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Hybridization-induced band gaps in transition-metal aluminides

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The occurrence of hybridization gaps around the Fermi level in ordered binary and ternary transition-metal aluminides is investigated using first-principles electronic structure calculations. Hybridization between transition-metal atoms and Al and the *lack* of transition-metal–Al d-d hybridization are both found to be important for the formation of the hollows or pseudogaps in the density of states. Whether these hollows become actual gaps, as predicted for $RuAl_2$, $FeAl_2$, and Fe_2NbAl, depends on details of the electronic structure, including the relative positions of the atomic levels, the size of the atoms, the crystal structure, and the number of valence electrons. Although hybridization gaps resulting in true semiconductors are uncommon, at least among the aluminides, hollows in the density of states around the Fermi level are ubiquitous. [S0163-1829(98)08839-0]

I. INTRODUCTION

While alloys composed of metallic constituents are naively expected to be metallic, hybridization between transition-metals and main group elements such as Si and Al occasionally leads to gaps in the d bands around the Fermi level. The prototype of such systems is FeSi, which has a band gap describable in terms of traditional electronic energy-band theory, but optical and conducting properties that are not.[1,2] Of the several groups of phases to be discussed that have discernible hybridization gaps, two representatives have been reported experimentally. Basov *et al.*[3] observed that $RuAl_2$ (presumably in the Si_2Ti structure) is infrared active, indicating the presence of a gap. Nishino *et al.*[4] reported semiconductorlike behavior in the temperature dependence of the conductivity for Fe_2VAl and proposed that it might be a $3d$ heavy fermion system, although they note that photoemission indicates a metallic edge at the Fermi level. Since one of these systems is Al-rich while the other is transition-metal–rich, there is an expectation that the hybridization effects may well be different.

We have theoretically explored the occurrence of such gaps in some 150 ordered binary and ternary transition-metal aluminides in various crystal structures. These alloys include both observed and hypothetical aluminide phases involving mainly $3d$ (Ti, V, Fe, and Ni) and the $4d$ (Y through Pd) elements. In agreement with the experiment, $RuAl_2$ is found to be a semiconductor. The calculations indicate that the experimentally studied Fe_2VAl is a semimetal with a hybridization pseudogap in the density of states at the Fermi level, but in a closely related system, Fe_2NbAl, a true gap is predicted. As might be expected, in addition to hybridization, both crystal structure and d-band filling will be seen to be essential for the appearance of the gaps. Other aluminides with deep hollows in their calculated densities of states at the Fermi level also will be indicated. Some of these systems with gaps might be candidates for unusual transport and/or magnetic properties similar to those encountered in FeSi, although by some measures their gaps are larger than that inferred experimentally and calculated[5] for the silicide.

II. CALCULATIONS

The calculations employ the full-potential linearized augmented Slater-type orbital method[6] (FLASTO) in which Slater-type orbitals are used to construct wave functions in the interstitial region, augmented by explicit scalar-relativistic solutions of the radial wave equations within nonoverlapping spheres at each atomic site. The Hedin-Lundqvist form[7] for the local-density exchange and correlation potential is adopted. Slater-type orbital basis sets of varying size were employed with the largest having a 2 s-, 2 p-, 3 d-, 1 f-, and 1 g-like set of orbitals for the transition-metals and a 2 s-, 2 p-, 1 d-, and 1 f-like set for Al. With the normally used larger basis sets, FLASTO is one of the more accurate methods for dealing with systems involving transition metals, yielding charge densities, band structures, and estimates of energy differences among phases comparable in precision to converged calculations using the full-potential linearized augmented plane wave method.[8]

The sets of special k points used to obtain self-consistency were increased in size until details such as the behavior of the total energy in the vicinity of an extremum in the structural parameters were accurately established; charge densities and total energies were the main criteria used to determine k-point convergence. For the BiF_3 structure, calculations with 110 and 182 k points in the irreducible wedge yielded energies in essential agreement with each other. For other structures, comparable densities of k points in reciprocal space were used. Although converged from a total energy standpoint, k point sets of this size do not accurately define all the fine details of a density of states (DOS), but do serve to indicate the presence of the band gaps of concern here. The band structures lines were then obtained using the self-consistently determined density.

The possible existence of band gaps is most quickly determined from the calculated DOS, although direct evidence of the nature and occurrence of a gap requires a more detailed inspection of the underlying band structure itself. Direct comparisons of the band structures for different crystal structures and compositions are problematic, however, since there need not be any simple relationships between the high

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symmetry lines, etc.; for this reason, we have chosen to generally show densities of states. Although calculations including spin-orbit are routinely done for the alloys, the DOS to be shown were calculated without spin-orbit coupling in the valence bands since including it had little qualitative effect on the calculated DOS around the Fermi level. This situation would likely be different for some systems if the $5d$ aluminides had been considered in this paper since the spin-orbit splittings of level degeneracies would be larger. As a final caution, we note that the local-density approximation (LDA) has a well-known tendency to underestimate gaps, with the result that hollows in the DOS may be filled in compared to the exact result; however, the presence of a calculated gap should be taken seriously.

Local ℓ-dependent densities of states for nonoverlapping atomic spheres at the individual atomic sites will also be reported. While these quantities can be illustrative, too much weight should not be attributed to the exact numerical value of quantities such as the d electron count within some given transition-metal sphere. Such counts neglect the charge in the interstitial region outside the spheres and, more seriously, do not distinguish[9] between the direct (intrinsic to a site) and the—possibly substantial—overlap (associated with wave functions centered on other atomic sites) contributions to the charge counts. One consequence is that the ℓ dependence of the charge at a site is almost as much a function[9,10] of what and where the neighboring atoms are as of the site itself; in particular, the p-electron counts encountered in transition metal spheres are primarily due to overlap charge. However, even with these caveats, electron counts may still be useful by placing constraints on models.

