PHYSICAL REVIEW B VOLUME 44, NUMBER 16 15 OCTOBER 1991-II

Large low-energy oscillator strength for Ce 4*f* electrons in the solid state

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(Received 29 April 1991)

The conductivity sum rule applied to $LaSn_3$, $CeSn_3$, LaB_6, and CeB_6 between 1.5 and 4.35 eV shows that there is approximately one more electron contributing to the optical conductivity of the Ce compounds than to that of the analogous La compounds. From the data and band calculations we conclude that about 0.5 Ce 4*f* electron per atom contributes as initial states for $CeSn_3$ in the above energy range, and about half that number of 4*f* electrons serve as initial states in $LaSn_3$. This shift of oscillator strength from higher energies for atoms to lower energies for solids is attributed to hybridization. Much of the remaining Ce-La difference is from transitions to *p*-like final states, which are reduced in the La compounds due to hybridization with unoccupied 4*f* states.

It is well known that the cross section for the photoexcitation of 4*f* electrons on lanthanide atoms is very small near the ionization threshold. It peaks tens of eV above threshold and remains large to rather high energies. The reasons for this are the small radial extent of the 4*f* wave function and the fact that the majority of the transitions on the atom are of the type $4f \rightarrow \varepsilon g$, for which the cross section near threshold is small because the centrifugal potential keeps final-state wave functions with significant $l=4$ character from the origin until the final-state energy is large.[1,2] The same effects are widely believed to carry over to solids because of the atomic nature of the highly localized 4*f* states. Thus the contributions of 4*f* electrons to the optical conductivity are expected to be small in the 1–5-eV range. Indeed, in a study of the magneto-optical conductivity of Gd, Erskine and Stern[3] showed there was little 4*f* contribution below 6.1 eV. In the following we report measurements of the optical conductivity of $LaSn_3$ and $CeSn_3$ in the 1.5–4.35-eV range. We also make use of a previous study[4] of the optical conductivity of LaB_6 and CeB_6. The sum rule on the conductivity suggests that, for both types of compounds, the additional states with 4*f* character contribute strongly to the optical conductivity in this energy region, serving as initial and final states in both La and Ce compounds. Band calculations for $LaSn_3$ and $CeSn_3$ confirm that hybridization mixes considerable 4*f* character into the band states responsible for the transitions.

The samples were single crystals with a (100) face ($LaSn_3$) and a (111) face ($CeSn_3$). They were mechanically polished, finishing with 0.05-μm-diam alumina, rinsed in acetone and methanol, and then placed quickly in a vacuum chamber, which ultimately reached a pressure of 1×10^{-10} Torr. The complex dielectric functions were measured between 1.5 and 4.35 eV with a rotating-polarizer-analyzer ellipsometer.[5] The spectral bandpass was less than 0.02 eV. No attempt was made to sputter and anneal the surfaces in vacuum because of the difficulty of maintaining stoichiometry. These materials are reactive and so were covered with an oxide layer of unknown thickness. However, other runs were made in which the samples were held in air for a more extended period before being placed under vacuum. Such treatment produced a lower value of the optical conductivity than that reported here, but only by about 10%. The optical measurements sample a depth of about 500 Å.

Figure 1 shows the optical conductivities for $LaSn_3$ and $CeSn_3$. The most obvious difference is the much larger values in $CeSn_3$. Both compounds have the same crystal structure and nearly the same lattice parameter. There is one extra electron per formula unit in $CeSn_3$, the 4*f* electron.

The conductivity sum rule

$$\int \sigma(\omega)d\omega = \pi N e^2/2m \ ,$$

where N is the number density of electrons, may be applied, but with caution. When used over a finite energy

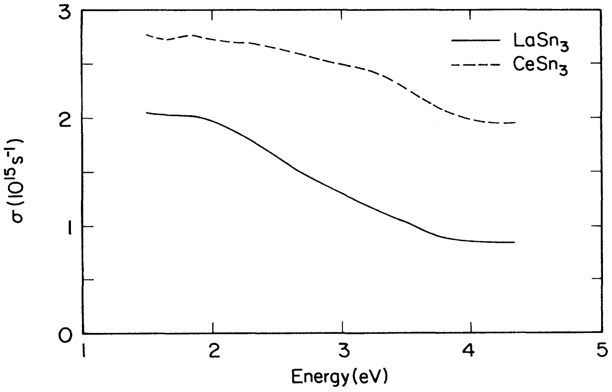

FIG. 1. Measured optical conductivity of $LaSn_3$ and $CeSn_3$. These spectra include an intraband (Drude) contribution.

