Ab initio theory of valency in ytterbium compounds

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The electronic structure of 26 Yb compounds is calculated with the *ab initio* self-interaction-corrected local-spin-density approximation. In this approach f electrons can be described as either localized or delocalized. Hence a divalent Yb ion is represented with a completely localized f^{14} shell, while a trivalent Yb ion is represented with a localized f^{13} shell with the remaining 14th f electron giving rise to a very narrow f resonance, which straddles the Fermi energy. The systems studied comprise the Yb monopnictides and monochalcogenides as well as a series of intermetallic compounds. Experimental equilibrium volumes are well reproduced. The results provide quantitative support to the experimental classification of Yb compounds in terms of effective valencies.

I. INTRODUCTION

Ytterbium compounds show a wealth of anomalous physical phenomena caused by the intricate electronic structure related to its f electrons.[1–3] In the atomic ground state Yb is divalent, with a filled f^{14} shell, but in the solid state the f electrons may play an active role in the bonding, giving rise to intermediate valent, heavy-fermion, or Kondo behavior as well as complex magnetic structures.[4] These phenomena are highly sensitive to chemical environment as well as external probes such as temperature, pressure, or magnetic field. The accurate theoretical description of Yb compounds remains a challenge. While conventional band theory, as implemented in the local-spin-density (LSD) approximation to density-functional theory,[5] has been rather successful in describing solid-state properties, it generally fails for f-electron systems. The large correlation effects involved for the atomiclike f-electron states are inadequately accounted for by the homogeneous electron gas underpinning the LSD. By applying self-interaction corrections (SIC's) to LSD a scheme is obtained which allows both an atomiclike description of f electrons and an itinerant description of other electronic degrees of freedom. Specifically, for Yb compounds, configurations assuming localized f^{13} and f^{14} shells on the Yb atom can be studied and their energies compared. The SIC introduces a localization energy, and whether it is more favorable to localize the entire f shell or only 13 f electrons becomes a trade-off between this localization energy and the energy which the 14th electron may gain by hybridizing into the conduction states. The present work aims at investigating this balance of energies for a selection of 26 Yb compounds comprising Yb monopnictides, monochalcogenides, and intermetallics. The primary goal is to demonstrate that a valid description of the bonding properties and effective valencies of Yb systems is achieved. In addition, a detailed electronic structure picture provided will be discussed.

For the configurations with localized f^{13} or f^{14} shells there are, respectively, three or two Yb electrons left over for band formation, and we shall identify this number with the

(nominal) Yb valency. We note that in the nominal trivalent case, where Yb possesses a localized f^{13} shell, the 14th f electron forms a very narrow band situated among the normal s-d-derived conduction states. In all the cases studied here the Fermi level is pinned to this narrow band which becomes partially occupied. As a consequence the total f occupancy is noninteger, and falls in between 13 and 14, and the nominally trivalent Yb configuration therefore describes a mixed-valent state. The more conventional definition of valency for rare earths identifies the valency with the number of non-f electrons,[1] which we shall here call the effective valency. Compared with the LSD, the SIC-LSD description reduces the fluctuation of the f-electron number. In the LSD all the f states are pinned at the Fermi energy, and therefore the number of occupied f electrons fluctuates between none and all occupied, while in the SIC-LSD description with a localized f^{13} shell this fluctuation is reduced to one possible f state. The ground state is, however, still described by a single Slater determinant, and spin fluctuations, giving rise to the Kondo effect, are not considered. Therefore, for cases where a significant energy contribution is associated with Kondo fluctuations, the SIC-LSD description could lead to errors.

The remainder of this paper is organized as follows: In Sec. II the SIC-LSD method is outlined, while Sec. III presents results. In Sec. III A the cohesive properties and effective valencies of Yb compounds are discussed. A brief account of part of these results was already given in Ref. 6. In Sec. III B the electronic structure of the Yb monopnictides is discussed in detail. Finally, Sec. IV presents conclusions and the outlook of the present work.