The crystalline structural parameters of the alloys have been determined by energy optimization. Although some of the alloys form in simple fcc- or bcc-like structures, such as the cubic BiF_3 structure, many have more complicated structures involving both c/a (and b/a) ratios and internal atomic positions whose values are not determined by symmetry. It is well established that LDA-based calculations yield lattice volumes that are smaller than those observed experimentally, and this difference is of numerical significance to the calculated ΔH. These lattice contractions are more important for the $3d$ elements and compounds than for the $4d$ and $5d$ counterparts. Our general experience for full-potential calculations is that the calculated c/a ratios of the hexagonal and tetragonal structures (and b/a for the orthorhombic systems) are close to the observed values, and that the differences between the experimental and calculated values of these ratios have only a modest consequence on the energy. Nevertheless, since all the structural parameters must be determined for the systems for which there is no crystallographic data, all the results discussed here (with one exception[11]) were obtained for the optimized structures.

To reiterate, the FLASTO method used in the calculations is an accurate full-potential method. Since the primary purpose of the set of aluminide calculations was the determination of the heats of formation of different competing phases, the demands on the precision of the calculations are higher than what is normally encountered. For this reason, it was necessary to use large basis and k point sets, and to perform full structural optimizations. While the higher precision used in the present calculations compared to typical calculations does change some details of the electronic structure, the gross features of the DOS are rather insensitive to these differences and the physical origin of the formation of (pseudo)gaps is unchanged.

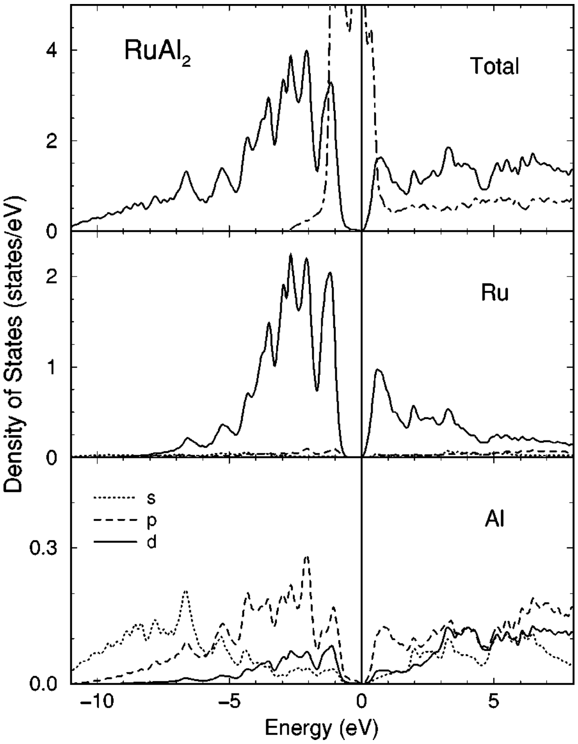

FIG. 1. The total density of states for $RuAl_2$ in the Si_2Ti structure is shown in the top panel. The s, p, and d local DOS within nonoverlapping atomic spheres are shown for the Ru and Al sites in the lower two panels. The Fermi level is the zero of energy. The dot-dash curve of the upper panel is the total DOS for the crystal with the Al atoms removed. Note that the vertical scales of the three panels differ.

III. $RuAl_2$ AND $FeAl_2$

There have been a number of published calculations for $RuAl_2$ both in the observed Si_2Ti structure[12–15] and in the other observed low-temperature $MoSi_2$ structure.[12] (The $5d$ counterpart $OsAl_2$ also forms in the $MoSi_2$ structure.) With one exception[14] that differs as to where the maximum in the valence bands occurs, the various calculations (including ours) are in essential agreement, although the small differences can affect details of the calculated band gap. Determining the lattice constants and atomic positions variationally, which was not done previously, has little effect on the results for $RuAl_2$.

Calculated total and local densities of states for $RuAl_2$ in the observed Si_2Ti structure are given in Fig. 1. The Si_2Ti structure is face-centered orthorhombic ($oF24$). As seen in the figure, a band gap at the Fermi level is found. If the low density of states at the bottom of the gap is overlooked, the calculated width of the gap appears to be slightly less than 1 eV. The dot-dash curve in the figure shows the narrow metallic[16] Ru bands, which result if the Al atoms are removed from the lattice. The significant increase in the Ru d band width when Al is present provides evidence of the strong hybridization between the Ru d and Al sp states that is also responsible for opening up the band gap in the middle of the Ru d bands. The distortion of the Al local DOS from the expected nearly free-electron form, especially around the Fermi level (E_F) where there is little Al wave function character, and the image of the Ru d bands in the Al DOS between -1 and -4 eV further reflect the Ru-Al hybridization.

Inspection of the band structure throughout the whole zone, not just the high-symmetry lines, indicates a valence band maximum at the center of the Brillouin zone Γ and the conduction band minimum on the (010) line near the zone face, with a calculated indirect gap of about 0.27 eV. The calculated minimum direct gap is removed from either of these k points and is 1.24 eV. Assuming that direct transitions control the infrared activity, it would appear that the calculations are in accord with the experimental infrared results of Basov and coworkers.[3] For comparison, the calculated[5] hybridization band gap for FeSi is roughly one fourth that encountered here.

The occupied d component of charge within the Ru atomic sphere is somewhat less than six electrons worth. This value, and inspection of the wave function character above and below the Fermi level, seems to indicate that the band gap is associated with a splitting of the d-like e_g and t_{2g} cubic states. However, the d-count extrapolated to the space-filling Wigner-Seitz sphere is measurably above 6. Although the tailing of wave function character attributable to neighboring atomic sites makes significant[9] contributions for both the atomic and Wigner-Seitz spheres counts, reasonable attributions of charge still lead to more than 6 Ru d electrons. The conclusion that can be drawn from these d counts is that the opening of a gap is not simply a case of Ru-Al hybridization increasing the t_{2g}-e_g splitting, but there must also be significant mixing between nominally t_{2g} and e_g orbitals, i.e., simple t_{2g}-e_g arguments in less than cubic systems such as we have here (or even in cubic systems) should be taken with caution. Rather, hybridization[13] between Al sp and Ru d orbitals, along with some charge transfer,[12] is the origin of the gap. It should also be noted that the Ru s- and p-like (and higher ℓ) components shown in the middle panel are measurably less than would be the case if Ru had been alloyed with another transition-metal, suggesting that Al introduces significantly less tailing charge at neighboring atomic sites than does a transition-metal.

