

## Covalent insulator CeO<sub>2</sub>: Optical reflectivity measurements

F. Marabelli and P. Wachter

*Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule Zürich, 8093 Zürich, Switzerland*

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The optical reflectivity of CeO<sub>2</sub> single crystals has been measured from 1 meV to 12 eV at 300 K and then analyzed in terms of a Kramers-Kronig transformation. Static and optic dielectric constants, TO- and LO-phonon frequencies, the effective charge, and the degree of covalency have been obtained. It can be asserted that CeO<sub>2</sub> is not of intermediate valence but it is a covalent insulator.

### INTRODUCTION

Since 1981 there has been a long-standing controversy about the valency of Ce-based compounds or alloys. In that year Wohllaben claimed that all Ce compounds are of intermediate valence.<sup>1</sup> This statement has been opposed by Wachter,<sup>2</sup> who measured the magnetization, susceptibility and optical absorption of CeO<sub>2</sub> and on that basis tried to show that in this material Ce is integral tetravalent and that CeO<sub>2</sub> is a covalent insulator.

This controversy has led (to the knowledge of the authors) to about 30 papers discussing the problem of valency in CeO<sub>2</sub> and using as experimental methods mainly high-energy probes, such as x-ray (XPS) and uv (UPS) photoemission spectroscopies, bremsstrahlung isochromat spectroscopy (BIS), *L-M*-edge spectroscopy, electron-energy-loss spectroscopy (EELS), and x-ray absorption spectroscopy (XAS). On this basis about two-thirds of the papers, e.g., Refs. 3–6 come to the conclusion that CeO<sub>2</sub> is of intermediate valence; however, one-third of the authors, e.g., Refs. 7 and 8, using the same experimental techniques, interpret their findings with tetravalency of Ce in CeO<sub>2</sub>. Thus, either there is a genuine physical contradiction, or the methods used for the investigation are not adapted to the problem.

For the investigation of intermediate-valence materials photoemission is a widely used method, since it is thought that in photoemission intermediate valence of the initial state  $a |4f^n\rangle + b |4f^{n-1}5d\rangle$  is reflected also in the final state after the emission of a  $4f$  electron, namely  $a |4f^{n-1}\rangle + b |4f^{n-2}\rangle$ .<sup>9</sup> The integration of the  $4f^{n-1}$  and  $4f^{n-2}$  spectra, separated by the Coulomb correlation energy, in principle, can yield the degree of valence mixing of the initial state. Problems arise when these methods should distinguish between inhomogeneously or homogeneously mixed valence or better termed mixed or intermediate valence. In the former case one has a mixture of different integer-valence ions, as in Fe<sub>3</sub>O<sub>4</sub>, Eu<sub>3</sub>O<sub>4</sub>, Eu<sub>3</sub>S<sub>4</sub>, and Sm<sub>3</sub>S<sub>4</sub>. The localized *d* or *f* states with different, but integer occupation already in the initial state, are separated by the Coulomb correlation energy,<sup>10–12</sup> and the integration of the final-state spectra yields a valence mixing of 2.66. When the materials are insulators or large-gap semiconductors, as Eu<sub>3</sub>O<sub>4</sub> and Eu<sub>3</sub>S<sub>4</sub>, a distinction between intermediate valence and mixed valence is possible, since the Fermi level  $E_F$  usually

is not in the lowest-energy *f* peak, but above it. However, when the materials are metals (as Fe<sub>3</sub>O<sub>4</sub> at 300 K) or have a gap of less than the standard resolution of XPS (0.8 eV) as, e.g., Sm<sub>3</sub>S<sub>4</sub> with  $E_g = 0.14$  eV,<sup>12</sup> this distinction is experimentally not observable by the photoemission methods alone since  $E_F$  is found in the *f* peak. Even though today a more modern analysis of the data is performed using the Gunnarson-Schönhammer mechanism,<sup>13</sup> the experimental methods are still the same. In other words, one cannot in all cases conclude from the measured spectra and Coulomb correlation energy of the final state whether the initial state consists also of two integral-valence states separated by the Coulomb correlation energy or of one intermediate-valence state where each ion has the same, noninteger, valence.