II. SIC-LSD METHOD

In the SIC-LSD approach[7] the total energy functional of the LSD approximation is corrected for the spurious self-interaction of each occupied electron state,

$$E^{SIC} = E^{LSD} - \sum_{\alpha}^{occ.} \delta_{\alpha}^{SIC}, \tag{1}$$

where α labels the occupied states, and δ_α^{SIC} is the self-interaction correction for state α. As usual, E^{LSD} can be decomposed into a kinetic energy T, a Hartree energy U, the interaction energy with the atomic ions, V_{ext}, and the exchange and correlation energy E_{xc}.[5] The self-interaction is defined as the sum of the Hartree interaction and the exchange-correlation energy for the charge density of state α:

$$\delta_\alpha^{SIC} = U[n_\alpha] + E_{xc}[n_\alpha]. \tag{2}$$

For itinerant states, δ_α^{SIC} vanishes identically. The advantage of functional (1) is that various valency scenarios can be explored by assuming atomic configurations with different total numbers of localized states. In particular, these different scenarios constitute local minima of the functional, and their total energies may be compared. The state with the lowest energy defines the ground-state configuration. Note that, if no localized states are assumed, E^{SIC} coincides with the conventional LSD functional, i.e., the Kohn-Sham minimum of the E^{LSD} functional is also a local minimum of E^{SIC}. The interesting question is whether competing minima with a finite number of localized states exist. This is usually the case in f-electron systems and some $3d$ transition metal compounds,[8–11] where the respective f and d orbitals are sufficiently spatially confined to benefit appreciably from the SIC.

The SIC-LSD approach still considers the electronic structure of the solid to be built from individual electron states, but offers an alternative description of the single-electron states to the Bloch picture, namely, in terms of periodic arrays of localized atom-centered states (i.e., the Heitler-London picture in terms of Wannier orbitals). Nevertheless, there still exist states which will never benefit from the SIC. These states retain their itinerant character of the Bloch form, and move in the effective LSD potential. The resulting many-electron wave function will be a Slater determinant consisting of both localized and itinerant states. In contrast to the LSD Kohn-Sham equations, the SIC electron states, minimizing E^{SIC} in Eq. (1), experience different effective potentials. This implies that to minimize E^{SIC} it is necessary to explicitly ensure the orthonormality of the one-electron wave functions by introducing a Lagrangian multiplier matrix. Furthermore, the total energy is no longer invariant with respect to a unitary transformation of the one-electron wave functions. Both of these aspects make the energy minimization more demanding to accomplish than in the LSD case. The details of the present implementation can be found in Ref. 12.

III. RESULTS AND DISCUSSION

In this section we present the results obtained for the 26 Yb compounds studied using the SIC-LSD scheme outlined above. Section III A is devoted to trends in bonding properties and effective valencies, while Sec. III B describes details of the electronic structures of the Yb monopnictides.

A. Bonding and valencies

The calculated equilibrium volumes in the divalent and trivalent states are listed in Table I together with the experi-

TABLE I. Energy difference ΔE in mRy per Yb atom, between the nominal divalent and trivalent states of Yb compounds. A negative sign means that the trivalent state is favored. For the cases marked by an asterisk (*), the spin-orbit correction has not been included in the calculations, while for those cases not marked by an asteriks the spin-orbit coupling has been self-consistently included. Also listed are the computed effective valencies n_{eff}, the theoretical volumes in the two valency states V_{III} and V_{II}, and the experimental volume V_{expt} in a.u. per formula unit. The calculated ground-state volume is underlined to ease comparison with experiment.