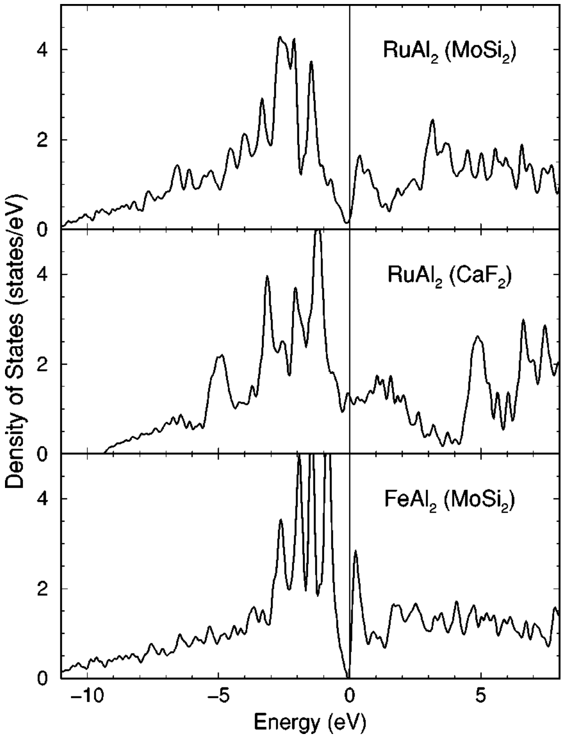

FIG. 2. Densities of states for RuAl$_2$ in the MoSi$_2$ and CaF$_2$ structures, and for FeAl$_2$ in the MoSi$_2$ structure. The Fermi level defines the energy zero.

Figure 2 displays the DOS for RuAl$_2$ in two other structures. RuAl$_2$ has also been reported to occur in the MoSi$_2$ structure, the observed structure for OsAl$_2$, although the lattice constants reported by Villars and Calvert[17] yield an improbable molecular volume. This structure corresponds to a (tetragonally distorted) aab stacking of (001) layers of a bcc lattice. The optimum c/a ratio indicates a compression along the c axis, in which case this structure is sometimes referred to as C$_2$Ca. As can be seen in the top panel, the calculated hollow around E_F just misses being a gap. Inspection of the band structure indicates that the top of the valence band lies $\sim$0.10 eV above the bottom of the conduction band, in agreement with the results of Springborg and Fischer.[12] Thus, RuAl$_2$ in the MoSi$_2$ structure is a semimetal with a hole pocket on the zone face and an electron pocket in the interior along a (110) line. The calculated minimum direct band gap is 0.62 eV, and so RuAl$_2$ in this structure might display some mixed semiconducting and metallic behavior. The calculated DOS for the CaF$_2$ structure is also shown in the figure because this is a plausible structure for dialuminides formed with transition-metals in this region of the periodic table. No hint of a gap is to be found for this case, nor for RuAl$_2$ in the MoSi$_2$ structure with the c/a ratio corresponding to a fcc lattice (not shown). These results demonstrate that hybridization-induced (pseudo)gaps/hollows in the DOS are strongly dependent on the structure of the lattice. This conclusion is to be expected since symmetry controls the hybridizations that may occur.

The bottom panel of Fig. 2 shows the calculated density of states for FeAl$_2$ in the MoSi$_2$ structure. This structure has not been reported experimentally, but its calculated heat of formation is such that it is stable with respect to a two-phase mix of FeAl (a nearby observed phase) and of pure Al, suggesting that it may be at least metastable. The results show the system in this structure to be a semiconductor with a minimum indirect band gap of about 0.17 eV, involving a valence-band maximum and conduction-band minimum like those for RuAl$_2$ in this structure, and direct band gaps in excess of 1 eV. The rapid rise in the density of states to either side of the gap suggests that there may be strong optical absorption in this energy range. The reported[17] structure for this system, however, is triclinic with eighteen atoms. The DOS obtained[11] using a limited number of k points shows a hollow at the Fermi level, but one that is far from being a gap. Crude as they are,[11] the results suggest that it is unlikely, but not impossible, that the reported triclinic FeAl$_2$ system is a semiconductor.

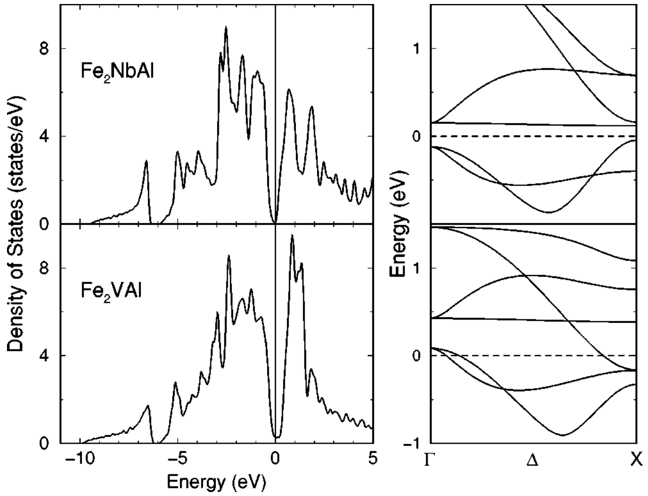

FIG. 3. Densities of states and band structures along Γ-X (along which the valence and conduction band extrema lie) for Fe_2NbAl and Fe_2VAl in the BiF_3 structure. The Fermi level defines the energy zero.

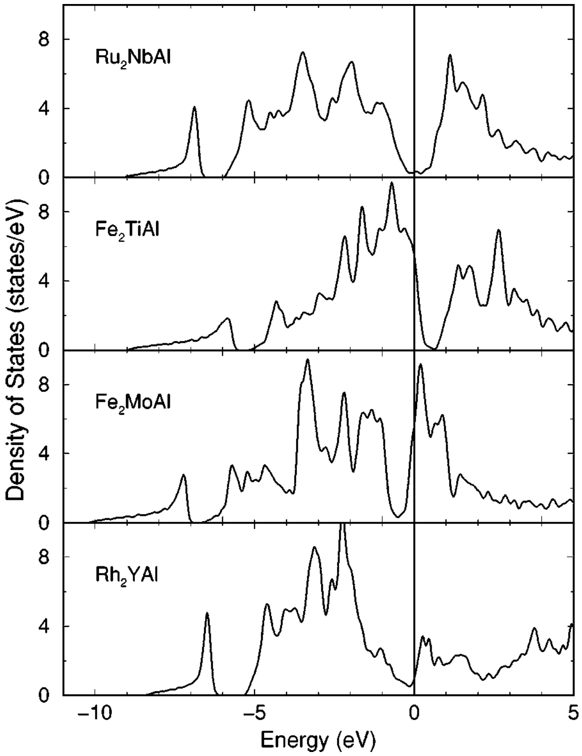

FIG. 4. Densities of states for several ternary transition-metal aluminides in the BiF_3 structure with varying electron counts. The Fermi level defines the energy zero.