With regard to true intermediate valence as in, e.g., SmB<sub>6</sub>, “gold” SmS, antiferromagnetic TmSe, or YbB<sub>12</sub>, photoemission or other high-energy methods have not up to now revealed the existence of a hybridization gap with  $E_F$  being in the gap.<sup>14–16</sup> This electronic structure, however, determines all the thermodynamic and transport properties of the quasiparticles.

For Ce compounds the above-described valence-band spectroscopies fail for the determination of intermediate valence, because in Ce and its compounds the valence is expected to be between 3 and 4, but tetravalent Ce has an empty  $4f$  level. For these materials core-level spectroscopies have instead been applied, where, e.g., a  $3d$  or  $2p$  electron is emitted or excited. The remaining configuration indeed exhibits in all investigated cases both, e.g.,  $3d^9 4f^0$  and  $3d^9 4f^1$  spectra, from which it is inferred that the initial state also has an intermediate-valence character.<sup>1,3–6</sup> However, it has not always been considered enough that 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  $4f^1$  configuration also appear to be present, which sometimes<sup>3–6</sup> has been interpreted as a fractional occupation of the initial state.

The theories used for the calculation of the initial intermediate-valence state are usually based on the Anderson impurity model.<sup>17</sup> Using this model, Gunnarson and Schönhammer have developed a method to calculate the initial state from the final-state photoemission spectra.<sup>13</sup> We find it somewhat surprising that all authors using UPS, XPS, and BIS methods on CeO<sub>2</sub> make use of the

Gunnarson-Schönhammer mechanism but nevertheless come to completely different conclusions regarding intermediate valency or tetravalency of CeO<sub>2</sub> (e.g., Refs. 3–7).

Therefore, it is very important that other experimental methods be used to decide on the valency of Ce in CeO<sub>2</sub>. The power of spectroscopic methods is well established in gaining information on the electronic structure of a material, and thus we have used optical reflectivity over a very large photon energy range (more than four decades of photon energy). It will be shown that “soft” optical spectroscopies have a simple answer to the question of valence mixing in the initial or final state.

### EXPERIMENTAL

We have grown single crystals of CeO<sub>2</sub> from the melt. For that purpose we started with commercial 99.99%-pure polycrystalline CeO<sub>2</sub>. To make the product more compact we sintered it overnight at 1000°C in 1 bar of oxygen in an Al<sub>2</sub>O<sub>3</sub> crucible. The ceramic then was placed into an electron-beam-welded tungsten crucible, heated for 2 h at 2275°C and afterwards slowly cooled for six days. In the crucible we found black single crystals of size 7×7×7 mm<sup>3</sup>. The black color had its origin in an absorption tail in the visible part of the spectrum and was due to oxygen deficiency. The crystal structure was of the CaF<sub>2</sub> type with some additional x-ray lines. However, we could bleach the crystals (usually after cutting, grinding, and polishing the surface) by annealing for 5 h at 500°C in a stream of oxygen. After this treatment the crystals were slightly yellow in color and transparent. The x-ray pattern now was purely of the CaF<sub>2</sub> type. The crystals now tended to exfoliate when mechanically strained, which was connected with the strain already introduced by the crystallographic transformation of oxygen-deficient parts of the samples (rhombohedral) to the CaF<sub>2</sub> structure of the more stoichiometric ones.

As a first measurement we repeated core-level XPS on the single crystals after scraping the surface in ultrahigh vacuum in the XPS machine.<sup>18</sup> The results obtained are absolutely comparable with those of other authors, especially regarding the existence of both 3d<sup>9</sup>4f<sup>0</sup> and 3d<sup>9</sup>4f<sup>1</sup> spectra. The existence of the 4f<sup>1</sup> spectra thus could not be blamed on a contamination of the CeO<sub>2</sub> with trivalent Ce<sub>2</sub>O<sub>3</sub>.