range, it is called a partial sum rule and represents the number of electrons per atom contributing to the conductivity in the energy range of the integral. It is applicable to an entire system of electrons, not to subsets of the system. However, in cases where the electronic structure is divided into shells with fairly well-separated binding energies, it may be applied to a shell or subshell. If the data of Fig. 1 are integrated from 1.5 to 4.35 eV, 1.2 more electrons per formula unit contribute to the conductivity of $CeSn_3$ than to that of $LaSn_3$ (see Table I). This probably represents an upper limit for the difference, since $LaSn_3$ oxidizes more rapidly than $CeSn_3$. However, the result is in qualitative agreement with the calculations described later. We carried out the same integration on the data for LaB_6 and CeB_6 of van der Heide *et al.*[4] and found that the latter had a contribution from an additional 0.8 electrons per formula unit. (A recent paper[6] compares the optical conductivities of many rare-earth hexaborides and shows very little difference between LaB_6 and CeB_6, unlike the data in Ref. 4.) Given possible experimental errors, 10–15 % or so, both these differences are probably best stated as about one electron per formula unit. An even larger sum-rule difference occurs for CeSb and LaSb.[7] Also, a comparison of the optical conductivities of $LaCu_6$ and $CeCu_6$ has been carried out, but shows very little difference in the 1–5-eV region due to the dominance of transitions from the Cu 3*d* states.[8]

The complete sum rule states that the conductivity of the Ce compounds will be larger in such a way that the integral will give one extra electron per formula unit when compared with the corresponding La compound. The conductivity of the former need not be higher everywhere, and there may be spectral regions where it is smaller than the conductivity of the latter. We see from our experimental results that, in the 1.5–4.35-eV spectral region, the full one electron per formula unit difference is obtained, although, according to our theoretical analysis, not all of this difference arises from 4*f* contributions to initial states. This spectral region contains contributions from only the valence electrons, derived from atoms of both types, and the 4*f* electrons. Given that the band structures of $LaSn_3$ and $CeSn_3$ are very similar except for the placement of the 4*f* band, it might seem reasonable to assign the difference in the sum-rule results to the presence of the extra electron in the Ce compounds, derived from the 4*f* electron on the Ce atom and to the relative placement of the empty (La compounds) or mostly empty (Ce compounds) "4*f* bands." This view is too simple, since hybridization must be taken into account.

The difference in the energy dependence of the 4*f* oscillator strength between the solids and free atoms certainly arises from the hybridization of the occupied 4*f* states with other states. This is a larger effect in Ce than in heavier rare earths for two reasons: because of the larger 4*f* average radius and because only the lowest, most bonding and most extended states are occupied. Even in La compounds, the empty 4*f* "level" will hybridize with states near the Fermi level, with weak hybridization even below it. Empty final states will also hybridize with the 4*f* states. We have approached this problem by carrying out band calculations for $LaSn_3$ and $CeSn_3$. The details of these calculations and the comparison with the data will be reported elsewhere. The calculation was a scalar-relativistic[9] self-consistent calculation, using warped-muffin-tin potentials.[10] The band structures were reported earlier and yielded Fermi surfaces in good agreement with experiment.[11] The band structures of $LaSn_3$ and $CeSn_3$ are very similar, except for the placement of the 4*f* bands. The decompositions of the valence-electron charge by atom and angular momentum are also nearly identical, except for one additional 4*f* electron in $CeSn_3$.[12] In addition, we calculated interband contributions to the optical conductivity by evaluating dipole-matrix elements. As an aid to interpretation, the degree of 4*f* admixture into the initial and final states important for the interband conductivity was monitored. The resultant conductivities are shown in Fig. 2. There is no adjusted normalization of the spectra in Fig. 2; the magnitudes of the conductivity spectra are set by the calculated electric dipole-matrix elements. The conductivity

TABLE I. Partial (1.5–4.35-eV) sum-rule results (electrons/formula unit).

Initial-state angular momentum	$CeSn_3$	$LaSn_3$	Difference
$l=0$ $(s \rightarrow p)$	0.66	0.49	0.17
$l=1$ $(p \rightarrow s,d)$	0.38	0.32	0.06
$l=2$ $(d \rightarrow p,f)$	1.39[a]	1.30[b]	0.09
$l=3$ $(f \rightarrow d)$[c]	0.47	0.24	0.23
Total	2.90	2.35	0.55
Experiment	2.83	1.65	1.18

[a] $d \rightarrow f$, 0.15.

[b] $d \rightarrow f$, 0.13.

[c] $f \rightarrow g$ is less than 0.01.