IV. BiF_3 STRUCTURE

The most common ordered structure for ternary transition-metal aluminides to form in is the BiF_3 structure. With composition M_2NA, the A atom may be a main group element such as Al, Si, Ge, Ga, or In, and M and N are transition metals, with M usually from the righthand half of the row and N from the left. The structure is a bcc lattice with the M atoms at the body corners, and the N and A atoms alternating in the body centers along the x, y, and z directions. This structure tends not to form[18] if the elemental atomic volumes of the A and N atoms differ by more than about 30%.

The experimental results of Nishino *et al.*[4] are for Fe_2VAl in this structure. Like $RuAl_2$, this system has an even number of valence electrons in the unit cell, consistent with filled bands and the possibility of a gap. In contrast to $RuAl_2$, Al is now the minority constituent and transition-metal–transition-metal bonding should be important. As shown in Fig. 3, the Al s-electron character for both Fe_2VAl and Fe_2NbAl is peaked up below the bulk of the bands. Although the Al s hybridization may be significant to the energetics of the alloy formation, in the vicinity of the gap the Al DOS is dominated by p and d character, with most of the d-like density arising from tailing of transition-metal wave function character onto the Al site. The most important feature in the densities of states for the purposes of this paper is the deep hollow around the Fermi level. The simplest explanation of this behavior is that a common d band is formed in the alloy; in bcc-like structures there is a hollow separating the bonding and antibonding states. The Fermi level will fall in this hollow when there are 5 d electrons per transition-metal atom, and the calculations for the compounds yield a total of almost exactly 15 d electrons in the three transition-metal spheres. While this picture is appealing in its simplicity, it is obviously incomplete. There are clear indications from the transition-metal local densities of states that there is not a common d band and that the distortion of the Al DOS involves hybridization between Al and the transition metals.

The bands responsible for defining the (pseudo)gaps in the DOS near the Fermi level (shown in Fig. 3) are along the Γ to $X[=2\pi(001)/a]$ line. [Although the (001) and (010) directions are symmetry equivalent, our particular choice for the X point has the advantage that the conventional choice of $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals are correctly symmetry-adapted.] In the case of Fe_2NbAl, there is a gap in the spectrum, with the minimum direct gap of ~0.16 eV at the X point. For Fe_2VAl, slight changes in the relative positions of the bands cause the conduction band minimum at X to fall below the valence band maximum, which is now at Γ. Thus, Fe_2VAl is a semimetal with hole pockets around Γ and electron pockets at X, consistent with the metallic character of the photoemission spectrum[4] and with the semiconductorlike conductivity because of the small number of carriers. Our bands for Fe_2VAl, including its semimetallic nature, are in agreement with other recent band calculations.[19,20] The readjustment of the bands at X and the shift relative to Γ on going from Fe_2NbAl to Fe_2VAl is even greater for the Ru counterparts, leading to larger electron and hole pockets. While Fe_2NbAl and the Ru counterparts have not yet been reported to occur, these alloys are predicted[18] to be stable relative to competing binary alloys.

The total densities of states of a number of other M_2NAl alloys in the BiF_3 structure are given in Fig. 4. As discussed above, the density of states of Ru_2NbAl is similar to that of Fe_2VAl, but with the (pseudo)gap being a bit wider and not as deep. These similarities among the different alloys point out the important role of structure in determining the hybridization leading to the formation of the pseudogap. The fact that the Fermi level falls in this hollow is a consequence of the total number of electrons. To emphasize this point, the middle two panels of Fig. 4 show the consequences of

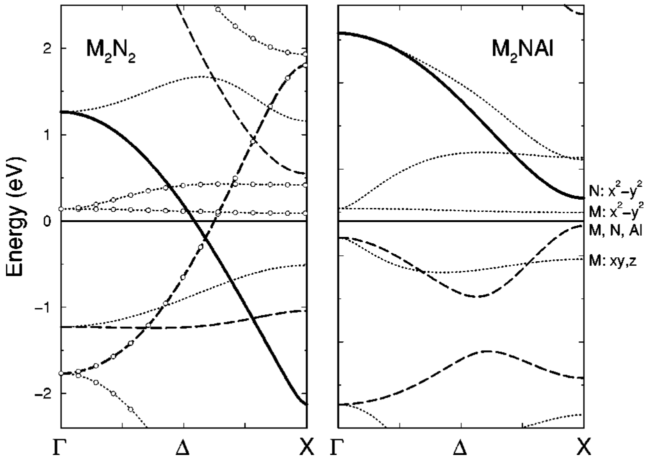

FIG. 5. Schematic of the bands along Γ-X of the BiF_3 structure for transition-metal aluminides M_2N_2 and M_2NAl, with parameters appropriate for $M=$Fe and $N=$Nb. Dashed (dotted) lines represent doubly (singly) degenerate bands, and the heavy solid line represents the N $d_{x^2-y^2}$ band (at X) discussed in the text. Note that M_2N_2 is actually in the CsCl structure; bands originating from the R-M line of the CsCl structure are marked by circles. The bands for M_2N_2 have been shifted to align the energy of the flat band at Γ with the similar band of M_2NAl.

changing the N-site valence electron count by one. While there are obviously changes in the details of the bands, there is an almost rigid bandlike shift in the position of the hollow. Furthermore, the effect of maintaining the total valence electron count by changing the charge of the M atom by $+1$ and that of the N by -2 is shown in the bottom panel for Rh_2YAl. In this case the centers of gravity of the Rh and of the Y d states are more widely separated than those of the compounds above and the Y d bands are much wider, yet a hybridization hollow can still be discerned at the Fermi level. Rh_2YAl is predicted[18] not to occur, but size factors are more favorable for Rh_2ScAl and for Co_2ScAl. If these alloys occur, they are not expected to have as ''exotic'' properties as Fe_2VAl simply because the sharp rise in the DOS to either side of the hollow is missing. The conclusions that can be drawn from the results shown in Fig. 4 are that the basic hybridization effects are related mainly to the crystal structure, and whether the Fermi level falls in one of these hybridization hollows is related to the total number of electrons.

