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Optical spectroscopy of the covalent insulator CeF_4

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The optical reflectivity of polycrystalline CeF_4 has been measured at room temperature over four orders of photon energy (1 meV–12 eV) using four spectrometers. The data have been analyzed with the Kramers-Kronig relation in order to obtain the optical constants. Interband transitions and phonons are discerned. Just as in CeO_2 the lowest energy interband transition is from the p band of the anions into empty $4f$ states. The material is a covalent insulator and cannot be classified as an intermediate valent material.

INTRODUCTION

It has been suggested that insulating transition-metal, rare-earth, and actinide compounds may be of intermediate valence character.[1–4] This suggestion is based on the experimental observation that in high-energy spectroscopies, such as x-ray photoelectron spectroscopy (XPS) or *L*-*M*-edge absorption (XANES), a multiple-peak structure is observed that has been interpreted as a mixed valency in the initial state. There are definitely compounds or alloys that behave metallically at ambient temperature (at which temperature most of the XPS or XANES experiments are performed) and are genuinely intermediate valent, as also judged by many other physical methods. Ce compounds or alloys differ from other rare-earth compounds that one of the possible valence states 3 or 4 no longer has a $4f$ occupation; therefore, core-level XPS and *L*-edge XAS have been adopted, where, e.g., a $3d$ or $2p$ electron is emitted or excited. The final state reached by electron emission or excitation exhibits in all investigated cases a multiple-peak structure due to $4f^0$-, $4f^1$-, and $4f^2$-derived states, from which it has been inferred that the initial state also has an intermediate valence character.[1–5] However, the creation of a core hole renormalizes all energies of the outer electron shells, including that of an empty $4f$ shell. Thus, in the final-state, amplitudes of a $4f^1$ and $4f^2$ configuration also appear to be present, which sometimes has been interpreted as a fractional occupation of the initial state.

Theories used for the calculation of the initial intermediate valence state are usually based on the Anderson impurity model.[6] Gunnarson and Schönhammer[7] have developed a method to calculate the initial state from the final-state photoemission data. In Ce alloys or compounds and even in insulating compounds like CeO_2,[8] the experimental core-level data, with its multiple peaks, and with the standard theory of Gunnarson and Schönhammer[7] have in many cases been interpreted as an intermediate valence configuration in the initial state.[1–5] However, it has been shown that the same core-level spectra arise either when a $4f$ level is mixing with a conduction band[7] in the initial state (intermediate valence metal) or when a $4f$ level is mixing with a filled valence band of an insulator (covalency).[9–11] The latter is the case in the covalent insulator CeO_2,[8] and we will show that the same is true for CeF_4, where core-level spectroscopies have already been performed.[12]

EXPERIMENT

In order to investigate the optical properties of CeF_4, we have performed reflectivity measurements using four spectrometers from 1 meV to 12 eV to cover the whole spectral range. The sample was a polycrystalline and sintered piece of irregular shape, approximately $2\times2\times3$ mm^3 large and of a yellowish white color. We performed a first and rough dry polishing of one surface and measured the reflectivity, and then did a more perfect job and polished the surface as smoothly as we could until a shiny surface was achieved. Then the reflectivity measurement was repeated. But only in the ultraviolet spectral range above about 4 eV did we obtain in the latter case slightly higher values of the reflectivity. The best results are shown in Fig. 1(a) for the high-energy photon range and in Fig. 1(b) for the low-energy range.

Despite the very low values obtained in the high-energy region, they were well above the limit of detectability, and the measurements were always clear and reproducible. The sample exhibits a strong diffusion and scattering of light for energies below above 3 eV, and a large anomalous bump in the reflectivity is observed between 0.5 and 2 eV. To illuminate this aspect further, we have measured in an Ulbricht sphere the total diffuse reflectance of the sample and compared it with a mirror. The sum of the reflectance in all directions is about 90% below 2 eV (see Fig. 2). At the same time, the transmission reaches values up to 10%, so it can be concluded safely that strong absorption sets in at about 2 eV (see Fig. 2). We measured also the reemission in the Ulbricht sphere by comparison with a perfect white diffuse reflecting ZnO or MgO standard. The rough reverse side of the sample and the polished side gave nearly the same result, namely that the reemission is constant at the lower energies, and then above the absorption edge at 2 eV it decreases and tends towards zero (Fig. 2). This kind of behavior must probably be ascribed to some porosity being homogeneously distributed in the sample, which scatters the light in the range of transparency due to the corresponding size of the individual particles of the polycrystalline sample and the wavelength of light.