We then performed optical reflectivity measurements between 1 meV and 12 eV at 300 K, using four spectrometers. The results are shown in Fig. 1. The spectrum is obviously that of an insulator with only one phonon band at low energies and interband transitions above 3 eV. Group theory tells us that only one triple-degenerate T<sub>1u</sub> infrared-active phonon exists in the CaF<sub>2</sub> structure. It is remarkable that the reflectivity spectrum of the black (as-grown) crystals exhibits three phonon bands as typical for the rhombohedral, oxygen-deficient phase. In other words, the symmetry reduction has lifted the degeneracy of the phonons. The reflectivity peak somewhat below 4 eV shows also a fine structure for the stoichiometric, transparent crystals, which is displayed in detail in the inset of Fig. 1.

The reflectivity spectrum has been analyzed in terms of a Kramers-Kronig transformation, where the spectrum

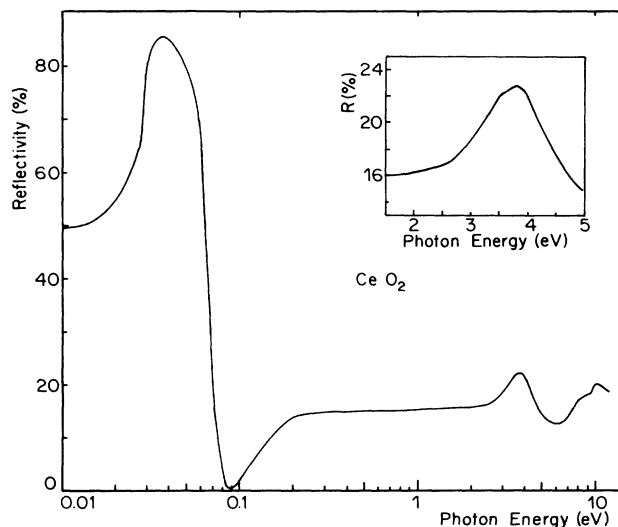


FIG. 1. The reflectivity spectrum of CeO<sub>2</sub> single crystals at 300 K. The inset shows the details of the lowest-energy interband transition at about 4 eV.

has been extrapolated for  $\omega$  towards zero in such a way as to obtain values consistent with the Lyddane-Sachs-Teller relation. For energies larger than 12 eV and up to 18 eV the reflectivity has been assumed to drop off as  $\omega^{-2}$ , for still higher energies as  $\omega^{-4}$ . The dielectric functions ( $\epsilon = \epsilon_1 - i\epsilon_2$ ) obtained are plotted for the high-energy range in Fig. 2 and for the low-energy range in Fig. 3.

The reflectivity spectra for the black and the yellow, transparent crystal in the high-energy region, especially between 2 and 4 eV, are practically the same. However, the absorption tail below about 3 eV, visible in  $\epsilon_2$  in Fig. 2, gets significantly enhanced for the black crystal and is due to oxygen deficiencies (*F* centers).

It is well known that optical transitions having small

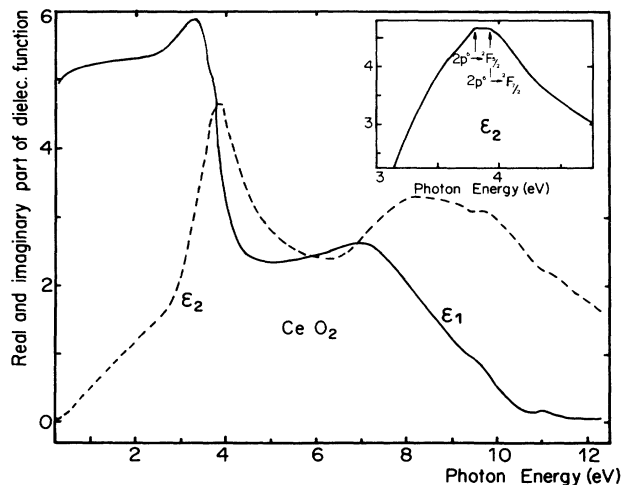


FIG. 2. The dielectric functions  $\epsilon_1$  and  $\epsilon_2$  of CeO<sub>2</sub> in the high-energy photon range. The inset shows  $\epsilon_2$  near the lowest-energy interband transition with the spin-orbit splitting of the empty 4f<sup>1</sup> state indicated.