The bands along Γ-X for an M_2NAl alloy in the BiF_3 structure are sketched in the righthand part of Fig. 5. While the bands represent a case like Fe_2NbAl with a gap, the important band structure features of all of these alloys are similar. The wave function character of the bands at X near the Fermi level are also labeled in Fig. 5. Naively, the t_{2g}-e_g convention might seem a natural way to discuss the bonding in this cubic system, but such a division is inadequate for understanding the formation of gaps in the BiF_3 structure. The individual members of the t_{2g} or e_g manifolds belong to different irreducible representations along Δ; it is these irreducible representations that determine the allowed hybridizations and interactions, and hence the (pseudo)gaps. (If these alloys were highly localized systems with little hybridization among the sites, a description in terms of t_{2g}-e_g or t_2-e states, depending on the site, might be appropriate. This limit, however, is not the correct one for these alloys.)

Just below the Fermi level for M_2NAl in Fig. 5 are a doubly degenerate (dashed line) band and a singly degenerate (dotted) band. At X, the singly degenerate band is a mixture of M (Fe) d_{xy} and p_z states, while the doubly degenerate state is a mixture of $M(d_{xz}, d_{yz}, p_x, p_y)$, $N(p_x, p_y)$, and Al (p_x, p_y) orbitals. The flat band above the Fermi level is composed of M (Fe) $d_{x^2-y^2}$ orbitals, and the band marked with the heavy solid line is composed entirely of N (Nb) $d_{x^2-y^2}$ orbitals at X because, by symmetry, there is no coupling between the $d_{x^2-y^2}$ orbitals on the M and N sublattices. From inspection of a large number of band structures for different alloys in the BiF_3 structure, the relative position of this N $d_{x^2-y^2}$ state at X is found to be the major factor determining whether or not a gap forms.

Around the Fermi level there is very little Al character, just as in $RuAl_2$. Because of this depletion of Al character, it is not obvious at first glance that Al plays any significant role in the formation of the gaps. However, calculations that simply ignore the Al atoms (the CaF_2 structure) show that the gaps are destroyed (as well as shifting the Fermi level), demonstrating that the Al atoms do play an important, if indirect, role. We will return to this issue later.

The origin of the (pseudo)gaps in the density of states for the BiF_3 structure can be understood using simple tight-binding arguments. In this structure, there are four atoms per unit cell and three symmetry inequivalent sites. As discussed above, states with $d_{x^2-y^2}$ character around the Fermi level play an important role in determining the existence of the (pseudo)gaps. Along Γ-X, all $d_{x^2-y^2}$ orbitals belong to either the Δ_2 or Δ_1' irreducible representations; conversely, no other s, p, or d orbitals on any of the atoms belong to these irreducible representations. For a general M_2NA alloy, the symmetry at X dictates that the $d_{x^2-y^2}$ orbitals on the M sublattice do not interact with those on the N-A sublattice. Thus, the four bands at X derived from the $d_{x^2-y^2}$ orbitals split into two sets of bonding and antibonding levels. The tight-binding energies[21] of the states derived from the orbitals centered on the M sublattice are

$$E_1^M(X)=\epsilon_d^M+3V_{dd\sigma}^{MM}, \tag{1}$$

$$E_2^M(X)=\epsilon_d^M-3V_{dd\sigma}^{MM}, \tag{2}$$

and for orbitals on the N-A sublattice, the energies are

$$E_{\pm}^{N-A}(X)=\frac{\epsilon_d^N+\epsilon_d^A}{2}\pm\left[\left(\frac{\epsilon_d^A-\epsilon_d^N}{2}\right)^2+(3V_{dd\sigma}^{NA})^2\right]^{1/2}. \tag{3}$$

In these equations, the usual notation is used: ϵ_d^{α} is the tight-binding on-site energy parameter for the d electrons of atom α, and $V_{dd\sigma}^{\alpha\beta}<0$ is a second neighbor interatomic potential matrix elements between atoms α and β. (The small $V_{dd\delta}$ terms have been neglected.) The state corresponding to $E_1^M(X)$ is below the bottom of Fig. 5, the energy of the flat band just above the Fermi level corresponds to $E_2^M(X)$, and the state labeled ''N:x^2-y^2'' corresponds to one of the pair of $E_{\pm}^{N-A}(X)$. Note, the energies given in Eqs. (1)–(3) do not correspond[22] to the energy of the zone center e_g level in the bcc lattice of the elemental system.

For the case that the A atom is Al, the intrinsic Al d levels are much higher in energy than for the transition-metal, and the interaction between the d states on the N and Al sites is vanishingly small. The effective lack of d orbitals on Al can be expressed as $|V_{dd\sigma}^{N-\mathrm{Al}}/(\epsilon_d^{\mathrm{Al}}-\epsilon_d^N)|\rightarrow 0$. In this case the two eigenvalues at X of Eq. (3) are simply a very high-lying state at ϵ_d^{Al} (not shown) and one, marked with a heavy line in Fig. 5, at ϵ_d^N. Hence, the position of the N $d_{x^2-y^2}$ state at X for M_2NAl is determined not by any transition-metal d and Al p hybridization, but rather by the *lack* of N–Al d-d hybridization. This result, unexpected perhaps, is essential in order to understand the formation of the gap in these systems.

