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Supercell calculations of the valence photoemission spectra of CeSb, PrSb, and NdSb

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Photoemission spectra, as calculated using a transition-state analysis within a supercell approach, are found to be in good agreement with experimental data for both PrSb and NdSb. The model assumes localized f electrons in the ground state and a localized f photohole in the final state. By comparing these results to previous ones for CeSb, we determine how the photoemission peak due to f emission moves further away from the Fermi energy for higher Z. Finally, we predict where a second f feature might be seen if resonant photoemission were done on these two compounds.

I. INTRODUCTION

Photoemission spectra in rare-earth compounds are now yielding a large amount of information about the behavior of their $4f$ electrons which questions current theoretical understanding of these systems. Previously, we discussed the origin of the two-peak structure due to f emission seen in the valence photoemission spectra of cerium and many of its compounds.[1,2] By assuming two different final states, an f-screened f hole and a d-screened f hole, the photoemission spectra were calculated for several of the cerium pnictides that were in good agreement with experiment. In particular, an f peak near the Fermi energy (f-screened hole) and another about 2.5 eV below the first (d-screened hole) were found. The same method was also applied to explain the two-peak structure seen in bremsstrahlung isochromat spectroscopy (inverse photoemission).[3]

Recently, Parks *et al.*[4] and Wieliczka *et al.*[5] noticed that the two-peak structure present in cerium systems also appeared in Pr and Nd systems, but the structures there were further removed from the Fermi energy. This seems to rule out a Kondo explanation for the upper peak since in that model such a feature is inherently tied to the Fermi energy. It is, therefore, of some interest to see whether the approach followed for the Ce compounds would explain the Pr and Nd pnictides in the same manner as it did the Ce pnictides. Since photoemission data exist on PrSb and NdSb (unfortunately, not resonance data), we decided to study these two systems.

II. CALCULATIONAL PROCEDURE

The ground state of each compound was determined by performing a standard local-density band calculation using the self-consistent warped-muffin-tin linearized augmented-plane-wave method in a semirelativistic approximation with a perturbative spin-orbit correction.[2] Since one expects the f electrons to be localized in PrSb and NdSb, the f electrons were treated as $j=\frac{5}{2}$ states in an overlapping (nonfrozen) core model.[6] We emphasize that this is a departure from standard density-functional theory. In particular, it is being assumed that the charge density is not just a sum of squares of Bloch wave functions, but a sum of squares of non-f Bloch wave functions plus a sum of squares of localized f wave functions. We believe that this is a more proper description of the localized electrons. In particular, the exact density-functional theory for these compounds should predict localized f levels with integer occupations, or else a separation of the f levels from the Fermi energy would not be possible using Fermi-Dirac statistics. A full exchange-correlation potential was used, the correlation part being that of von Barth and Hedin (vBH).[7] Some calculations were also performed with an exchange-only, or Kohn-Sham (KS) potential; the differences due to choice of potential will be elaborated on below. We shall also contrast the results obtained for CeSb when treating the f electrons as itinerant or localized in the ground state.

As discussed extensively in our examination of the series of Ce pnictides,[2] the localized nature of the excitation precludes the straightforward use of ground-state eigenvalues to determine the excitation spectrum. One must determine the total energy difference between the ground and excited state. This can be done using as a basis a transition-state analysis which must be applied specifically to each case.

Having noted that one generally cannot use the ground-state eigenvalues, we first consider the fully screened final state (the f-screened hole) which can be approximately described using the ground-state eigenvalues. The essential idea is that the screening charge is sufficiently close to the charge removed by the excitation that the energetics of the system is essentially that of the effective one-particle eigenvalue. More precisely, we use the idea that the occupation-number derivative of the total energy is this eigenvalue, $dE/dn=\epsilon$, and ϵ is essentially unchanged because of the nature of the screening. Thus, the eigenvalue ϵ is equal to the integral of dE/dn for a change of one in the excitation charge which is just the change in total energy, i.e., it is the excitation energy. If the f states are then assumed to be localized, this energy can fall below the Fermi energy even though not all of the f levels are occupied. This occurs because the eigenvalue is a local derivative of the total energy and the significant factor in determining the occupation of states is the change in energy for a complete change of occupation by unity. Viewed as a series of incremental changes, the eigenvalue of this localized state will rise with increased occupation such that by the time the occupation of the level is increased by one the level is above the Fermi energy. The total energy is then higher with the additional electron placed in the local states than if it is placed in the conduction states at the Fermi energy even though the ground-state eigenvalue is below the Fermi energy. Note that this will occur only if the bandwidth of the local levels has collapsed such that one can only have an integral change of occupancy. If a partial occupancy of those levels is possible, they will be pinned to the Fermi energy with some fractional occupancy. Thus, the ground-state f levels must be fully decoupled from the conduction bands. The apparent dilemma that one must have coupling to the f levels to achieve f screening is easily resolved by noting that such coupling can and will occur in excited states reached by the excitation process.

