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Supercell calculation of the bremsstrahlung isochromat spectrum of cerium phosphide

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The supercell technique with a local-density potential as described in the preceding paper is used to calculate the inverse photoemission spectrum of cerium phosphide. The results yield a double-peaked structure due to f states with one peak at 0.4 eV and another peak at 4.4 eV above the Fermi energy. Although bremsstrahlung isochromat spectroscopy has not yet been applied to CeP, the theoretical spectrum is very similar to experimental spectra of other cerium compounds. The peak at 0.4 eV is interpreted as a "fully relaxed" peak where the final state closely approximates the ground state (i.e., the f electron hops off the site involved). The second peak at 4.4 eV is due to a localized $f^1 \rightarrow f^2$ transition with associated repulsion of d charge off that site (antiscreening).

INTRODUCTION

Much interest has been generated by the two-peak feature due to f emission present in the photoemission spectra of cerium and many of its compounds.[1] In the preceding paper we have applied supercell techniques utilizing a standard local-density potential to calculate the photoemission spectra of three of the cerium pnictides.[2] The results yield spectra in good agreement with experiment. The peak at 3 eV below the Fermi energy (the so-called poorly screened peak) was derived by simulating a d-screened f hole. The peak near the Fermi energy was derived from an ordinary band calculation and interpreted as an f-screened f hole.

A similar two-peak structure is seen in the inverse photoemission [bremsstrahlung isochromat spectroscopy (BIS)] spectra of cerium[3] and several of its compounds[4] (in a BIS experiment, one adds an electron to the system). The first peak is just above the Fermi energy (~ 0.5 eV) and is dominant in the more "itinerant" cerium compounds.[4] The second peak is located 4–5 eV above the Fermi energy and is due to localized $f^1 \rightarrow f^2$ transitions.[3,4] The BIS spectrum in certain ways thus mirrors what is seen in the photoemission spectrum. With this in mind, it was decided to apply the techniques of the preceding paper to determine the inverse photoemission spectrum of CeP. CeP was chosen since the experimental spectrum for that compound will hopefully be determined in the near future.[5]

CALCULATIONAL PROCEDURE

The use of supercell technique to calculate the photoemission spectra of cerium compounds has been extensively discussed in the preceding paper. A similar scheme can be used to calculate the inverse photoemission spectra. Here, a brief discussion of the supercell technique is given with emphasis on the changes needed to calculate the BIS spectra. Basically, we assume the f states are itinerant in the ground state (this is not necessary for the technique *per se*, but we feel it is appropriate for the model we wish to explore). We thus performed a self-consistent band calculation using the LAPW method with a local-density potential. We use the exchange-only approximation as electron gas correlation functionals are thought to be inappropriate for f electron systems.[6] The ground state should be equivalent to a "fully relaxed" final state of the photoemission or inverse photoemission process, and thus we use the f-band partial density of states from the band calculations as an approximation for the peak near the Fermi energy. To describe the other peak, we perform a band calculation but on a large unit cell (eight atoms for the cerium pnictides as opposed to two for the ground-state calculation). As described in the preceding paper, the excited state for the photoemission was obtained by not allowing any f occupation on the central cerium site. This simulates the f hole. Although the f hole is periodically repeated, the separation of f holes is sufficiently large not to affect things very much. The system was then allowed to relax resulting in d screening of the hole.

A similar procedure can be used to obtain the second peak in the BIS spectrum. Since this peak is supposedly due to a localized f bound state, we simulate this with the same supercell calculation as above (in other words, depopulate all f character inside the central Ce site by raising the $l=3$ LAPW energy parameter up into the $5f$ energy region as described in the preceding paper), but placing two f electrons in the "core" on the central site. By this we mean that the f electrons are treated as site localized (i.e., they are not allowed to hybridize), but in all other ways they are treated normally (i.e., they were not frozen). In fact, these f states were treated as $j=\frac{5}{2}$ states in an overlapping core model.[2] Once self-consistency was achieved, the final iteration was rerun setting the $l=3$ energy parameter back into the $4f$ energy region for the central site. This is done to see where the "unoccupied" f states lie in the new potential. The differences between these unoccupied eigenvalues and the supercell Fermi energy are taken, and the results divided by two. This yields the appropriate transition state values to be used in constructing the supercell contribution to the BIS spectrum.