Clearly, transition-metal–Al hybridization must play a role in the formation of the gap. To better understand the effect of Al on the formation of the (pseudo)gaps in M_2NAl alloys, it is instructive to consider the case $A=N$, i.e., the transition-metal binary MN alloy in the CsCl structure. These bands are shown in the left-hand part of Fig. 5 for the Δ line of the BiF$_3$ structure. Since M_2N_2 in the BiF$_3$ structure is a supercell of MN, half of the bands in Fig. 5 along Γ-X of the BiF$_3$ cell are from the Γ-X line in the CsCl simple cubic Brillouin zone and the other half come from the $R[=2\pi(\frac{1}{2}\frac{1}{2}\frac{1}{2})/a]$ to $M[=2\pi(\frac{1}{2}\frac{1}{2}0)/a]$ line; these latter states are marked with circles in the figure. States arising from the different lines in the CsCl Brillouin zone do not interact.

M_2N_2 does not have a gap because there are two bands with large dispersion passing through the gap region of M_2NAl. These bands are a doubly degenerate band (dashed line) coming from the R-M line dispersing upward, and a downward dispersing band (heavy solid line). As before, the band marked with the heavy solid line has N $d_{x^2-y^2}$ character at X, and is the counterpart of the "N:x^2-y^2" band of M_2NAl shown in the right-hand part of the figure. Because there are now $d_{x^2-y^2}$ orbitals on both N sites, the energy of this band at X is given by [cf. Eq. (3)] $\epsilon_d^N+3V_{dd\sigma}^{NN}$, which is $|3V_{dd\sigma}^{NN}|$ lower than the corresponding band of M_2NAl. This large reduction in the dispersion for the aluminide arising from the *missing* transition-metal–Al d-d hybridization is a necessary condition if a gap is to form.

The upwardly dispersing doubly degenerate band (dashed line with circles) that destroys the pseudogap in M_2N_2 arises from the R-M line of the CsCl Brillouin zone and crosses doubly degenerate bands originating from Γ-X of the CsCl zone. When one of the N atoms is replaced by Al, the artificial translational symmetry of the supercell is broken. Now all the doubly degenerate levels belong to the same irreducible representation and can hybridize, causing the band crossings to change into anticrossings. The size of the anticrossing gaps are related to the differences between the potentials of the N transition-metal and Al potentials. The accompanying level repulsions between the doubly degenerate bands determine the relative energy of the valence band maxima at Γ and X. The positions of these doubly degenerate states are dependent on the Al p and transition-metal d hybridization since the Al $p_{x,y}$ and transition-metal $d_{zx,zy}$ orbitals all belong to this irreducible representation. For the large potential difference corresponding to removing the Al atom entirely, i.e., the CaF$_2$ structure, the hybridization among the bands and the level repulsions are so large that the pseudogap structure is destroyed.

This analysis confirms that the relative positions of these different bands at X are the best indicators of whether a gap is formed in the M_2NAl alloys. In the case of Fe$_2$VAl, the V $d_{x^2-y^2}$ band dips far enough below the Fe $d_{x^2-y^2}$ to result in semimetallic behavior. For the Ru compounds, the N $d_{x^2-y^2}$ band at X is even farther below E_F. From the tight-binding results, we can make some further observations and predictions. To get a gap, the energy of the N $d_{x^2-y^2}$ band $[E^N(X)]$ should be as high as possible relative to the energy (E_2^M) of the flat M $d_{x^2-y^2}$ band: $E^N-E_2^M=\epsilon_d^N-(\epsilon_d^M-3V_{dd\sigma}^{MM})$ should be as positive as possible, recalling that $V_{dd\sigma}^{MM}<0$. This requirement can be satisfied by separating the d bands farther and/or decreasing the interaction between the M atoms. This latter condition suggests that larger N atoms (Nb vs V), which will expand the lattice and reduce the M-M interactions, are more likely to form gaps. This prediction is borne out by the calculations for both $M=$Fe and Ru. Moreover, if the lattice is expanded by about 6%, Fe$_2$VAl becomes an indirect gap semiconductor. On the other hand, the $V_{dd\sigma}^{MM}$ terms for the Ru compounds are significantly larger ($\sim 60\%$) than those of the Fe alloys, and is the major reason that gaps do not form in either Ru$_2$VAl or Ru$_2$NbAl.

The other term, the relative position of the transition-metal d levels, depends on a number of parameters, including the specific elements and the volume. From the calculated band structures, the Nb d levels are found to be higher than the V d levels in both the Fe and Ru alloys. Since the d bands in the $4d$ row are lower than those in the $5d$ row, our analysis predicts that replacing Nb with Ta should increase the tendency to form a gap by increasing $\epsilon_d^{\mathrm{Ta}}-\epsilon_d^{\mathrm{Fe,Ru}}$. As a test of this hypothesis, we have calculated Ru$_2$TaAl and find that $\epsilon_d^{\mathrm{Ta}}-\epsilon_d^{\mathrm{Ru}}$ is about 0.35 eV larger than $\epsilon_d^{\mathrm{Nb}}-\epsilon_d^{\mathrm{Ru}}$, while $V_{dd\sigma}^{\mathrm{Ru\text{-}Ru}}$ is approximately the same. The net result is that the pseudogap in the density of states at E_F for Ru$_2$TaAl is significantly deeper than for Ru$_2$NbAl. The detailed reason for this change is that the N $d_{x^2-y^2}$ state for Ru$_2$TaAl is above the doubly degenerate state at X, whereas in Ru$_2$NbAl it is below. Ru$_2$TaAl is still a semimetal, with the N $d_{x^2-y^2}$ state at X ~ 0.28 eV below the states at Γ. The density of states and band structure around the Fermi level, however, are rather similar to those of Fe$_2$VAl, suggesting that Ru$_2$TaAl might have properties very similar to those of Fe$_2$VAl.