Compound	ΔE	n_{eff}	V_{III}	V_{II}	V_{expt} [a]
YbN	-215.0	2.88	<u>184.8</u>	227	185
YbP	-117.0	2.69	<u>281.5</u>	362	289
YbAs	-109.0	2.63	<u>309.2</u>	381	312
YbSb	-18.2	2.53	<u>386.3</u>	432.3	379
YbBi*	-2.2	2.45	<u>413.2</u>	461.8	
YbO*	$+40.3$	2.00	181.1	<u>200.1</u>	196
YbS*	$+35.6$	2.00	267.0	<u>301.4</u>	309
YbSe*	$+38.1$	2.00	308.5	<u>345.4</u>	352
YbTe*	$+63.3$	2.00	397.6	<u>442.1</u>	434
YbPo*	$+68.2$	2.00	466.7	<u>513.4</u>	472
Yb	$+40.0$	2.00	212.5	<u>271.9</u>	278
YbRu*	-92.4	2.61	<u>248.0</u>	270.3	256
YbRh*	-33.6	2.54	<u>253.7</u>	291.1	253
YbIr*	-29.9	2.57	<u>249.5</u>	276.0	253
YbPd*	-10.5	2.49	<u>265.6</u>	285.0	275
YbAg*	$+14.7$	2.00	292.4	<u>324.5</u>	336
YbAu*	$+3.6$	2.00	286.1	<u>307.5</u>	311
YbZn*	$+13.9$	2.00	279.1	<u>327.4</u>	323
YbCd*	$+13.8$	2.00	324.7	<u>380.6</u>	373
YbIn*	$+37.4$	2.00	340.7	<u>370.4</u>	373
YbAl$_3$	-83.0	2.61	<u>466.2</u>	511.7	497
YbAl$_2^*$	-16.0	2.46	<u>376.0</u>	403.4	411
Yb$_3$Pd	$+24.2$	2.00	679.6	<u>776.2</u>	813
YbPd$_3$*	-66.0	2.54	<u>456.2</u>	475.1	444
YbPb$_3$	$+28.5$	2.00	714.9	<u>736.2</u>	776
YbBiPt*	-16.9	2.45	<u>497.4</u>	517.4	484 [b]

[a]Reference 13, except where noted.
[b]Reference 16.

mental volumes,[13] the calculated energy differences between the divalent and trivalent states, and the calculated effective valencies. The Yb compounds considered here can be divided into three groups, according to the size and sign of the energy difference between the divalent and trivalent states.

The group of strongly trivalent compounds comprises YbN, YbP, YbAs, YbRu, YbRh, YbIr, YbAl$_3$, and YbPd$_3$. For this group the trivalent configuration is favorable over the divalent configuration by more than 20 mRy per Yb atom. The effective valency ranges from 2.88 in YbN to 2.54 in YbRh and YbPd$_3$. In addition, the calculated equilibrium volumes for the trivalent configuration agree well with experimental volumes (within an average 2.2 % deviation). The worst case is represented by the YbAl$_3$ compound, for which the calculated equilibrium volume is 6% too low. By comparison, the calculated equilibrium volumes for the divalent Yb configurations are on average 14% too large for this group of compounds.

The second group consists of strongly divalent Yb compounds, encompassing the monochalcogenides YbO, YbS, YbSe, YbTe, and YbPo, as well as elemental Yb, Yb_3Pd, $YbPb_3$, and YbIn. Here the divalent Yb configuration is favored over the trivalent configuration by more than 20 mRy. Hence the effective valency is 2 for these compounds. In addition, the calculated volumes for the divalent configuration agree within an average 3.1% with the experimental volumes, whereas the equilibrium volumes for the trivalent state are too low by 11.2% on average. In this group, the worst case is YbPo, for which the calculated divalent volume is 9% larger than the experimental volume. The discrepancy is most likely due to the difficult experimental conditions.[14] In our calculations YbPo is the most distinctly divalent compound studied, and it is hard to see why this compound should behave differently from the other Yb monochalcogenides.