The reemission data have been used to correct the reflectivity data of Figs. 1(a) and 1(b) in order to obtain consistent values. The measurements in Fig. 2 have shown that the broad bump between 0.5 and 2 eV is mainly caused by light scattering due to the size effect of the grains and not so much by real absorption. The corrected reflectivity has been analyzed in terms of a Kramers-Kronig transformation. The extrapolation towards zero frequency was readily obtained, since below 10 meV the reflectivity tends towards the constant value of 38%. For energies larger than 12 eV and up to 18 eV, the reflectivity has been assumed to drop off as ω^{-2}, and

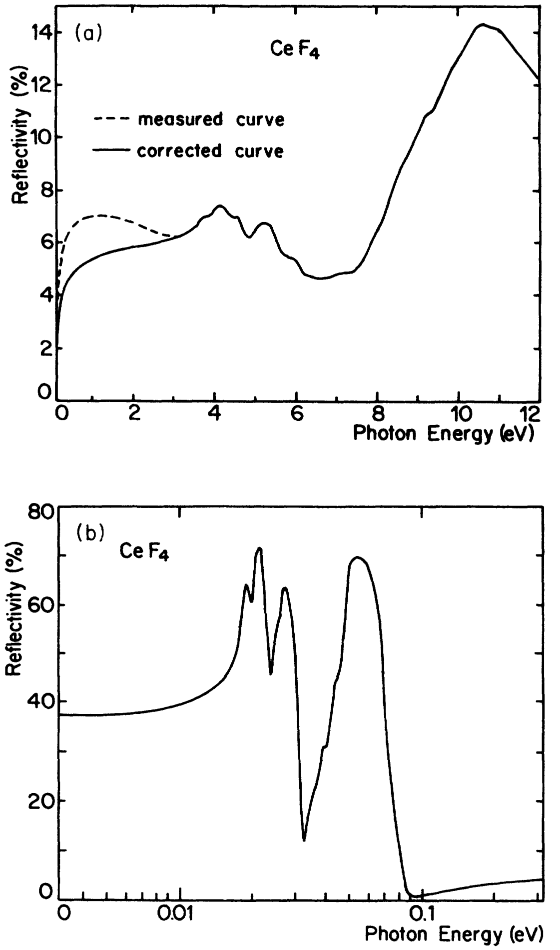

FIG. 1. (a) Optical reflectivity of CeF_4 at 300 K. The solid curve has been corrected with grain size scattering. (b) Reflectivity of CeF_4 in the far-infrared region at 300 K.

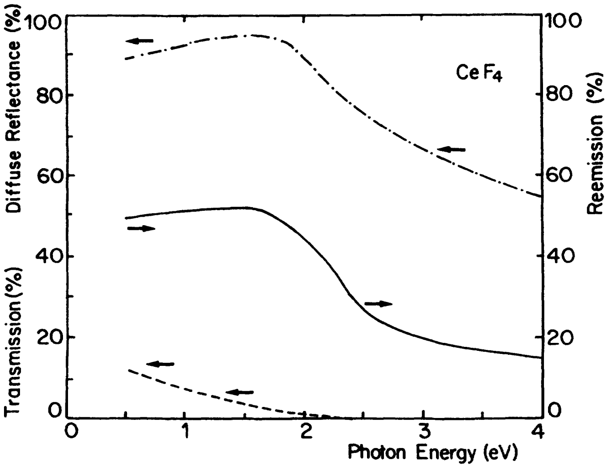

FIG. 2. Diffuse reflectance, transmission, and reemission of CeF_4 near the absorption edge.