The other relevant final state—the d-screened hole—does require a more involved analysis. For the d-screened hole, a calculation is performed on a large unit cell (eight atoms in the case of the pnictides) where the central rare-earth site is constrained to have an f hole. Since the f electrons are treated as localized, this is trivially done by reducing the occupation number of the f electrons by one on that site. Although this hole is periodically repeated, the separation of the holes is sufficiently large that hole-hole interactions are small. The supercell impurity hole state is then allowed to relax via self-consistent cycling, resulting in d screening of the hole. The full procedure is discussed in detail in Ref. 2. The final result is an eigenvalue for the f hole. To find the position of the f emission peak for the d-screened process we use a modified Slater transition-state technique:

$$\epsilon(\mathrm{TS})=[\epsilon(1)+\epsilon(0)]/2 ,$$

where $\epsilon(1)$ is the ground-state f eigenvalue and $\epsilon(0)$ is the eigenvalue of the f hole. The photoemission spectra are modeled by fitting Lorentzians to $\epsilon(1)$ (f-screened hole) and $\epsilon(\mathrm{TS})$ (d-screened hole), which are then combined with a Gaussian-broadened density of states obtained from the band calculation.

III. RESULTS

Table I shows the calculated peak positions for PrSb and NdSb using a full exchange-correlation (vBH) potential compared to their experimental values. A represents the f-screened hole, B the main peak in the Sb valence band, C the shoulder in the Sb valence band, and D the d-screened hole. Also shown are the results for CeSb, the first being our previous calculation [using an exchange-only (KS) potential] where the f electrons were treated as extended states in the ground state[2] plus two new calculations where the f electrons were treated as localized—one with a KS potential and the other with a vBH potential. The shoulder, peak C, is not seen in CeSb since it is masked by the screened-hole peak (D). The Expt.* columns represent shifting the experimental positions by a constant so that the Sb valence band (peak B) lines up with the theoretical prediction. This shift is 0.3 eV for PrSb and 0.0 eV for NdSb, indicating that there was probably a slightly incorrect experimental assignment of the Fermi energy for PrSb (the experimental resolution was 0.55 eV full width at half maximum). As can be seen, there is excellent agreement between experiment and theory for the two cases. The values for peak A constitute a prediction as to where an f-screened hole might be seen in these compounds if resonant photoemission is

TABLE I. Experimental and theoretical positions for the valence-band spectral peaks in CeSb, PrSb, and NdSb with respect to E_F (eV). A is the f-screened f hole, B is the main Sb p peak, C is the Sb p shoulder, and D is the d-screened f hole. KS stands for exchange—only and the vBH for von Barth—Hedin exchange-correlation potentials. The Expt.* values are shifted so that the Sb peak B lines up.

		PrSb (local)			NdSb (local)	
Peak	Expt.[a]	Expt.*	Theor. (vBH)	Expt.[a]	Theor. (vBH)	
A	?	?	−0.95	?	−2.95	
B	−2.1	−1.8	−1.8	−1.9	−1.9	
C	−3.4	−3.1	−2.9	−3.1	−3.1	
D	−4.7	−4.4	−4.4	−5.7	−5.75	

		CeSb (extended)			CeSb (local)	
Peak	Expt.[b]	Expt.*	Theor. (KS)	Expt.[b]	Theor. (vBH)	Theor. (KS)
A	−0.6	−0.05	−0.05	−0.6	−0.35	+0.10
B	−2.15	−1.6	−1.6	−2.15	−2.15	−2.15
D	−3.1	−2.55	−2.8	−3.1	−3.55	−3.1