The remaining compounds are characterized by having the calculated energies of the trivalent and divalent Yb configurations equal within 20 mRy. Therefore, effects of valency fluctuations may start to be important. We have found, however, that the weakly divalent compounds, the intermetallics YbCd, YbZn, YbAg, and YbAu, are in fact well described by the divalent configuration, as evidenced by the agreement between the calculated and experimental volumes (an average deviation of 2%). Hence for these compounds there seems to be no need for an additional cohesive contribution originating from valence fluctuations. An interesting behavior may be expected when pressure is applied to these materials, since the trivalent state will then become more favorable. However, we are not aware of any pressure experiments carried out on any of these Yb intermetallics. Finally, the compounds YbSb, YbBi, YbBiPt, YbPd, and $YbAl_2$ are weakly trivalent, i.e., according to the calculations the trivalent state is favored by less than 20 mRy. Among these, YbBiPt and $YbAl_2$ are known heavy-fermion compounds,[16,17] and YbPd is believed to be a mixed-valent system, with approximately equal proportions of Yb^{2+} and Yb^{3+} ions.[18,19] YbBi has never been synthesized, while YbSb in most respects resembles the other predominantly trivalent Yb pnictides, though with a somewhat unusual low-temperature magnetic behavior.[15] Hence, for the compounds in this group, the valence fluctuation phenomena seem to be significant. The calculated effective valencies range from 2.53 in YbSb to 2.45 in YbBi and YbBiPt. The heavy-fermion character of YbBiPt was previously confirmed by local density approximation (LDA)+U calculations.[20]

We conclude that the valency classification of Yb compounds, based on the SIC-LSD total energies, maps very well onto the physical properties observed experimentally. In particular, in the third group of compounds this allows us to identify the heavy-fermion and mixed-valent systems on the trivalent side, and, on the divalent side, those systems which are likely to undergo pressure induced valence transitions. Note, however, that this division should not be interpreted too rigorously. For example, spin-orbit coupling, which was not included in some of the calculations presented in Table I, may lead to minor shifts in the energy balance between divalent and trivalent configurations. On the other hand, some overestimation of the bonding in the trivalent configuration
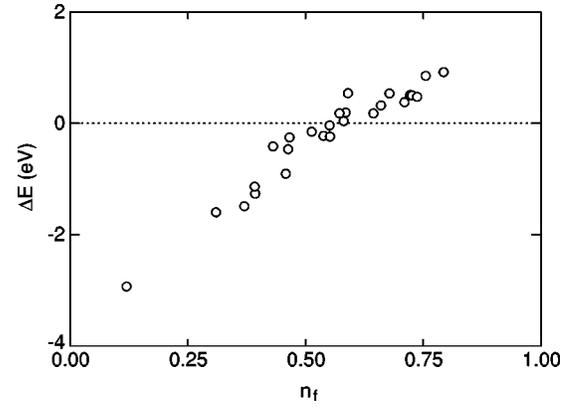
FIG. 1. Divalent-trivalent energy difference (in eV per Yb atom) of Yb compounds vs the number of band f electrons, n_f, in the trivalent configuration. A negative sign means that a trivalent state is favored.

may be explained by the general tendency of LSD to overbind (there being more ''normal'' band electrons in the trivalent Yb compounds).

The trends in effective valency and trivalent-divalent energy difference show some universal features, which are displayed in Fig. 1. Here the calculated energy difference is plotted against the occupancy of the narrow f band in the nominal trivalent state. All 26 compounds studied fall on the same curve, demonstrating that the valence energy balance is solely determined by the relative position of the narrow f band with respect to the other valence bands. When the f band lies relatively high, the f-band occupancy is low, and the divalent configuration is energetically very unfavorable, while when the f band lies relatively low, its occupancy is closer to 1, and the divalent configuration is more favorable. At a critical filling around 0.6 the energy balance tips, and for fillings above this number the ground state will be the ideal divalent configuration. The approximately linear relationship between the valence energy difference and the f-band occupancy can be rationalized by assuming that the major difference in electronic structure between the competing local minima of the SIC energy functional is a promotion of electrons on the Yb atom from non-f character to f character, when going from the nominal trivalent to the nominal divalent configuration. We may further assume that the cost of this promotion is a constant, $E(d \rightarrow f)$, *per electron* to be promoted. If the band occupancy in the trivalent calculation is n_f, the number of non-f electrons to be promoted is $1 - n_f$, and the energy difference becomes

$$-\Delta E \equiv E(II) - E(III) = (1 - n_f)E(d \rightarrow f) - \delta_f^{SIC}, \quad (3)$$

since once the entire f-electron has become occupied it gains the self-interaction energy [Eq. (2)] by localization. From Fig. 1 we may estimate the slope $E(d \rightarrow f) \sim 6$ eV. The self-interaction energy is $\delta_f^{SIC} = 1.5$ eV invariably in all Yb compounds, so that the above simple analysis would lead to a critical filling of $n_f \sim 0.75$, in reasonable agreement with the value of ~ 0.6 actually calculated.