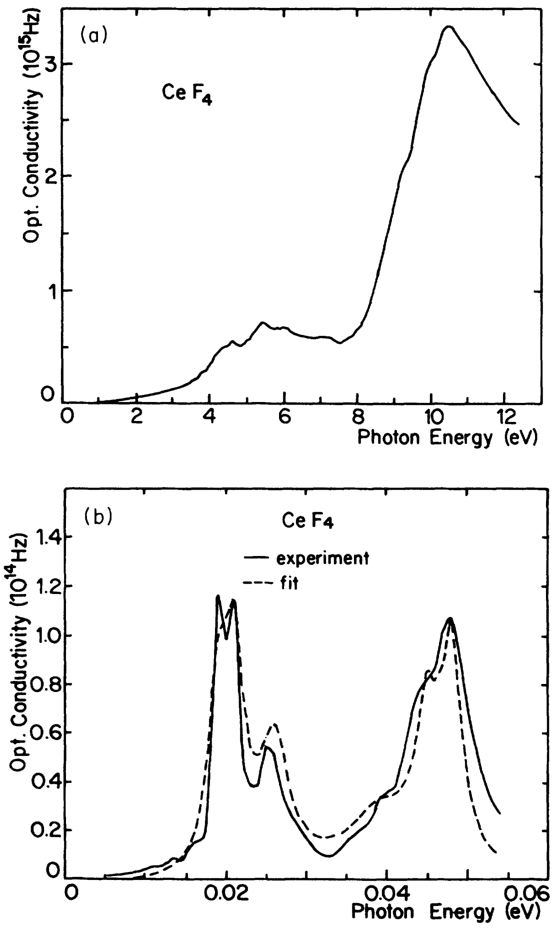

FIG. 3. (a) The optical conductivity of CeF_4 at 300 K. (b) The optical conductivity of CeF_4 in the far-infrared region. The fit is with a six-oscillator Lorentz model.

for still higher energies as ω^{-4}. The dielectric functions and the optical conductivity thus obtained are plotted in Figs. 3–5.

After long-time exposure to air, the sample changed its color to light pink. A further series of measurements indicates that the only change occurs in the absorption tail between 2 and 4 eV. This is probably due to an increasing loss of fluorine, causing F centers.

DISCUSSION

Since we are dealing with an insulating material, we can easily separate the discussion into two parts concerning the phonon modes in the far-infrared region and the electronic properties above the absorption edge at 2 eV. The conductivity spectrum in the far-infrared region, between 0 and 0.1 eV, is characterized by several peaks: three well-separated peaks between 15 and 30 meV form a first group; a second group of superimposed structures is found at 40–55 meV [Fig. 3(b)]. The structure of the molecule of CeF_4 is tetrahedral, with Ce symmetrically surrounded by the four F atoms, so one should expect two IR-active modes.[13,14] The two modes are triply degenerate. However, the crystal structure is much more complicated. We deal with a monoclinic cell with spatial group C_{2h-6} and 12 formula units per cell,[13–15] which will remove the degeneracy. In this scheme, the two observed groups of optical structures correspond to the two IR modes of the molecule, and each of these modes is split into three crystalline modes.

This splitting and the complex crystal structure render very difficult the analysis of the optical results in order to calculate the effective charge. As a matter of fact, it is not possible to identify a single value for the frequency of the transversal and longitudinal components ω_t and ω_l, so one cannot apply the usual expressions (e.g., the Szigeti formula[16]). A fit with six Lorentz oscillators on the split structures has been performed by assuming the same oscillator strength for each one [Fig. 3(b)]. Every group of three structures, corresponding to the same mode in the tetrahedral symmetry, should have a total strength directly proportional to the square of the effective charge (in principle the same for both modes). From the results of the fit we obtained a Ce ionic charge q/e of about 3. A similar result can also be obtained by integrating the conductivity spectrum (this is equivalent to the well-known f-sum rule). One obtains a curve with two steps, both representing for each mode a density $n=(q/e)^2N/\mu$,

