Perceiving Molecular Themes in the Structures and Bonding of Intermetallic Phases: The Role of Hückel Theory in an Ab Initio Era

Timothy Stacey and Daniel C. Fredrickson

Department of Chemistry, University of Wisconsin-Madison,

1101 University Avenue, Madison, WI 53706-1322

Supporting Information

Density Functional Theory Calculations. For the elemental and Laves phases studied, the Vienna Ab initio Simulation Package (VASP)[1–4] was used for geometrical optimization of crystal structures, calculation of band energies, and generation of projected DOS curves. Depending on the cell geometry, differing routes of geometry optimization were taken: for cubic cells with atoms only on special positions, only cell volume optimization and static single-point energy calculations were performed, but for the elemental phases with *hcp*-type structure, an additional step was taken for cell shape optimization. Details of the execution of these calculations are listed in Table S1. For the steps of cell volume and shape optimization, two k-point meshes, one relatively coarse and one slightly finer, were used at each step. For the static calculations, 2-3 k-point meshes of increasing fineness were used to ensure that convergence was obtained. The two k-point meshes used in geometry optimization and the finest k-point mesh employed in the static calculation are all specified in Table S1. Each calculation was run in the high precision mode, corresponding to the energy cutoffs specified in Table S1, using the Density Functional Theory with the Generalized Gradient Approximation, and the Projector Augmented Wave potentials supplied with the package. The number of bands employed in each calculation roughly approximated nine times the number of ions.

Projected DOS curves were obtained by defining a fixed sphere around each atomic position and then projecting the wavefunctions within the sphere onto spherical harmonics corresponding to the pertinent atomic orbitals. The magnitude of the sphere radii were determined by taking the ratio of the Wigner-Seitz radii specified in the potential files and keeping the ratio fixed while adjusting the magnitude of the radii such that the sum of the sphere volumes equaled the unit cell volume (see the VASP manual).

Hückel Theory Calculations. Hückel calculations were performed using the YAeHMOP package,[5] specifying keywords DIAGWO and NONWEIGHTED to employ the simple Hückel, or orthogonal tightbinding mode and to turn off the correction for counterintuitive orbital mixing.[6] Hückel calculations performed in this paper follow the classic Wolfsberg-Helmholtz approximation[7] for calculation of off diagonal Hamiltonian matrix elements (H_{ij} terms). The Hückel parameters in Table S2 were obtained with the method in the main article. All Laves phases for μ_3-acidity analysis, both real and hypothetical, were fit using the $MgCu_2$-type structure.

Table S1. Details of DFT calculations

CsCl map calculation details

Stochiometry	Structure type	k-point meshes	Energy cutoff (eV)
Sc	*hcp*	5x5x3 10x10x6 20x20x12	193.5
Ti	*hcp*	5x5x3 10x10x6 20x20x12	223.0
V	*bcc*	5x5x5 10x10x10 15x15x15	240.7
Cr	*bcc*	5x5x5 10x10x10 15x15x15	283.9
Mn	α-Mn	3x3x3, 5x5x5, 13x13x13	337.4
Fe	*bcc*	5x5x5 10x10x10 15x15x15	334.9
Co	*hcp*	5x5x3 10x10x6 20x20x12	335.0
Ni	*fcc*	5x5x5 10x10x10 15x15x15	337.0
Cu	*fcc*	5x5x5 10x10x10 15x15x15	341.6
$ScCu_2$	$MgCu_2$	9x9x9, 11x11x11, 13x13x13	341.6
$ScNi_2$	$MgCu_2$	9x9x9, 11x11x11, 13x13x13	337.0
$ScCo_2$	$MgCu_2$	9x9x9, 11x11x11, 13x13x13	335.0
$ScFe_2$	$MgCu_2$	9x9x9, 11x11x11, 13x13x13	334.9
$ScMn_2$	$MgCu_2$	9x9x9, 11x11x11, 13x13x13	337.4
$TiCu_2$	$MgCu_2$	9x9x9, 11x11x11, 13x13x13	341.6
$TiNi_2$	$MgCu_2$	9x9x9, 11x11x11, 13x13x13	337.0
$TiCo_2$	$MgCu_2$	9x9x9, 11x11x11, 13x13x13	335.0
$TiFe_2$	$MgCu_2$	9x9x9, 11x11x11, 13x13x13	334.9
$TiMn_2$	$MgCu_2$	9x9x9, 11x11x11, 13x13x13	337.4
VCu_2	$MgCu_2$	9x9x9, 11x11x11, 13x13x13	341.6
VNi_2	$MgCu_2$	9x9x9, 11x11x11, 13x13x13	337.0
VCo_2	$MgCu_2$	9x9x9, 11x11x11, 13x13x13	335.0
VFe_2	$MgCu_2$	9x9x9, 11x11x11, 13x13x13	334.9
VMn_2	$MgCu_2$	9x9x9, 11x11x11, 13x13x13	337.4
$CrCu_2$	$MgCu_2$	9x9x9, 11x11x11, 13x13x13	341.6
$CrNi_2$	$MgCu_2$	9x9x9, 11x11x11, 13x13x13	337.0
$CrCo_2$	$MgCu_2$	9x9x9, 11x11x11, 13x13x13	335.0
$CrFe_2$	$MgCu_2$	9x9x9, 11x11x11, 13x13x13	334.9
$CrMn_2$	$MgCu_2$	9x9x9, 11x11x11, 13x13x13	337.4