The trends in bonding in the Yb intermetallic compounds are displayed in Fig. 2, which shows the chemical variations in trivalent-divalent energy difference. For 50-50 binary compounds, a marked dependency on ligand is seen in the
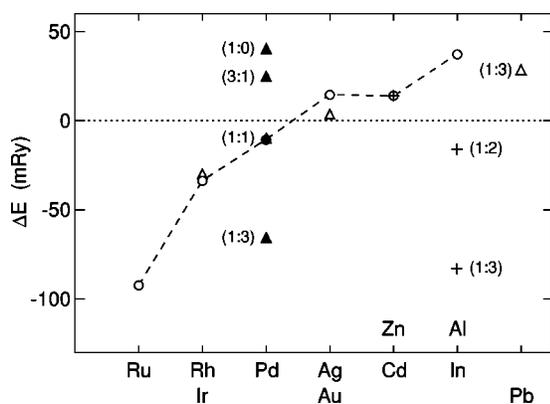
FIG. 2. Divalent-trivalent energy difference (in mRy per Yb atom) of Yb intermetallics. A positive energy means that the divalent configuration is favored. The sequence through the $4d$ series from Rh to In is shown with open circles and a dashed line to guide the eye. Triangles show results from the $5d$ series, and pluses results from the $3d$ series. Filled triangles are results for Pd compounds. For compounds of stoichiometry different from 50-50, the stoichiometry is given in parentheses with the Yb fraction quoted first. Yb metal is plotted as an $(1:0)$ Yb_1Pd_0 compound.

FIG. 3. Divalent-trivalent energy difference (in mRy) of Yb monopnictides (filled circles) and monochalcogenides (open circles). The triangle marks the YbBiPt ternary compound.

series with ligand $Z = 44-49$ (Ru-In, dashed line in Fig. 2). For Ru and Rh, which are far into the $4d$ transition series the f^{13} configuration of Yb is strongly favored because the 14th f electron lowers the overall energy by entering into the d bands, i.e., an $f \rightarrow d$ charge transfer occurs. In YbPd, the two valencies are almost degenerate, while in the alloys with normal sp elements, Cd and In, the divalent state is favored. Alloys with the $5d$ elements Ir and Au as well as the $3d$ element Zn follow roughly the same curve.

For the three $(1:3)$ compounds $YbPd_3$, $YbAl_3$, and $YbPb_3$, the trivalent configuration is favored in $YbPd_3$ and $YbAl_3$, while the divalent state is the ground state of $YbPb_3$. This can be explained as a volume effect, since the atomic volumes of Pd and Al metal are much smaller than that of Yb metal, so that Yb in $YbPd_3$ and $YbAl_3$ is subject to a large lattice pressure, converting the Yb ion into a trivalent ion. Decreasing the Al concentration in going from $YbAl_3$ to $YbAl_2$ leads to a less stable trivalent Yb configuration. The 50-50 compound YbAl does not exist, but assuming it to form in the CsCl structure we have found that this compound would still be on the nominally trivalent side, albeit with only 8 mRy lower energy than in the divalent configuration.