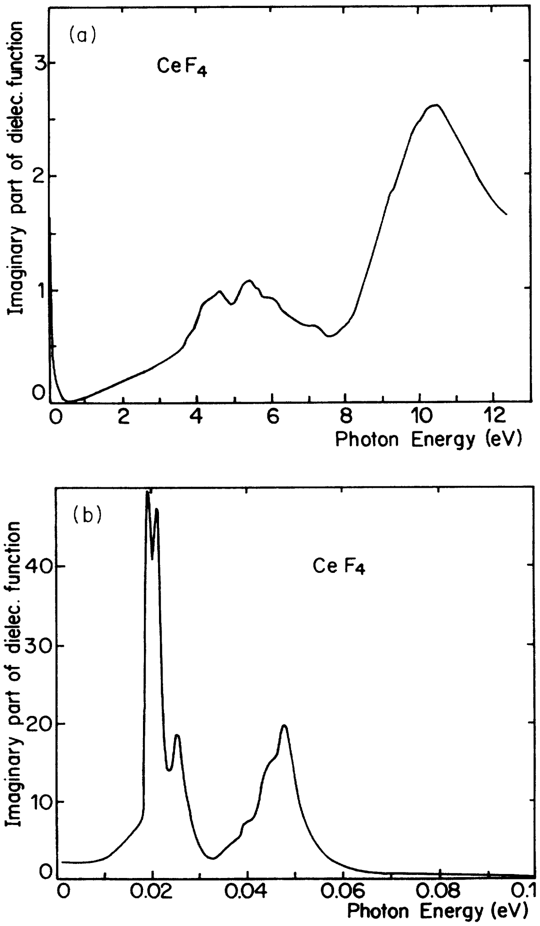

FIG. 4. (a) The imaginary part of the dielectric function of CeF_4. (b) The imaginary part of the dielectric function of CeF_4 in the far-infrared region.

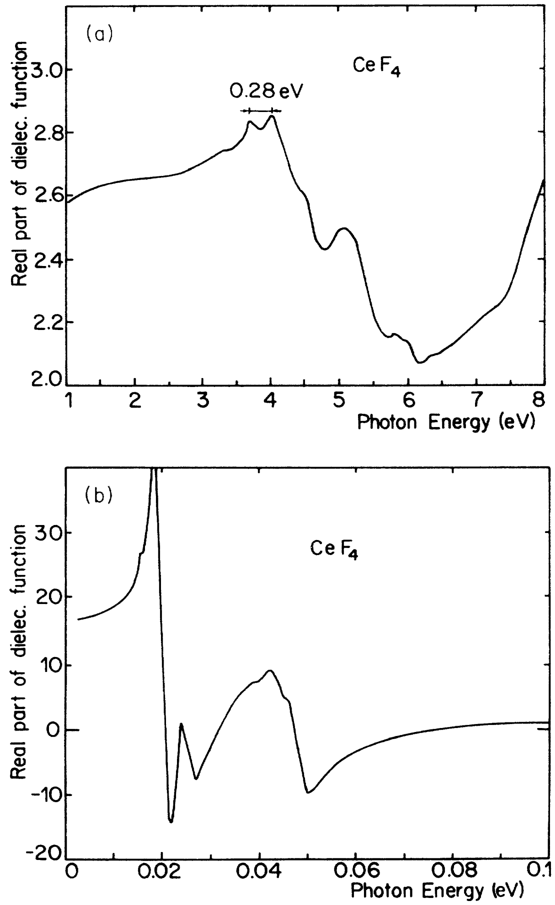

FIG. 5. (a) The real part of the dielectric function of CeF_4. (b) The real part of the dielectric function of CeF_4 in the far-infrared region.

where q is the effective charge in electron charge units, N the density of Ce atoms, and μ the molecular reduced mass $\mu=(M_{Ce}4M_F)/(M_{Ce}+4M_F)$ in atomic masses. The two methods are not exactly equal. This can be due to a different screening effect in the two modes, but also to some uncertainty in the Kramers-Kronig transformations, where a very small error for the value of the reflectivity minimum at 90 meV can have a large effect on the calculated conductivity. Regardless, assuming the density $N=1.34\times10^{22}$ atoms/cm^3,[8] one obtains from the experiment an effective charge q ranging between 2.9 and 3.6 electronic charges. This value corresponds to the ionicity of CeF_4 and has no relation with the valency of cerium, which remains 4, as in the case of CeO_2. Compared to CeO_2 [$q/e=2.48$ (Ref. 11)] CeF_4 shows a stronger ionic character, in agreement with the larger electronegativity of fluorine with respect to oxygen.