V. OTHER SYSTEMS

There are a number of other transition-metal aluminides that have low densities of states in the midst of the d-bands near the Fermi level; three are shown in Fig. 6. Both NbAl$_3$ and VAl$_3$, which form in the TiAl$_3$ structure, have an even number of valence electrons per unit cell. Although there are hybridization hollows, NbAl$_3$ and VAl$_3$ are not semimetals like Fe$_2$VAl and are better classified as metals, i.e., these systems do not have the compensating localized (in k space) electron and hole pockets generally associated with a semimetal. Within a rigid band model, substituting $\sim 5\%$ Cr or

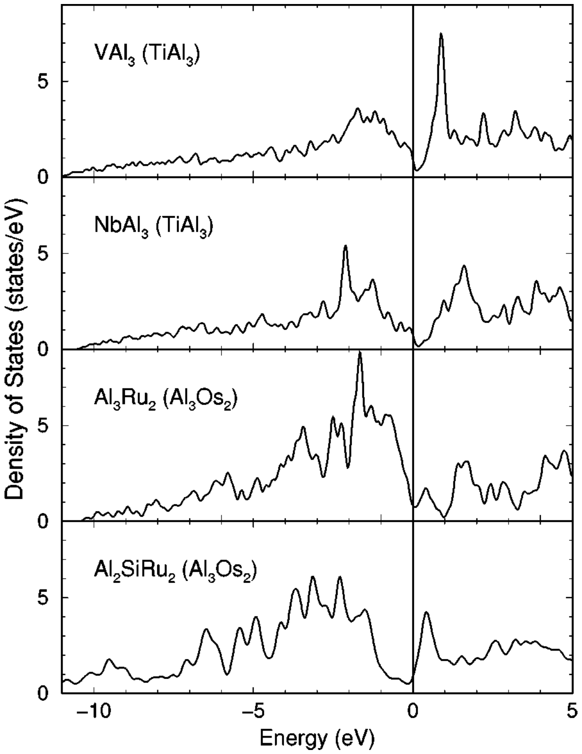

FIG. 6. Densities of states for VAl_3 and $NbAl_3$ in the observed $TiAl_3$ structure, and for Al_3Ru_2 and Al_2SiRu_2 in the Al_3Os_2 structure. The Fermi level defines the energy zero.

Mo for V or Nb causes the Fermi level to fall at the minimum of the DOS, at which point the extra charge is contained in electron pockets at X; virtual crystal calculations for $V_{1-x}Cr_xAl_3$ support this basic picture. Because these systems are Al-rich and V (and Nb) are near the beginning of the transition-metal row, the type of missing d-d hybridization between Al and the transition-metal that was important for the M_2NAl BiF_3 alloys is not present.

Also shown in Fig. 6 is Al_3Ru_2 in the Al_3Os_2 structure. This structure is an *abccb* stacking of bcc (001) planes, the fivefold analog of the $MoSi_2$ structure. Because Al_3Ru_2 has an odd number of valence electrons per unit cell, it cannot have a band gap at the Fermi level, even though there is a modest hollow. At about 1 eV above the Fermi level, corresponding to having added one valence electron to the chemical unit, there is a deep hollow that can be reached by substitution of higher valence elements for either Al or Ru. The density of states for an ordered hypothetical Al_2SiRu_2 phase in the Al_3Os_2 structure (often labeled C_2IrU_2 when a ternary) is shown in the bottom panel of the figure. The Fermi level now falls near the minimum of the density of states, but since there are several bands crossing the Fermi level, the system is metallic. While Al_2SiRu_2 has not been reported, the calculated heat of formation (optimizing the structural parameters) is substantial, on the order of -0.62 eV/atom. This heat, however, is calculated to be just slightly unstable relative to the competing binaries, but the possibility exists that this system might be at least metastable.

There are a few other observed binary aluminides whose densities of states at the Fermi level are of the order of those displayed in Fig. 6, including AlRh (in the CsCl structure), $Al_{12}Mo$ and $Al_{12}Tc$ ($Al_{12}W$ structure), and Al_3Zr. All of these, however, are not as easily describable as near semimetals/semiconductors as the cases considered above. Most ordered ternary aluminides that do not form in the BiF_3 structure involve one transition-metal from the upper end of the row and the other from the Sc or Ti columns, just the circumstances under which strong line compound formation occurs for the binary transition-metal alloys. Then the situation is similar to that encountered in Fig. 4 for Rh_2YAl, where the centers of the two sets of d bands are far apart and the Fermi level falls between them. Such a situation has been encountered in calculations for the observed Al_5Ni_2Zr phase (a $tI16$ structure), where there is the suggestion of a weak hybridization hollow in what is already a low density of states region.

VI. CONCLUSION

Hybridization between transition metals and main group elements may lead to gaps or to deep hollows (pseudogaps) in the density of states. If the total electron counts are such that the Fermi level falls in one of these hollows, the transport properties are not what one would naively expect for alloys composed of good metallic constituents. A few cases, such as $RuAl_2$, $FeAl_2$ in the $MoSi_2$ structure, and Fe_2NbAl (and also[12] Al_2Os and Ga_2Ru), are predicted to be semiconductors, and one, $RuAl_2$, has been observed.[3] In other cases, such as Fe_2VAl, the system is best described as a semimetal with a low-carrier concentration. Whether the band structure alone can describe all the properties[4,19,20] of Fe_2VAl is an open question, but the results presented here demonstrate that the existence of (pseudo)gaps in the density of states can be understood from hybridization arguments without the necessity of invoking correlation effects.

Some of the systems considered in this paper, especially $RuAl_2$, have been studied previously.[12–15] We have extended those studies to related compounds (e.g., $FeAl_2$), and shown that the basic features of the bands are similar. We have also briefly discussed a number of other systems with hollows in their density of states around the Fermi level. These systems vary widely in their crystal structures and band structures, but hybridization between the transition-metals and Al are essential for the formation of the hollows in their DOS. For a system with a low density of states at the Fermi level, our admittedly somewhat arbitrary classification as either a metal or a semimetal is based on the topology of the bands, rather than transport properties: A semimetal has compact electron and hole pockets *and* will result in a semiconductor with reasonably small shifts of the bands (cf. Fe_2VAl). In contrast, the topology of the bands crossing the Fermi level in a metal is such that a clear separation into conduction and valence bands may be difficult. Thus, simple shifts of the bands in a ''metal'' will not open up a gap and, by these criteria, the hollows in the DOS are not pseudogaps.