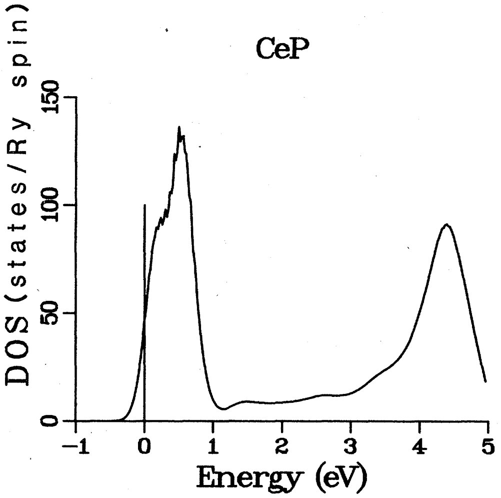

FIG. 1. Calculated BIS spectrum for CeP. This was formed by combining the unoccupied band density of states with the unoccupied f density of states for the supercell Ce central site as described in the text. The Fermi energy is at zero. A Gaussian broadening factor of 0.2 eV was employed as well as a temperature broadening factor of 0.025 eV.

RESULTS

In Fig. 1 the combined spectrum is shown. This is obtained by taking the unoccupied density of states from the band calculation and adding in the unoccupied f density of states inside the central muffin tin for the supercell (this latter is found as described in the last few sentences of the preceding section). We see a two-peak structure with the peak at 0.4 eV above the Fermi energy coming from the band calculation and the peak at 4.4 eV coming from the supercell calculation. The state forming the peak near the Fermi energy are largely pure f with some d admixture from both Ce and P sites. The states from the upper peak contain a good bit of hybridization with d character on the Ce and P sites as well as p character on the phosphorus sites, although only the f character inside the central Ce muffin tin was used to construct the upper peak in Fig. 1. In Table I angular momentum decompositions of the charge for the band calculation and the supercell calculation are compared. One sees an enhancement of p character inside the central Ce muffin tin. This is because the semicore Ce $5p$ states have risen over 5 eV in response to the now more repulsive core and have begun to hybridize more with the valence states. We also see significant depletion of d character out of the central site as expected. There is a slight depletion of the p character inside the nearest-neighbor phosphorus sites as well as f character on the other cerium sites. Part of this effect is due to the fact that the electron filling factor for the valence states in the supercell has been reduced from 28 to 26 to accommodate two f electrons in the "core." Also in Table I are total charges inside and outside the muffin tins. As can be seen, there is a significant reduction of interstitial charge in the supercell.

TABLE I. Angular momentum charge decompositions inside the muffin-tin spheres as well as total charges for the band and the BIS supercell calculations. A lattice constant of 11.15 a.u. and the muffin-tin radii of 3.025 (Ce) and 2.550 (P) were employed. Ce(1) is the modified Ce site, Ce(2) the other three equivalent Ce sites, P(1) are the three equivalent P sites which border Ce(1), and P(2) is the odd phosphorus site. The interstitial charge for the band calculation was multiplied by four since there are four formula units within the supercell.

		Band	Supercell
Ce(1)	s	0.13	0.10
	p	0.17	0.25
	d	1.04	0.54
	f	0.94	2.03
	total	56.15	56.69
Ce(2)	s	0.13	0.13
	p	0.17	0.18
	d	1.04	1.09
	f	0.94	0.89
	total	56.15	56.16
P(1)	p	2.53	2.49
	d	0.06	0.05
	total	14.37	14.39
P(2)	p	2.53	2.52
	d	0.06	0.07
	total	14.37	14.43
Interstitial		9.92	9.23

DISCUSSION

Setting two f electrons in the core on the central site as well as depleting all other f character out of this site is simply a device used to obtain the appropriate potential with which to analyze the unoccupied states. As such this method is very general. We have used this device to analyze the spectrum of a two-f-electron bound state on a cerium site, but one could easily simulate other many-body excitations (two-hole bound states, for example).

