experiment cannot be explained by errors in the magnetic contributions because the errors should largely cancel since calculated moments for both Fe_2NiAl and the elements are similar. For this and other reasons,[1] this system is most likely metastable. Further experimental and theoretical work is needed to clarify the situation regarding the contribution of magnetism to the heats of formation and the errors associated with the spin-polarized LDA (and GGA).

D. Ternaries

As mentioned in the Introduction, one of the reasons for developing a data base of binary heats is to provide the basis for considering the stabilities of ternary and higher order alloys. The heats of five (six, if Fe_3Al is included) experimentally reported M_2NAl ternaries in the BiF_3 structures are given in Tables I and II. The stabilities of these, and a large number of other such ternaries, have been discussed previously.[1] Here we will consider several other aspects of ternary stability.

The stable M_2NAl BiF_3 ternaries generally have the M atom from the right-hand side of the transition-metal row, and the N atom from the left. As an example, Fe_2VAl is calculated[1] to be stable and it is observed. For comparison, ΔH for FeV_2Al, i.e., the role of the M and N atoms reversed, is also given in Table II, and is found to have a near zero heat. Since the Fe site is magnetic, albeit with a reduced moment of $1.15\mu_B$, a possible error in the magnetic contribution cannot explain the small value of ΔH. While perhaps a bit surprising, a small ΔH can be rationalized in several ways. First, the d electron to (transition-metal) atom ratio puts the system in a region where ΔH is expected to be small based on the trend of the binary heats for Ti-Al and V-Al. Second, since the calculated heats for V-Fe and for V-rich aluminides are relatively small, the main contribution should come from Fe-Al bonding. By making the Fe the minority constituent, the heat is expected to be smaller. Moreover, when Fe is the majority atom in the BiF_3 structure, each Al has eight Fe nearest neighbors and six V next nearest neighbors, but for FeV_2Al the Al nearest neighbors are all V. Because the atomic size of V is larger than Fe (as seen from the difference in lattice constants), the Al-Fe interactions are weakened even further. All these effects together suggest that the heat should be small and that BiF_3 ternaries with the M atom from the left-hand end of the row are unlikely to be stable.

As discussed above, Ti_3Al forms in the hexagonal Ni_3Sn structure, whereas V_3Al may or may not form in the Cr_3Si structure. The question arises as to the extent that a Ni_3Sn phase, rather than a fcc or bcc phase, may extend for compositions around TiV_2Al. First consider the fcc and bcc lattices. The heats for the ordered bcc BiF_3 and fcc CuAu-I structures are given in Table II. Clearly the fcc lattice is more favored than the bcc, but both of these ordered phases are unstable relative to a two-phase mixture of V and TiAl. That the ternary heat is small is not too surprising since Ti-V alloys have small heats of formation because they are next to each other in the Periodic Table. The relative stability of the fcc over the bcc phase is consistent with the heats of Ti_3Al and V_3Al in the BiF_3 and CuAu-I structures: V_3Al shows a small preference for the bcc lattice, but Ti_3Al—with its larger heat—strongly favors the fcc case, with the net result that an fcc ordering is favored. A simple estimate of the ternary fcc heat can be obtained by averaging the fcc (Cu_3Au) heats of V_3Al and Ti_3Al. This value, the same as the calculated one to within roundoff, suggests that V and Ti may well be disordered on an fcc lattice.

We now return to the hexagonal case. For Ti_3Al, the hexagonal and fcc phases are basically degenerate. For a hexagonal-based ternary with the same Al concentration, but now with equal amounts of Ti and V, we consider a variant of the Ni_3Sn structure where there are alternating V_3Al and Ti_3Al hexagonal planes. This heat, given in Table II, is the same as for fcc-based TiV_2Al. This phase is unstable relative to two- and three-phase mixtures of binaries. (The heat of TiAl is the controlling heat.) Taken in the virtual crystal approximation, with V and Ti on a disordered sublattice, the estimated ΔH becomes -0.21 eV/atom. This heat is still slightly unstable relative to three-phase mixtures of V-Ti_3Al-TiAl, but granting the shortcomings of the approximation, the results suggest that disorder may stabilize a $(Ti_xV_{1-x})_3Al$ phase, and that a hexagonal Ni_3Sn or fcc phase may extend well into the transition-metal-rich ternary regime.

Up to now, the emphasis has been on transition-metal-rich ternaries. We now shift our attention to Al concentrations around 50%. While the transition-metal-rich Fe_2NiAl has a rather small ΔH and is probably metastable,[1] the heat for $FeNiAl_2$ in the BiF_3 structure is calculated to be rather large, -0.57 eV/atom. This increased binding is expected since both NiAl and FeAl have significant heats. In fact, the calculated heat for the competing two-phase mixture of FeAl and NiAl is -0.56 eV/atom, suggesting that there is not a strong tendency for ordering. Moreover, since both FeAl and NiAl are also in bcc structures, our results would predict that this $FeNiAl_2$ would be a disordered bcc system, in agreement with the reported[3] CsCl phase.