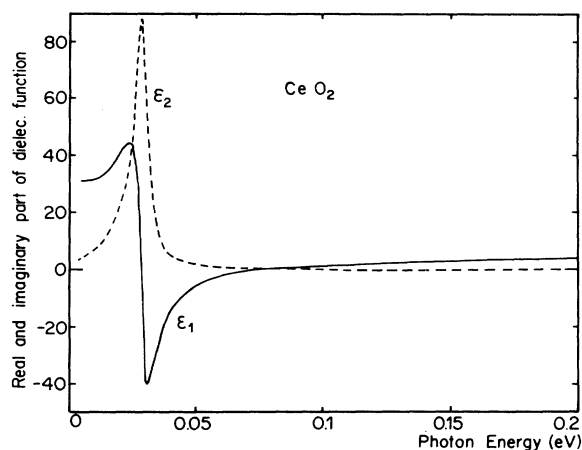


FIG. 3. The dielectric functions  $\epsilon_1$  and  $\epsilon_2$  of  $\text{CeO}_2$  in the low-energy photon range.

oscillator strengths cannot be observed in the reflectivity spectrum. Such transitions are, e.g., intra- $4f$  transitions having an oscillator strength of about  $10^{-6}$ . In order to test whether there is any  $4f$  occupation in the ground state as in  $\text{Ce}^{3+}$  ions ( $4f^1$ ) we can perform an optical transmission experiment in which such intra- $4f$  transitions can readily be seen.<sup>2</sup> One can expect a transition to the next spin-orbit state  $^2F_{5/2} \rightarrow ^2F_{7/2}$  which in the free atom is at  $2300 \text{ cm}^{-1}$  or  $4.3 \mu\text{m}$ . The material which definitely has 100%  $\text{Ce}^{3+}$  ions is  $\text{CeF}_3$ , which we thus wanted to compare with  $\text{CeO}_2$ . Since we only had polycrystalline  $\text{CeF}_3$  we used also polycrystalline  $\text{CeO}_2$ , and we performed between  $0.4$  and  $2.5 \mu\text{m}$  an optical reemission experiment in an Ulbricht sphere, the results of which are shown in Fig. 4(a). This experiment, in fact, corresponds to an optical transmission experiment, but nothing spectacular is seen in this wavelength range, except that both materials are highly transparent. Since the spectrometer used for longer wavelengths was not equipped with an Ulbricht sphere, we used mixtures of 1% or 2%  $\text{CeO}_2$  or  $\text{CeF}_3$  in KBr pressed pills on which

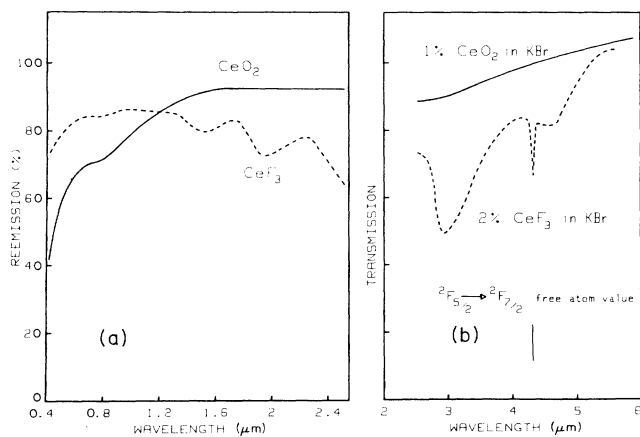


FIG. 4. (a) Reemission of polycrystalline  $\text{CeO}_2$  and  $\text{CeF}_3$ . (b) Optical transmission on pressed KBr pills containing 1%  $\text{CeO}_2$  and 2%  $\text{CeF}_3$ , respectively.

we made transmission experiments [Fig. 4(b)]. In  $\text{CeF}_3$  the intra- $4f$  transition is clearly observable, whereas in  $\text{CeO}_2$  nothing similar is found.

Furthermore, it has been shown in Ref. 2 that the magnetic susceptibility of  $\text{CeO}_2$  is paramagnetic, but corresponds only to a spin concentration on the order of  $1/1000$  per formula unit that can be easily associated with  $\text{Ce}^{3+}$  impurities induced by residual oxygen vacancies. The magnetization at 90 kOe is also a factor 1000 less than compared with  $\text{CeF}_3$ , which again is due to  $\text{Ce}^{3+}$  impurities.