As was discussed in the preceding paper, we do not yet have a way of calculating the intensity ratios of the two peaks. In principle, the full many-body matrix elements can be set up, but some way of approximating them must be found to make their evaluation tractable. The combined spectrum of Fig. 1 was obtained by simply adding the two base spectrum together. The result is to grossly exaggerate the feature at E_F. Recent BIS spectra for CeAs and CeSb (Ref. 7) show no feature near E_F. The reason for this is that there is virtually no pnictide p character above E_F which implies that f-p coupling in that energy region is extremely weak. Thus, one would expect to see at most a small bump near E_F in CeP if at all. This is in contrast to CeN where a large peak is seen near E_F as well as one about 5 eV above E_F.[8] The intensity of the peak near E_F is understandable in CeN since this compound appears to be an ordinary f-band metal which would imply a large probability for f hopping. Of course in a model theory such as that of Gunnarsson and Schönhammer,[9] intensity ratios come out naturally and the reader is referred to their paper to see how the ratio is dependent upon the various model parameters.

Although the effect of the spin-orbit interaction was included for the band peak, it was not for the supercell peak since the effect was thought to be too small to be worth the effort (the two f electrons in the core used to construct the potential were treated as $j=\frac{5}{2}$ states, though). Multiplet effects were also not taken into account. In principle, this can be done in the local-density formalism,[10] but has not been applied to solids to the author's knowledge. If multiplet effects turn out to be crucial for interpreting the BIS spectra of cerium pnictides, then an effort could be made to incorporate those effects into the calculation.

A discussion of the peaks themselves is now in order. The first peak represents the extra f electron hopping away and is thus located just above the Fermi energy. This peak will be strong in itinerant f systems since the probability for f hopping will be greater. The second peak due to a two-f bound state is at 4.4 eV above the Fermi energy. This is very encouraging since the experimental spectra indicate this peak at 4—5 eV for cerium metal[3] and in the various compounds.[4] The reason this peak is not higher is that the final energy is lowered by d charge moving off the site in response to the extra f electron (antiscreening). This is simply the mirror process of the d-screened f hole discussed in the preceding paper. The antiscreening can be seen by observing the difference in charges between the band and supercell calculations given in Table I which shows significant depletion of central-site Ce d character as well as interstitial charge. In fact, plots made of the difference in charge density between the two calculations inside the central Ce muffin tin show depletion of charge from 2 a.u. outwards. Plots of the radial wave functions also reveal that the supercell $4f$ function drops off more rapidly in this region than does the corresponding band function, indicating more localization for the two-f bound state. The d antiscreening, though, makes the $f^1 \rightarrow f^2$ excitation more extended than the corresponding $f^1 \rightarrow f^0$ photoemission process. In the future it will be necessary to test the dependence of the results on the supercell size. This, of course, will be very expensive from a computational standpoint.

CONCLUSIONS

Using simple assumptions about the nature of the final states in a BIS experiment, *ab initio* calculations have been performed to obtain a BIS spectrum for CeP which appears very similar to experimental spectra of other Ce compounds. In particular, peaks at 0.4 and 4.4 eV above the Fermi energy are predicted. In a BIS experiment, an f electron is added to a Ce site. This electron can either hop away (0.4-eV peak) or remain localized resulting in antiscreening by the d states (4.4-eV peak). The generality of this method would allow it to be applied to many other systems. In particular, we plan to apply the methods of the preceding paper and this one to a praesodymium system. Of course, rare earths are only a small subset to be considered. In fact, supercell techniques were used several years ago in an attempt to discuss various excitations in the alkali halide LiF.[11]

We hope to see these methods gain wider use. In fact, work similar to that of the preceding paper has been done for metallic cerium.[12,13] To our knowledge, though, this is the first *ab initio* calculation for a BIS spectrum involving both localized and "delocalized" excitations, and we hope that others might apply these techniques to other rare-earth and actinide systems as well as transition-metal systems.

ACKNOWLEDGMENT

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[1] See the extensive set of reference given in the preceding paper.

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