Table S2: DFT-calibrated Hückel parameters

Parameters for elemental phases

Compound, RMS deviation**	Atom	Orbital	H_{ii} (eV)	c_1	ζ_1 (a_o^{-1})	c_2	ζ_2 (a_o^{-1})
Sc, 0.070002 eV	Sc	Sc 4*s*	-3.678		1.8418		
		Sc 4*p*	-1.892		1.7017		
		Sc 3*d*	-5.158	0.4228	4.3824	0.7368	1.6386
Ti, 0.083302 eV	Ti	Ti 4*s*	-4.175		2.0531		
		Ti 4*p*	-2.054		1.9004		
		Ti 3*d*	-6.530	0.4228	4.2694	1.7625	1.9528
V, 0.155167 eV	V	V 4*s*	-4.279		2.1804		
		V 4*p*	-1.941		1.9963		
		V 3*d*	-7.977	0.4228	8.5631	0.7411	2.1054
Cr, 0.145661 eV	Cr	Cr 4*s*	-4.607		2.2994		
		Cr 4*p*	-2.034		2.1110		
		Cr 3*d*	-8.878	0.5680	10.8679	0.8859	2.2377
Mn, 0.126104 eV	Mn	Mn 4*s*	-4.764		2.3817		
		Mn 4*p*	-1.523		2.0601		
		Mn 3*d*	-9.129	0.4228	4.4781	1.0440	2.3231
Fe, 0.105060 eV	Fe	Fe 4*s*	-4.904		2.3986		
		Fe 4*p*	-2.077		2.1910		
		Fe 3*d*	-9.054	0.4228	4.5466	0.6528	2.2791
Co, 0.063276 eV	Co	Co 4*s*	-5.546		2.4962		
		Co 4*p*	-2.335		2.3072		
		Co 3*d*	-9.035	0.4228	3.4563	0.2739	2.1403

Parameter table continued on next page

**RMS deviation: root-mean-squared deviation between the GGA-DFT and Hückel energies fit to DFT results for the conventional cell, considering all occupied valence bands up to the Fermi energy (E_F plus some additional low-lying unoccupied bands (usually up to 1 eV above E_F).

Compound, RMS deviation	Atom	Orbital	H_{ii} (eV)	c_1	ζ_1 (a_o^{-1})	c_2	ζ_2 (a_o^{-1})
Ni, 0.071565 eV	Ni	Ni 4*s*	-4.635		2.3730		
		Ni 4*p*	-1.674		2.0795		
		Ni 3*d*	-8.637	0.4228	8.3565	0.4036	2.2683
Cu, 0.072147 eV	Cu	Cu 4*s*	-5.280		2.4197		
		Cu 4*p*	-2.092		2.1994		
		Cu 3*d*	-8.461	0.4228	3.8882	0.2250	2.0774
Parameters for Laves phases							
$ScCu_2$, 0.035522 eV	Cu	Cu 4*s*	-5.419		2.4845		
		Cu 4*p*	-2.514		2.2611		
		Cu 3*d*	-9.350	0.4228	3.6830	0.2404	2.1976
	Sc	Sc 4*s*	-4.126		1.8847		
		Sc 4*p*	-2.213		1.8008		
		Sc 3*d*	-4.870	0.4228	4.5794	0.7963	1.6459
$ScNi_2$, 0.031758 eV	Ni	Ni 4*s*	-5.520		2.5470		
		Ni 4*p*	-2.510		2.3497		
		Ni 3*d*	-9.052	0.4228	3.4832	0.2815	2.2059
	Sc	Sc 4*s*	-4.569		1.9600		
		Sc 4*p*	-2.396		1.8732		
		Sc 3*d*	-5.651	0.4228	4.4006	0.7978	1.7011
$ScCo_2$, 0.031628 eV	Co	Co 4*s*	-5.818		2.6378		
		Co 4*p*	-2.707		2.4084		
		Co 3*d*	-9.136	0.4228	3.6172	0.4462	2.2720
	Sc	Sc 4*s*	-4.508		1.9349		
		Sc 4*p*	-1.857		1.7872		
		Sc 3*d*	-6.105	0.4228	4.2752	0.7008	1.7246
$ScFe_2$, 0.033720 eV	Fe	Fe 4*s*	-5.872		2.6468		
		Fe 4*p*	-2.747		2.4091		
		Fe 3*d*	-9.127	0.4228	3.6631	0.5499	2.2649
	Sc	Sc 4*s*	-4.538		1.9243		
		Sc 4*p*	-2.020		1.8075		
		Sc 3*d*	-6.056	0.4228	4.2907	0.9300	1.7631