Figure 2 also shows the trends of the Yb divalent-trivalent energy difference for Pd alloys with various Yb concentrations. In Yb_3Pd, as in pure Yb metal, the f^{14} configuration is favored, while in the Pd-rich case $YbPd_3$, the trivalent f^{13} configuration is most favorable. The 50–50% alloy is in between, according to calculations favoring the trivalent state with moderately 10.5 mRy. This energy difference of only 10.5 mRy between divalent and trivalent Yb in YbPd could plausibly indicate that within the accuracy of the SIC-LSD method these states could be degenerate. Experimentally, YbPd is found to be mixed valent, with a fraction around 35% (Ref. 18) or 52% (Ref. 19) of Yb(3+) ions. The Mössbauer experiment gives evidence for YbPd being heterogeneously mixed valent[19], since the recorded spectrum reveals coexistence (in approximately equal proportions) of the f^{13} and f^{14} configurations of Yb. We have tried to model
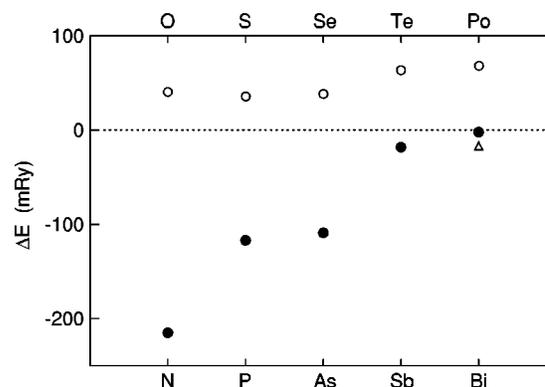
this situation by computing the energy of a Yb_2Pd_2 supercell. Since YbPd has a CsCl structure, the Yb sublattice is bipartite, and we can make an ordered $Yb(f^{13})Yb(f^{14})Pd_2$ compound. However, we find no energy gain associated with this arrangement, although the calculated equilibrium volume for the $Yb(f^{13})Yb(f^{14})Pd_2$ case coincides with the experimental value. The energy is to a good approximation additive, i.e., as a function of volume the energy of the $Yb(f^{13})Yb(f^{14})Pd_2$ system is just the sum of the energy of $Yb(f^{13})Pd$ and $Yb(f^{14})Pd$.

In short, from Fig. 2 we see that the SIC-LSD method is successful in describing the chemistry of Yb compounds, and in particular the energy balance associated with f-electron localization on the scale of the chemical and volume effects in these materials. This is further corroborated by the trends of the energy difference between the divalent and trivalent states of the Yb monopnictides and monochalcogenides depicted in Fig. 3. For the pnictides a strong tendency toward the trivalent Yb configuration is seen in the early pnictides, dropping to almost zero for YbSb and YbBi. In fact, we may speculate that the reason that YbBi has never been synthesized in the solid state could be due to the trivalent configuration no longer being stable in this compound. When Pt is introduced on every second interstitial site, the ternary compound YbBiPt is formed, for which Yb is found to be weakly trivalent, i.e., the addition of Pt stabilizes the trivalent configuration. The strong tendency toward trivalency in the earlier pnictides can be understood by the electronegativity of the pnictide, by which pnictide p bands are filled by Yb donating three electrons. YbN is the most trivalent compound studied, but even in this case the band of the 14th f electron falls at the top of the N p band, leading to a high density of states at the Fermi level. In YbN this band is filled by 0.12 electrons, while in YbP and YbAs this band is filled with 0.31 and 0.37 electrons, respectively. Experimentally, the position of the f^{14} band is found ~ 0.2 eV above the Fermi level in YbN, YbP, and YbAs.[21] Other experiments revealed heavy-electron behavior in Yb pnictides,[22] but this can be a reflection of sample nonstoichiometry.[21] The discrepancy between the present electronic structure and the picture provided by Ref. 21 can be due to the LSD approximation, since the position of the narrow f^{14} band in the theory is solely determined by the LSD potential (no SIC). In a more complete treatment some correlations beyond the

FIG. 4. Valence-band density of states of YbN, YbP, YbAs, and YbSb. Units are states/eV per unit cell. The zero of the energy axis coincides with the Fermi energy.

too low positioning of the *f* band does not affect the bonding too much, since the calculated equilibrium volumes are quite accurate in YbN, YbP, and YbAs.

For Yb chalcogenides, the divalent state is seen to be favored in all cases, by $\sim 35-70$ mRy. In these cases, two Yb electrons are needed to fill the ligand *p* band, while no particular favorable itinerant state is available for a possible third Yb valence electron, which therefore localizes and completes the f^{14} shell.