[a] Reference 17.
[b] Reference 18.

done to enhance that feature. It is quite possible, however, that the *f* electrons are so localized in the ground state that the intensity of this feature might be too small to resolve; experiments are being planned to test this prediction.[8]

CeSb is a more difficult system. In Table I, the first column presents results of the previous calculation[2] where the *f* states were treated as Bloch states in the ground state. As can be seen, a 0.55-eV shift is needed to get the Sb valence peak (peak *B*) to line up. It was speculated in Ref. 2 that this might be due to the fact that experimentalists place the Fermi energy near the upper edge of peak *A* instead of close to the centroid as the calculation suggests is appropriate (see Fig. 1 for the CeSb results). When this shift is applied, peak *A* now lines up, but peak *D* overshoots by 0.25 eV. It was also speculated in Ref. 2 that this might be due to the fact that 1.07 *f* electrons were found in the ground state so that possibly too much *f* charge was removed in the excited state (the eigenvalues in the local-density approximation are highly sensitive to occupation number). Also, when a linear correction is made for that removal of one *f* electron, the results are then brought into excellent agreement. Because a single electron was found for CeP, this problem did not exist and the results were much better. To probe further this limitation of the previous results and to explore the effect of using a local-orbital approach, CeSb calculations treating the *f* electrons as localized in the ground state (with an occupation number of 1) were performed. The results are shown in the next two columns of Table I. It is seen