Parameter table continued on next page

Compound, RMS deviation	Atom	Orbital	H_{ii} (eV)	c_1	ζ_1 (a_o^{-1})	c_2	ζ_2 (a_o^{-1})
$ScMn_2$, 0.037426 eV	Mn	Mn 4*s*	-5.113		2.5362		
		Mn 4*p*	-2.344		2.2966		
		Mn 3*d*	-8.888	0.4228	3.1956	0.6301	2.2616
	Sc	Sc 4*s*	-4.421		1.8870		
		Sc 4*p*	-1.903		1.7246		
		Sc 3*d*	-6.163	0.4228	4.4861	0.8303	1.7272
$TiCu_2$, 0.027530 eV	Cu	Cu 4*s*	-5.812		2.5631		
		Cu 4*p*	-2.854		2.4672		
		Cu 3*d*	-9.508	0.4228	3.8127	0.2327	2.1836
	Ti	Ti 4*s*	-5.058		2.0592		
		Ti 4*p*	-2.153		1.8780		
		Ti 3*d*	-5.673	0.4228	4.4212	0.6348	1.7212
$TiNi_2$, 0.029690 eV	Ni	Ni 4*s*	-5.529		2.5675		
		Ni 4*p*	-2.371		2.3666		
		Ni 3*d*	-9.242	0.4228	3.5808	0.2935	2.2284
	Ti	Ti 4*s*	-5.108		2.0928		
		Ti 4*p*	-2.723		2.0138		
		Ti 3*d*	-6.671	0.4228	4.4483	0.5541	1.7942
$TiCo_2$, 0.034734 eV	Co	Co 4*s*	-5.407		2.5811		
		Co 4*p*	-2.346		2.3839		
		Co 3*d*	-9.234	0.4228	3.3808	0.3507	2.2675
	Ti	Ti 4*s*	-5.230		2.0954		
		Ti 4*p*	-2.740		1.9982		
		Ti 3*d*	-6.965	0.4228	5.0301	0.6789	1.8527
$TiFe_2$, 0.037276 eV	Fe	Fe 4*s*	-5.011		2.5377		
		Fe 4*p*	-2.186		2.3405		
		Fe 3*d*	-9.180	0.4228	3.2562	0.5137	2.3280
	Ti	Ti 4*s*	-5.163		2.0684		
		Ti 4*p*	-2.691		1.9487		
		Ti 3*d*	-7.077	0.4228	5.0003	0.7498	1.8587

Parameter table continued on next page

Compound, RMS deviation	Atom	Orbital	H_{ii} (eV)	c_1	ζ_1 (a_o^{-1})	c_2	ζ_2 (a_o^{-1})
$TiMn_2$, 0.040948 eV	Mn	Mn 4*s*	-4.910		2.5458		
		Mn 4*p*	-2.142		2.3342		
		Mn 3*d*	-8.943	0.4228	2.8784	0.4158	2.2961
	Ti	Ti 4*s*	-5.102		2.0132		
		Ti 4*p*	-2.662		1.8865		
		Ti 3*d*	-7.094	0.4228	4.6842	1.0813	1.8867
VCu_2, 0.033439 eV	Cu	Cu 4*s*	-5.622		2.5278		
		Cu 4*p*	-2.236		2.2851		
		Cu 3*d*	-9.666	0.4228	3.8342	0.2274	2.1847
	V	V 4*s*	-5.439		2.1981		
		V 4*p*	-3.018		2.1563		
		V 3*d*	-6.139	0.4228	8.5800	0.8490	1.9826
VNi_2, 0.029004 eV	Ni	Ni 4*s*	-5.935		2.6776		
		Ni 4*p*	-2.468		2.4389		
		Ni 3*d*	-9.360	0.4228	3.6595	0.3032	2.2458
	V	V 4*s*	-5.272		2.1245		
		V 4*p*	-2.640		2.0401		
		V 3*d*	-7.195	0.4228	8.7857	0.4482	1.9105
VCo_2, 0.038531 eV	Co	Co 4*s*	-5.517		2.6009		
		Co 4*p*	-2.249		2.3852		
		Co 3*d*	-9.355	0.4228	3.4473	0.3082	2.2253
	V	V 4*s*	-5.786		2.2172		
		V 4*p*	-3.374		2.1914		
		V 3*d*	-7.615	0.4228	8.2923	0.6903	2.0385
VFe_2, 0.039521 eV	Fe	Fe 4*s*	-5.353		2.6206		
		Fe 4*p*	-2.253		2.4191		
		Fe 3*d*	-9.287	0.4228	3.1304	0.3227	2.2638
	V	V 4*s*	-5.845		2.1794		
		V 4*p*	-2.987		2.0549		
		V 3*d*	-7.798	0.4228	9.0523	0.8645	2.0625