Similarities between CeO_2 and CeF_4 can also be found for the electronic properties above the absorption edge. The absorption edge is placed at 2 eV, as described above. Below this energy, the material is completely transparent, due to transmission and reemission measurements. Above 2 eV the curvature of the reflectivity changes [Fig. 1(a)] and the reflectivity rises to a maximum at about 4 eV, in strong similarity with CeO_2, even though the values are lower.[8] Nevertheless, between 4 and 6 eV, CeF_4 shows a series of peaks that are not present in the oxide.[8]

Due to a lack of theoretical investigations on the electronic structure of CeF_4, we can only present some considerations starting from the analysis of CeO_2.[8] The highest occupied valence band in CeO_2 is a "nominal" $2p$ band; i.e., it has a strong d admixture.[11] The first optical structure at 3.9 eV has been associated with a transition from this band into empty $4f$ states of cerium. In the CaF_2 structure the $2p$-like valence band shows four branches that are doubly degenerate at the Γ_{15} and Γ_{25} points. Some metal f character is present in Γ_{15}, whereas the bottom of the p band, originating in Γ_{25}, has metal d character admixed. Since $p\rightarrow f$ or $f\rightarrow f$ transitions are, in principle, forbidden, or in the solid have a rather low oscillator strength, the most important contribution to the oscillator strength comes from the d component of the band. By fitting the CeO_2 data with a classical Lorentz oscillator, one finds an oscillator strength of ~0.1, which is in fair agreement with a $d\rightarrow f$ transition. Since the empty f states of Ce are localized, the width of the 3.9-eV peak must be ascribed to the width of the oxygen nominal p band ($W=3.2$ eV).[8]

The fingerprint of the final f state is the trapezoidal shape of the reflectivity peak at 3.9 eV, where the kinks are separated by 0.28 eV. This number closely agrees with the well-known $^2F_{5/2}\rightarrow{}^2F_{7/2}$ spin-orbit splitting of the Ce $4f^1$ state. Such a feature is also particularly evident in CeF_4: the spectrum of the dielectric constant ϵ_1 in Fig. 5(a) shows the two well-separated substructures near 4 eV.

The assumption of a completely empty localized f state in the ground state is fully consistent with XAS, XPS, and soft x-ray-absorption measurements.[12,17–19] These measurements reveal a $4f$ ligand hybridization in CeF_4 as well as in CeO_2, which results in a covalent bonding but keeps the tetravalency of Ce. CeF_4 shows a lower degree of covalency with respect to the oxide; this behavior may actually be expected due to the higher ionicity of this compound and is in agreement with our analysis of the ionic charge.

Despite the different and much more complicated crystal structure, CeF_4 seems to have essentially the same electronic configuration as CeO_2. On the other hand, the isostructural non-$4f$ reference compound ZrF_4 shows a large gap of the order of 10 eV between the valence band, about 5 eV wide and characterized by fluorine states, and the conduction band, originating in the metal d and s states.[20]

Let us consider the basic tetrahedral structure of the molecule CeF_4 as observed in the phonon spectrum. This symmetry is similar to that of CeO_2. Thus the $2p$ states of fluorine should originate in four triply degenerate branches similar to those of CeO_2. The reduction of the symmetry in the CeF_4 crystal compared to CeO_2 eliminates the degeneracy and splits the band into several different branches. Yet we must notice that the total number of electrons in the band is 24 electrons per formula unit (288 electrons per cell), higher than in CeO_2 (12 electrons per formula unit; 48 electrons per unit cell). This is probably the origin of the peaks in the conductivity spectrum [Fig. 3(a)] at 4.5, 5.4, 6, and 7.2 eV, all of which correspond to p-f transitions from the different branches of the nominal $2p$ band. The oscillator strength, calculated on the whole structure between 3.5 and 7.5 eV, results in $f\sim0.05$, about one half the value in CeO_2.

Above 8 eV, the reflectivity increases rapidly up to a maximum at 10.6 eV. In the optical conductivity, a corresponding structure with a maximum five times larger than the one at 4.5 eV is placed at the same energy [Fig. 3(a)]. This large intensity agrees with the attribution of such a structure to transitions from the valence $2p$ band into the conduction $5d$ or $6s$ band, where the $p\rightarrow d$ transitions are typically allowed. In fact, the oscillator strength calculated from our data results in $f\sim0.25$ for this transition.