B. Electronic structure of Yb monopnictides

Figures 4(a)–4(d) show the density of states for YbN, YbP, YbAs, and YbSb in the nominal trivalent state (assuming a ferromagnetic ordering for simplicity). One notes the pnictide *p* bands, which are intersected at the top by the narrow *f* band, which pins the Fermi level. Hence a few holes in the P *p* bands occur, while some (heavy) *f* electrons are present right at the Fermi level. These plots show that the Fermi energy moves progressively into the *f* peak as the ligand *p* states move up in energy in going from N to P to As to Sb. As this happens the compounds become less and less trivalent, and for YbSb the energy balance in favor of trivalency is less than 10% of that for YbN. These densities of states provide a simple chemical picture that can be associated with the trend in the valence energy difference of trivalent Yb monopnictides.

IV. CONCLUSIONS

The self-interaction-corrected local-spin-density approximation has been used to describe the electronic structure of Yb compounds. This approximation allows for a description with either a completely localized f^{14} shell on the Yb atom or a partially occupied (in practice f^{13}) localized shell with the remaining *f* degrees of freedom available for band formation. The two configurations constitute two competing minima. The trends in valency of Yb systems are reproduced spanning from the most trivalent YbN compound to the most divalent Yb compounds, which are the Yb chalcogenides. The equilibrium volumes are generally calculated accurately, demonstrating that the bonding properties of Yb systems are well accounted for by the present scheme.

In nominally trivalent cases, where a localized f^{13} shell is assumed, the 14th *f* state appears as a narrow band in the conduction states, and the relative stability of the valence configurations is determined by the degree of filling of this band. When the filling exceeds a critical value of 0.6 the ideal divalent configuration becomes the lowest in energy. Consequently, the effective valency of Yb compounds is either exactly 2 or higher than 2.4. The generally good description of bonding properties that we obtain means that compounds with a valency close to 2 are well represented by the ideal divalent configuration corresponding to a localized f^{14} shell, while compounds with Yb valency significantly higher than 2 are well represented by a localized f^{13} shell together with a partially filled, uncorrelated *f* band.

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LSD should be invoked for these band *f* states. Such correlation effects would lead to a repulsive potential, since the LSD generally overestimates the self-exchange for partially filled narrow bands. We note that, apparently, this slightly

[1] P. Wachter, *Handbook on the Physics and Chemistry of Rare Earths* (North-Holland, Amsterdam, 1993), Vol. 19, Chap. 132.

[2] En-Jin Cho, J.-S. Chung, S.-J. Oh, S. Suga, M. Taniguchi, A. Kakizaki, A. Fujimori, H. Kato, T. Miyahara, T. Suzuki, and T. Kasuya, Phys. Rev. B **47**, 3933 (1993).

[3] J. J. Joyce, A. B. Andrews, A. J. Arko, R. J. Bartlett, R. I. R. Blythe, C. G. Olson, P. J. Benning, P. C. Canfield, and D. M. Poirier, Phys. Rev. B **54**, 17 515 (1996).

[4] P. Bonville, J. A. Hodges, F. Hulliger, P. Imbert, G. Jéhanno, J. B. Marimon da Cunha, and H. R. Ott, J. Magn. Magn. Mater. **76&77**, 473 (1988); A. Dönni, P. Fischer, A. Furrer, and F. Hulliger, Solid State Commun. **71**, 365 (1969); A. Dönni, P. Fischer, A. Furrer, W. Basca, and P. Wachter, Z. Phys. B: Condens. Matter **80**, 269 (1990); A. Dönni, A. Furrer, P. Fischer, F. Hulliger, P. Wachter, and H. R. Ott, J. Magn. Magn. Mater. **90&91**, 143 (1990); L. Keller, P. Fischer, A. Furrer, A. Dönni, D. X. Li, and T. Suzuki, Physica B **186-188**, 553 (1993).

[5] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. A **140**, 1133 (1965); R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989).