The other experimentally studied[4] ''semiconducting'' transition-metal aluminide is Fe_2VAl. Rather than simply limiting ourselves to this single phase, we have considered a number of related compounds in the BiF_3 structure, also the most common crystal structure in which ternary aluminides form. Our analysis concentrated on these alloys, both because compounds in this structure are predicted to have well-defined (pseudo)gaps around the Fermi level and because little previous work addressing these issues has been reported. By showing which bands and hybridizations are responsible for the formation of the (pseudo)gap in these structures, and how the bands vary with parameters such as atomic size and *d* band position, we have been able to go beyond handwaving ‘‘*p*-*d*’’ hybridization arguments—which, for these alloys, are incomplete at best—to make concrete predictions, that have then been verified by detailed calculations. The tight-binding analysis shows that Al having no *d* electrons available to hybridize with the transition-metals is just as important as hybridization involving Al *p* electrons in determining whether a (pseudo)gap forms in the BiF_3 structure.

The results of this paper demonstrate that the crystal structure of the alloy plays an essential role in determining the band structure, with different structures allowing significantly different hybridizations. For transition-metal-rich aluminides, both hybridization and the *lack* of *d*-*d* hybridization between the transition-metal atoms and *d*-less Al atoms are found to be important ingredients in the formation of hollows in the density of states. Whether these hollows become actual gaps depends on details of the electronic structure, including the relative positions of the atomic levels and the relative sizes of the atoms, but the overall band structures are qualitatively similar for sets of related compounds. Although hybridization gaps leading to semiconductors are uncommon, at least among the aluminides, hollows are ubiquitous, and these systems show behavior running the gamut from metallic to semiconducting.

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[1] V. Jaccarino, G. K. Wertheim, J. H. Wernick, L. R. Walker, and S. Arajas, Phys. Rev. **160**, 476 (1967).

[2] Z. Schlesinger, Z. Fisk, H.-T. Zhang, M. B. Maple, J. F. DiTusa, and G. Aeppli, Phys. Rev. Lett. **71**, 1748 (1993).

[3] D. N. Basov, F. S. Pierce, P. Volkov, S. J. Poon, and T. Timusk, Phys. Rev. Lett. **73**, 1865 (1994).

[4] Y. Nishino, M. Kato, S. Asano, K. Soda, M. Hayasaki, and U. Mizutani, Phys. Rev. Lett. **79**, 1909 (1997).

[5] L. F. Mattheiss and D. R. Hamann, Phys. Rev. B **47**, 13 114 (1993).

[6] G. W. Fernando, J. W. Davenport, R. E. Watson, and M. Weinert, Phys. Rev. B **40**, 2757 (1989).

[7] L. Hedin and B. I. Lundqvist, J. Phys. C **4**, 2064 (1971).

[8] E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, Phys. Rev. B **24**, 864 (1981).

[9] R. E. Watson, M. Weinert, and G. W. Fernando, Phys. Rev. B **43**, 1446 (1991).

[10] R. E. Watson and M. Weinert, Phys. Rev. B **49**, 7148 (1994).

[11] The one exception is $FeAl_2$, where the reported triclinic structure was used. The low symmetry and eighteen atom unit cell of this system made a complete optimization impractical. Another complication is that the experimental data were determined from an alloy off stoichiometry, thus requiring assumptions concerning the Fe vs Al occupancies at three sites in order have a 2:1 composition. Furthermore, because of the cell size, the calculation was done employing a single-ζ basis set. Finally, besides questions of the accuracy of the reported atomic positions, there are questions whether they are appropriate for the stoichiometric system. Granted these several factors, the most important being that the phase was observed off stoichiometry, any conclusions concerning the presence of a gap in the triclinic structure are at best tentative.

[12] M. Springborg and R. Fischer, J. Phys.: Condens. Matter **10**, 701 (1998).

[13] D. Nguyen Manh, G. Trambly de Laissardiere, J. P. Julien, D. Mayou, and F. Cyrot-Lackmann, Solid State Commun. **82**, 329 (1992).

[14] S. E. Burkov and S. N. Rashkeev, Solid State Commun. **92**, 525 (1994).

[15] S. Ogut and K. M. Rabe, Phys. Rev. B **54**, R8297 (1996).

[16] Ru, as well as other transition metals, in the standard high-symmetry crystal structures (fcc, bcc, diamond, etc.) is metallic. It is not inconceivable, however, that at certain volumes there exist (high energy) structures in which Ru is semiconducting. Although such cases may seem unlikely, examples of elemental systems that are either metallic or semiconducting depending on the crystal structure can be found both in theoretical calculations and even in nature: Sn exists both as a zero gap semiconductor (gray tin) and as a metal (white tin).

[17] P. Villars and L. D. Calvert, *Pearson’s Handbook of Crystallographic Data for Intermetallic Phases, 2nd ed.* (American Society for Metals, Materials Park, OH, 1991).

[18] R. E. Watson, M. Weinert, and M. Alatalo, Phys. Rev. B **57**, 12 134 (1998).

[19] D. J. Singh and I. I. Mazin, Phys. Rev. B **57**, 10 598 (1998).

[20] R. Weht and W. E. Pickett, Phys. Rev. B **58**, 3855 (1998).

[21] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

[22] From a cursory glance at the band structure of M_2NAl or M_2N_2, one might infer that the flat band, which is doubly degenerate at Γ, should be associated with the energy of the zone center e_g level of the elemental system. This expectation, however, is wrong. To understand why, let all the atoms in the BiF_3 structure be of type M. The system is then simply a supercell of the bcc structure, with a one-to-one correspondence between bands in the BiF_3 and bcc structures. Although the $d_{x^2-y^2}$ orbitals nominally belong to the e_g manifold, the energies given in Eqs. (1)–(3), including $E_2^M(X)$, differ from the zone center bcc e_g energy:

$$E_{e_g}(\Gamma)=\epsilon_d^M+\frac{16\pi}{3}V_{dd\pi}+3V_{dd\sigma}^{MM}.$$

In this equation, the tight-binding parameter $V_{dd\sigma}^{MM}$ is again a second-neighbor interaction and $V_{dd\pi}$ is a nearest-neighbor in-

teraction. The simple explanation for the differences is that the flat band and the one that is degenerate with it at Γ are bands from the outer part of the bcc Brillouin zone; the differences in energy are related to the dispersion of the bcc bands. As an aside, there are no $V_{dd\pi}$ contributions to the band energies in Eqs. (1)–(3) because the phase factors associated with $V_{dd\pi}$ vanish at X; elsewhere along Δ these terms do contribute to the energies.