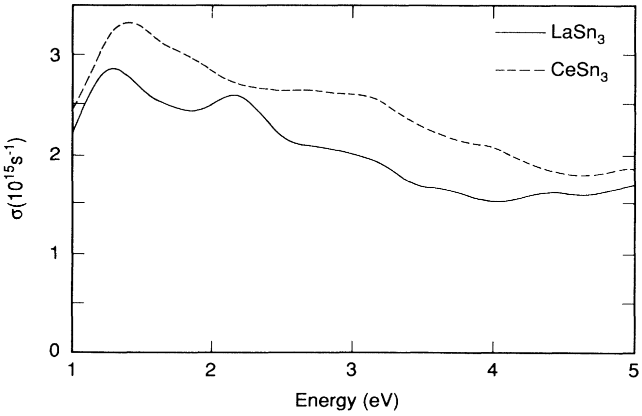

FIG. 2. Calculated interband optical conductivity of $LaSn_3$ and $CeSn_3$. The calculated spectra have been broadened with a Lorentzian with a full width at half maximum of 0.2 eV. These spectra do not contain a Drude contribution. (An attempt was made to estimate Drude contributions from the dc resistivity and expected valence, but at 1 eV, the resultant values were unrealistically large.)

partial-sum-rule difference between $LaSn_3$ and $CeSn_3$, using the calculated conductivities, is 0.55 electrons per formula unit between 1.5 and 4.35 eV, about half the difference found in the measured spectra. Detailed agreement for all structures in the spectra was not achieved. Close agreement was not expected since the precise evaluation of the positions of structures in the conductivity spectrum for systems with strong electron correlations requires a more elaborate determination of the excited quasiparticle self-energies. This can lead to some redistribution of oscillator strength.

Not all of the calculated optical conductivity difference can be assigned to $4f$ electrons. In $LaSn_3$ the peak at 3 eV (Fig. 2) arises from transitions involving states with only small amounts of $4f$ character. Table I shows the contributions to the partial sum rule from transitions with different angular momentum values in the initial states. The largest contribution to the Ce-La difference is from the extra $4f$ weight in the initial states of $CeSn_3$. The next-largest contribution is from the $s \rightarrow p$ transitions. Here $LaSn_3$ loses oscillator strength with respect to $CeSn_3$ because the $4f$ hybridization with La p states pushes some states with p character up in energy, causing their contributions as final states to occur at higher energies.

Band theory is not expected to be accurate for materials with highly localized $4f$ states. Even for the ground-state properties of these systems, calculations using the local-density approximation do not accurately treat the strong correlations of the $4f$ shell and result in nonintegral "band" occupations and overestimates of the $4f$ hybridization with the conduction electron (s,p,d) states. In $CeSn_3$, where the $4f$ states are not so localized, the hybridization given by band theory is, in fact, important for producing agreement with de Haas–van Alphen experiments.[11] It also seems likely that band theory gives a reasonable picture for the low-energy optical excitations in this compound, except for optical transitions to final states with significant $4f$ character, where the Coulomb interaction with the occupied $4f$ states (not $4f \rightarrow 4f$ transitions) will be inadequately treated. Such transitions will occur at higher energies than predicted by band models. The other extreme model for $4f$ systems is a localized one, with hybridizing interactions with the conduction electrons.[12] To date, however, such calculations have been carried out only with very simple models for the valence states, e.g., no wave-vector dependence of the energy. These calculations do show, however, that $4f$-valence hybridization is very important for an explanation of many spectroscopic properties of $4f$ systems, especially light rare earths, and that the hybridization is larger than previously thought. The optical data presented here arise from excitations close to the adiabatic limit, while the localized model treats more energetic photoexcitations in the sudden approximation. The large low-energy oscillator strength found in $CeSn_3$ and CeB_6, unexpected from an atomic picture, is described qualitatively by the hybridization resulting from the band calculation. We expect that for systems containing rare earths, where there is little $4f$ hybridization (localized $4f$ states), the $4f$ oscillator strength will peak at higher energies, similar to the atomic case. In fact, it might be possible to use the shift in oscillator strength as a means of determining the degree of localization of the $4f$ states.

This work was supported by the U.S. Department of Energy, Office of Energy Research, Division of Materials Sciences, by the Ames Laboratory, operated for U.S. DOE by Iowa State University under Contract No. W-7405-ENG-82, and by Argonne National Laboratory under Contract No. W-31-109-Eng-38. Part of this work was accomplished through a grant of computer time on the Cray computers at the National Energy Research Supercomputer Center.

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