[6] W. M. Temmerman, Z. Szotek, A. Svane, P. Strange, H. Winter, A. Delin, B. Johansson, O. Eriksson, L. Fast, and J. M. Wills, Phys. Rev. Lett. **83**, 3900 (1999).

[7] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[8] A. Svane and O. Gunnarsson, Phys. Rev. Lett. **65**, 1148 (1990); Z. Szotek, W. M. Temmerman, and H. Winter, Phys. Rev. B **47**, 4029 (1993).

[9] Z. Szotek, W. M. Temmerman, and H. Winter, Phys. Rev. Lett. **72**, 1244 (1994); A. Svane, *ibid.* **72**, 1248 (1994).

[10] A. Svane, W. M. Temmerman, Z. Szotek, H. Winter, Solid State Commun. **102**, 473 (1997); A. Svane, Z. Szotek, W. M. Temmerman, J. Lægsgaard, and H. Winter, J. Phys.: Condens. Matter **10**, 5309 (1998); A. Svane, W. M. Temmerman, and Z. Szotek, Phys. Rev. B **59**, 7888 (1999).

[11] P. Strange, A. Svane, W. M. Temmerman, Z. Szotek, and H. Winter, Nature (London) **399**, 756 (1999).

[12] W. M. Temmerman, A. Svane, Z. Szotek, and H. Winter, in *Electronic Density Functional Theory: Recent Progress and New Directions*, edited by J. F. Dobson, G. Vignale, and M. P. Das (Plenum, New York, 1998.), p. 327.

[13] P. Villars and L. D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, 2nd ed. (ASM International, Materials Park, OH, 1991).

[14] C. J. Kershner, R. J. De Sando, R. F. Heidelberg, and R. H. Steinmeyer, J. Inorg. Nucl. Chem. **28**, 1581 (1966).

[15] A. Oyamada, K. Hashi, S. Maegawa, T. Goto, D. X. Li, T. Suzuki, A. Dönni, and F. Hulliger, Physica B **199&200**, 42 (1994); T. Kasuya, J. Phys. Soc. Jpn. **63**, 843 (1994); D. X. Li, A. Oyamada, K. Hashi, Y. Haga, T. Matsumara, H. Shida, T. Suzuki, T. Kasuya, A. Dönni, and F. Hulliger, J. Magn. Magn. Mater. **140-144**, 1169 (1995).

[16] R. A. Robinson, A. Purwanto, M. Kohgi, P. C. Canfield, T. Kamiyami, T. Ishigaki, J. W. Lynn, R. Erwin, E. Peterson, and R. Movshovich, Phys. Rev. B **50**, 9595 (1994).

[17] E. E. Havinga, K. H. J. Buschow, and H. J. van Daal, Solid State Commun. **13**, 621 (1973).

[18] A. Iandelli, G. L. Olcese, and A. Palenzona, J. Less-Common Met. **76**, 317 (1980).

[19] P. Bonville, J. Hammann, J. A. Hodges, P. Imbert, and G. J. Jéhanno, Phys. Rev. Lett. **57**, 2733 (1986).

[20] P. M. Oppeneer, V. N. Antonov, A. N. Yaresko, A. Ya. Perlov, and H. Eschrig, Phys. Rev. Lett. **78**, 4079 (1997).

[21] L. Degiorgi, W. Bacsa, and P. Wachter, Phys. Rev. B **42**, 530 (1990); L. Degiorgi, S. Teraoka, G. Compagnini, and P. Wachter, *ibid.* **47**, 5715 (1993).

[22] H. R. Ott, H. Rudigier, and F. Hulliger, Solid State Commun. **55**, 113 (1985); T. Sakon, N. Sato, A. Oyamada, N. Takeda, T. Suzuki, and T. Komatsubara, J. Phys. Soc. Jpn. **61**, 2209 (1992); N. Takeda, K. Tanaka, M. Kagawa, A. Oyamada, N. Sato, S. Sakatsumi, H. Aoki, T. Suzuki, and T. Komatsubara, *ibid.* **62**, 2098 (1993).