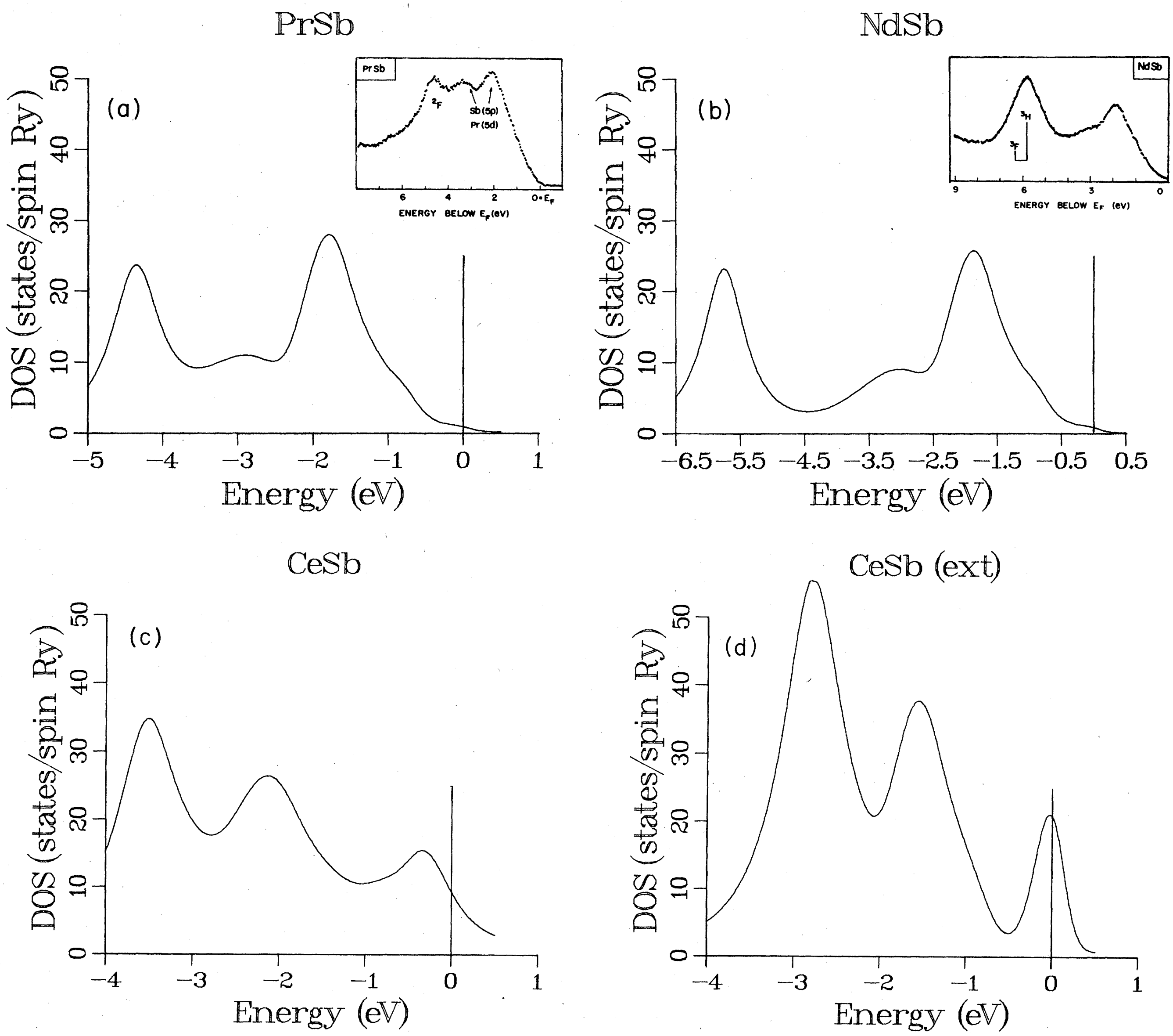

FIG. 1. Local *f* spectra for CeSb, PrSb, and NdSb using a vBH potential. CeSb (ext) is the spectrum obtained when the *f* electrons are treated as extended in the ground state using a KS potential.

that in the local f case, no shift is needed to get the valence-band peak B to line up but, for the vBH potential which worked very well for PrSb and NdSb, there is an overshoot of 0.45 eV for peak D and an undershoot of 0.25 eV for peak A. In other words, the separation of the two f emission peaks overshoots by a full 0.7 eV. The effect of reducing the correlation by using the KS potential is to shift both f emission features up to 0.45 eV, yielding the same separation between the peaks with peak D lined up with experiment, but peak A above the Fermi energy.

In Fig. 1, we show the vBH spectra for CeSb, PrSb, and NdSb with the f states treated as local plus the CeSb spectrum with the f electrons treated as extended. These spectra were formed by taking the calculated density of states and Gaussian broadening with an instrument broadening factor of 0.2 eV, temperature broadening with $T=0.025$ eV, and including a lifetime broadening factor $a(e-E_F)^2$ where E_F is the Fermi energy and a is set at 0.05 eV^{-1} (see Ref. 9). To this was added a Lorentzian of width 0.4 eV centered at the position of the d-screened hole for the local f CeSb spectrum (in the extended spectrum, of course, the ground-state f levels are hybridized with the other states and are thus already included). For the most part, the spectra agree rather nicely with experiment. The discrepancies are discussed in the next section.

IV. DISCUSSION

We need to touch on several points now. First, we need to analyze the trend in the f emission features as one proceeds from CeSb to PrSb to NdSb. We see that the separation of the f emission features is not constant, but still does not vary too much (note that there is no correlation between the separation and atomic number). We do see, however, a dramatic drop in the absolute positions of these peaks as one proceeds from CeSb to PrSb to NdSb, just as was observed by Parks *et al.*[4] and by Wieliczka *et al.*[5] In fact, the positions of our peaks are in the same general energy range as found in Ref. 4 for a variety of Pr and Nd compounds. Theoretically, this result may be extremely important since this means that even for localized states, the local-density ground-state eigenvalues may have physical meaning as fully screened eigenvalues. This finding should not be hard to accept since the major error in local-density eigenvalues is the self-interaction error,[10] and full screening should be equivalent to compensating for the self-interaction error. Of course, full screening is equivalent to the f hole hopping off the site via coupling to the Sb p states. In fact, this explains why Parks *et al.*[4] see such a huge dispersion in the upper peaks (f-screened hole) in the various Pr and Nd compounds. If the f-screening electron originates from the Fermi energy, one would expect to see a sharp peak at the Fermi energy. Since this is not observed, the f screening occurs via coupling to the ligand p band (or d band for the transition-metal ligands). Since such a band is wide and has its main weight a few eV below the Fermi energy, the resulting f-screened feature is smeared out (although it is energetically centered about the position of the ground-state f eigenvalue). One can in fact see this if one attempts to simulate the excitation by using the model of Gunnarsson and Schonhammer.[11] In this model, one couples a localized f level to a valence band of a desired shape via an Anderson Hamiltonian. One sees that by adjusting parameters, the f-screened feature can be pulled down below the Fermi energy resulting in a large smearing out of that feature.[12] This model seems to simulate Pr spectra fairly well, but whether it will work as well for Nd systems where the f-screened feature is a full 3 eV below E_F remains to be determined.