Parameter table continued on next page

Compound, RMS deviation	Atom	Orbital	H_{ii} (eV)	c_1	ζ_1 (a_o^{-1})	c_2	ζ_2 (a_o^{-1})
VMn_2, 0.040720 eV	Mn	Mn 4*s*	-4.645		2.4516		
		Mn 4*p*	-1.687		2.2783		
		Mn 3*d*	-9.048	0.4228	3.0644	0.5341	2.3023
	V	V 4*s*	-6.576		2.2996		
		V 4*p*	-4.344		2.2609		
		V 3*d*	-7.983	0.4228	8.3894	0.8981	2.0638
$CrCu_2$, 0.024243 eV	Cu	Cu 4*s*	-6.388		2.7130		
		Cu 4*p*	-2.708		2.5205		
		Cu 3*d*	-9.614	0.4228	3.7188	0.2394	2.2340
	Cr	Cr 4*s*	-5.431		2.1522		
		Cr 4*p*	-2.474		2.0355		
		Cr 3*d*	-6.679	0.4228	8.7508	0.3777	1.8572
$CrNi_2$, 0.034483 eV	Ni	Ni 4*s*	-5.847		2.6636		
		Ni 4*p*	-2.323		2.4145		
		Ni 3*d*	-9.368	0.4228	3.7687	0.2975	2.2239
	Cr	Cr 4*s*	-5.620		2.2096		
		Cr 4*p*	-3.029		2.1704		
		Cr 3*d*	-7.556	0.4228	8.5195	0.4904	2.0262
$CrCo_2$, 0.041869 eV	Co	Co 4*s*	-5.359		2.6234		
		Co 4*p*	-2.250		2.3932		
		Co 3*d*	-9.342	0.4228	3.6243	0.3548	2.2405
	Cr	Cr 4*s*	-5.610		2.2004		
		Cr 4*p*	-2.628		2.0816		
		Cr 3*d*	-8.114	0.4228	8.1829	0.5853	2.0954
$CrFe_2$, 0.041097 eV	Fe	Fe 4*s*	-5.046		2.5994		
		Fe 4*p*	-2.127		2.3968		
		Fe 3*d*	-9.278	0.4228	3.3579	0.4015	2.2606
	Cr	Cr 4*s*	-5.876		2.2065		
		Cr 4*p*	-2.729		2.0354		
		Cr 3*d*	-8.414	0.4228	8.5054	0.7030	2.1351

Parameter table continued on next page

Compound, RMS deviation	Atom	Orbital	H_{ii} (eV)	c_1	ζ_1 (a_o^{-1})	c_2	ζ_2 (a_o^{-1})
$CrMn_2$, 0.043611 eV	Mn	Mn 4*s*	-5.030		2.6457		
		Mn 4*p*	-1.959		2.3897		
		Mn 3*d*	-9.089	0.4228	3.1902	0.5503	2.2965
	Cr	Cr 4*s*	-5.753		2.1257		
		Cr 4*p*	-2.965		1.9955		
		Cr 3*d*	-8.596	0.4228	8.2149	0.7959	2.1409

References

[1] Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *47*, 558–561.

[2] Kresse, G.; Hafner, J. *Phys. Rev. B* **1994**, *49*, 14251–14269.

[3] Kresse, G.; Furthmüller, J. *Comput. Mater. Sci.* **1995**, *6*, 15–50.

[4] Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169–11186.

[5] Landrum, G. A. *YAeHMOP: Yet Another extended Hückel Molecular Orbital Package, Version 3.0.*; YAeHMOP is freely available on the WWW at URL: http://sourceforge.net/projects/yaehmop/.

[6] Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Amer. Chem. Soc.* **1978**, *100*, 3686–3692.

[7] Wolfsberg, M.; Helmholz, L. *J. Chem. Phys.* **1952**, *20*, 837.