$FeTiAl_2$ is reported[3] to occur in the $Mn_{23}Th_6$ structure at this composition, in which case it must be disordered and/or have defects. At higher Al concentration, Fe-Ti-Al is reported in a fcc lattice. The question to address is whether an fcc-based ternary will extend down to lower Al concentrations. TiAl and FeAl, the main two phases competing with the ternary, both have large heats, but have different underlying lattices. The differences between the fcc and bcc phases for both TiAl and FeAl are substantial, 0.15–0.25 eV/atom. The calculated heats for the ternary show that the fcc-based lattice is more stable and, contrary to some of the ternaries considered above, the calculated heats are not simply averages of the corresponding bcc or fcc heats for the binaries. Thus, there is a tendency towards ordering for this system. However, the ternary in either structure loses out badly to a two-phase mixture of TiAl and FeAl ($\Delta H = -0.42$), a three-phase mixture of binaries (FeAl-$TiAl_3$-FeTi, $\Delta H = -0.44$), and a two-phase mixture of Fe_2TiAl-$TiAl_3$ ($\Delta H = -0.48$), suggesting that fcc-based ternaries near 50% Al are unlikely in this system.

The final ternary to be considered is $TiVAl_2$. This phase is reported[3] in the CuAu-I structure with Al on one sublattice, and V and Ti disordered on the other. The calculation for the CuAu-I structure, but with each atomic species placed on its own sublattice, yields $\Delta H = -0.30$ eV/atom. This ordered phase is calculated to be weakly unstable to both a mixture of TiAl and VAl (both in the CuAu-I structure), and a three-phase mixture of V_3Al-TiAl-$TiAl_3$; these mixtures are basically degenerate with $\Delta H = -0.31$ eV/atom. Using the same arguments as above, the fact that the heat of the two-phase mixture of TiAl and VAl is basically the same as the calculated heat for the ternary, we expect that $TiVAl_2$ will form on an fcc lattice, with disordered Ti and V. The virtual crystal scheme is used to estimate the effect of disorder, yielding a heat more bound by -0.06 eV/atom than the ordered system. Granting the shortcomings of the virtual crystal approximation and the error bar associated with the reference state, the fcc disordered phase would appear nevertheless to be stable with respect to competing phases at this composition, in agreement with experimental observations.

IV. CONCLUSIONS

In this paper the heats of formation for a variety of $3d$ aluminides in a diverse set of crystal structures have been calculated using the full-potential LASTO method and the local density approximation. An effort has been made to obtain values of ΔH to a common precision of ~ 0.01 eV/atom in order to allow for meaningful comparisons among different phases both at the same and at different concentrations. For the Ti, V, and Ni systems, the calculated heats are typically overestimated by ~ 0.02 eV/atom relative to the experimental numbers. Direct comparisons are hampered by the scatter in experiment, and by questions of if and how the experimental numbers have been corrected to a common (low) temperature since these temperature corrections often can be quite substantial. The scatter in experimental values appears to be particularly significant for the Fe compounds of concern here. Although experimental efforts to determine heats of formation of alloys and compounds are declining worldwide, the issue needs further investigation, both to understand the physical systems and as benchmarks for theory.

From comparisons between the calculated and experimentally derived heats for the nonmagnetic Fe-Al binary alloys, there is the suggestion that the local spin density approximation underestimates the on-site magnetic energy. While generalized gradient correction exchange-correlation potentials increase this magnetic energy,[10–13] the situation is more complicated since the apparent errors in ΔH do not simply scale with the number of Fe atoms in the alloys. In addition, full-potential treatments reduce[11] the GGA increase in the magnetization energy, and the values of this energy depend on which GGA functional is used, with the result that making any definite statements concerning the effect of GGA corrections to the magnetic energy is nontrivial. Future comparisons between experimental and theoretical values of ΔH of nonmagnetic Fe compounds may help serve as important tests of different exchange-correlation approximations. The list of available experimental heats for such Fe compounds, with whatever available second alloy constituent, is short and the accuracy of these values uncertain. Nevertheless, this issue deserves further investigation.

A major use of the calculated binary heats is in determining the stability of higher-order phases. Two- and three-phase mixtures of the binaries will be major competing phases that may suppress a ternary. The heat of a ternary was shown to depend on both crystal structure and composition. When ΔH of the ternary is close to the heat of a two-phase mixture of binaries with the same underlying lattice, configuration entropy will favor disordered on one or more sublattices, as seen for $FeNiAl_2$ and the Ti-V-Al system, although other binaries and ternaries may suppress such phases. The results presented in this paper add to the data base of calculated heats, which are necessary ingredients needed to tackle the complicated problem of phase stability of multicomponent alloys from first principles.

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