We now analyze the effect of choosing a particular potential. The effect of von Barth—Hedin correlation was seen to bring the f levels down by 0.45 eV relative to the KS results for CeSb both in the ground and excited state. Other correlation potentials should yield similar results. This is exactly the same shift as was found for the unoccupied f states in LaN,[13] and was also found for the ground-state calculations performed on PrSb. From Table I, we see that by using the vBH potential, we were able to get good results in PrSb and NdSb for the peak-D to peak-B separation. This means that we would have been half a volt off had we not included the fuller vBH correlation. One can contrast this to the case where the f electrons are treated as extended in the ground state. In that case, correlation would have little effect on the ground state, since if the f levels dropped in energy, the f occupation would go up resulting in an enormous Coulomb correlation effect (note that in the local calculations, the f occupation is frozen). This has been verified for $\mathrm{CeSn_3}$ where additional correlation had virtually no effect on the Fermi-surface topology.[14] This result implies that the peak separation between the d- and f-screened holes would be larger with the inclusion of correlation since in the excited state, the occupation number is frozen at an integer value and thus the f level will drop with inclusion of correlation. (As mentioned above, in the localized-f calculations, the peak separation remained the same.)

The final question to ask is the role and treatment of localized versus extended f states. In CeN, it was necessary to treat the f states as band states to get a specific heat in agreement with experiment, as well as to obtain a spectrum to agree with experimental photoemission data.[15] On the other hand, in PrSb and NdSb, it was completely necessary to treat the f states as localized in the ground state to get peak A to separate significantly from the Fermi energy. As can be seen from Table I, it seems hard to choose whether the local or extended calculation gives better results in the case of CeSb. In favor of the extended-f-electron calculation is the fact that the f-peak separation overshoots experiment by the smaller 0.25 eV as compared to 0.7 eV for the local calculation—although it must be remembered that the inclusion of correlation for the extended calculation would lead to a larger overshoot. In favor of the local f electron calculation is the experimental Fermi energy need not be shifted to get the experimental and theoretical valence bands to line up—although this in turn should be tempered by the fact that as can be seen in the figures, the theoretical Fermi energy is closer to the centroid of peak A than the standard experimental assignment. The situation is further complicated by the fact that our itinerant f calculations do not give precisely $\delta n_f = 1$. To shed some further light on this question, we have also performed local f electron calculations for the ground state of CeP with f occupation numbers of 0.93 and 1.00. From the results obtained it appears that the extended calculation does a better job for CeP than does either of the two local calculations. Perhaps the analysis of new optical data will provide a better clue to the nature of the f electrons in the paramagnetic phases of these systems,[16] since the truth may lie in between the two extremes presented.

Finally, we should comment on the spectra themselves. To begin with, the relative height of the Lorentzian for the localized f levels with respect to the Gaussian broadened density of states was simply set at some arbitrary value. It is of some importance to find a way to calculate such a value from first principles. Next, we need to comment on the valence-band shoulder, peak *C*. In NdSb, this shoulder agrees rather well with experiment, both in its small height and in its position. In PrSb, however, this shoulder differs by 0.2 eV from experiment and the calculation shows that it is as weak as its NdSb counterpart, whereas experimentally the shoulder has a rather large intensity. This might indicate that the valence-band density of states and the (f) peak *D* should be broadened more than we have done, although this would probably smear out the shoulder completely. Again, resonance data and better resolution would be helpful in clarifying this part of the spectrum.

In conclusion, good agreement between experiment and theory for PrSb and NdSb gives substantial support to the screening mechanisms assumed in carrying out these calculations. It should be emphasized that these are unadjusted impurity-like calculations using standard local-density potentials, which for localized excitations makes the good agreement with experiments even more remarkable. In fact, it seems that for localized levels, the local-density ground-state eigenvalues have physical meaning as fully screened eigenvalues. Finally, it is interesting to note that the inclusion of full correlations (say, via vBH potentials) yields correct absolute positions for the f peaks.

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