Also, the d band should be split by the crystal field into several bands. In effect, some small shoulders in the spectrum could account for this splitting, but it is not possible to do further speculations because the energy limit of our measurements is not great and the results become much more sensitive to surface defects at the higher energies.

CONCLUSION

We have shown in this paper that CeF_4 is an insulator, as verified by the absence of any free-carrier or plasma effects. An analysis in terms of Szigeti charges yields an ionicity between 2.9 and 3.6 compared with the formal valence of 4 of cerium. It is thus evident that the compound is about 25% covalent. Covalency means a hybridization between cation and anion wave functions, which is also obtained in the similar CeO_2, where band-structure calculations resulted in *d* and *f* character admixed with the nominal *p* character of the anion valence band.[11] In fact, we find that CeF_4 is less covalent or more ionic than CeO_2, which is reasonable in view of the stronger electronegativity of fluorine compared with oxygen.

The fingerprint of a transition involving the spin-orbit split 4*f* states of cerium is clearly observed in optical spectroscopy, best seen for CeF_4 in Fig. 5(a). There are no difficulties regarding initial- or final-state spectra in optical spectroscopy, provided one has a wide-range photon-energy spectrum available. If the 4*f* state would be the occupied ground state, one would observe in the infrared region an optical transition at 0.28 eV due to the spin-orbit splitting, as observed for CeF_3.[21] Such a transition is absent for CeF_4 (and also for CeO_2). On the other hand, when an empty 4*f* state is the final state, one observes an optical transition at large energies (e.g., 3.9–4.0 eV in CeF_4), which shows a double structure split by 0.28 eV. This is the case in CeF_4 and CeO_2. It is thus clear that the 4*f* states in CeF_4 are empty and not initial states. Since the material is also not a metal, the term intermediate valence is inappropriate, but the material is more properly termed a covalent insulator. In Fig. 6 we show a rough energy-level scheme of CeF_4, where localized states are plotted to the left and band states to the right of the figure.

Here a more general remark regarding intermediate valence is appropriate. Intermediate valence is the hybridization of generally *f* and *d* cation wave functions (not of the same cation). In some cases this *f* and *d* mixing can be turned on by external means (e.g., pressure) and thus can be followed in detail. The originally localized *f* states thus become narrow (1 meV wide) *f* bands with partial occupation, and at ambient temperatures (with *kT* much larger than the band width) these intermediate valence materials behave as metals. Only at very low temperatures does the observation of hybridization gaps become possible. It is thus clear that the mere observation of a wide-gap insulater at ambient temperature excludes the possibility of intermediate valence.

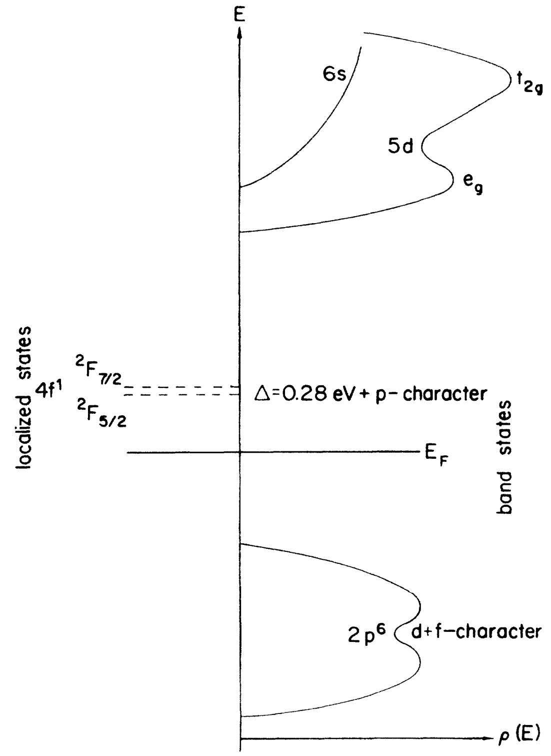

FIG. 6. A sketch of the electronic structure of CeF_4.

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