## DISCUSSION

The  $\epsilon_2$  spectrum in the visible and ultraviolet energy range presents (Fig. 2) a well-defined structure at 3.9 eV with a bandwidth of about 3.2 eV and a more complex structure near 9 eV. The highest occupied valence band in  $\text{CeO}_2$  is a "nominal"  $2p$  band,<sup>19</sup> where the  $\Gamma_{15}$  originating bands have some metal  $f$  character, but, in contrast to fcc-structure materials, the bottom of the  $p$  band, originating in  $\Gamma_{25}$ , has metal  $d$  character in this  $\text{CaF}_2$  structure. If we associate the lowest-energy optical transition near 4 eV with a transition from the  $2p$ -like valence band into empty  $4f$  states of cerium, we must realize that transitions from the  $\Gamma_{15}$  part of ( $p \rightarrow f$ ,  $f \rightarrow f$ ), in principle, are forbidden, or in the solid have a rather low oscillator strength. However, transitions originating from the  $\Gamma_{25}$   $d$ -like part are expected to have a rather large oscillator strength. In total, we have in the nominal  $p$  band 48 electrons per cell and  $6.319 \times 10^{21}$  cells per  $\text{cm}^3$ , but only half of them have  $d$  character. If we now calculate the oscillator strength of the lowest-energy transition at 4 eV by fitting the experimental data with a classical Lorentzian oscillator, we find  $f=0.1$ , which is in fair agreement with a  $d \rightarrow f$  transition from the nominal  $p$  band.

Since the empty  $f$  states of Ce in this compound certainly are localized the measured width of the 4-eV peak must be entirely ascribed to the width of the oxygen nominal  $p$  band. The measured width of 3.2 eV is in perfect agreement with values from the band-structure calculation of  $\text{CeO}_2$ ,<sup>19</sup> and it also agrees with the bandwidth determined from XPS valence-band measurements.<sup>7,20,21</sup>

A further support that transitions involving the  $4f$  states of Ce are present in the 4-eV peak of  $\epsilon_2$  is demonstrated in the inset of Fig. 2. This blown-up version of the 4-eV peak clearly shows a trapezoidal shape 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. Since optical transitions measure energy differences between initial and final states it is not obvious from this measurement alone whether the  $4f^1$  state is occupied or empty, acting as the initial or final state of the optical transition.

In contrast to high-energy XPS and similar methods, optics has the unique possibility to vary the excitation energy over many decades of photon energy towards very low energies. It is thus possible to clearly distinguish between a  $4f^1$  initial- or final-state excitation: When the  $4f^1$  state is occupied and thus the initial state of an optical transition we will find, with a photon energy corresponding to the spin-orbit splitting, an intra- $4f$  excitation.

This energy is at 0.28 eV, 2300 cm<sup>-1</sup>, or 4.3 μm. In Fig. 4(b) we give evidence for this in two examples. In CeF<sub>3</sub> this transition is clearly observed and thus the 4*f*<sup>1</sup> state is the occupied and initial state of the optical transition. In CeO<sub>2</sub> this transition is absent and thus the 4*f*<sup>1</sup> state is not occupied and must be the final state in the 4-eV transition of Fig. 2. With regard to the possibility of a fractional occupation of the 4*f*<sup>1</sup> state in CeO<sub>2</sub> in the sense of intermediate valence, we can state from the detection limit in Fig. 4 that a possible occupation must be less than 5%, in agreement with the susceptibility and magnetization results mentioned above. This is in sharp contrast to statements derived from *L*-edge<sup>1</sup> and other core-level spectroscopies, e.g., Refs. 3–6 regarding valence mixing and thus partial occupation of the 4*f*<sup>1</sup> state near 50%.

These optical techniques to decide on the initial or final state of 4*f* transitions have been known and practiced for a long time. To illustrate this we refer to the compound Eu<sub>3</sub>O<sub>4</sub>, a mixed-valence material containing Eu<sup>2+</sup> and Eu<sup>3+</sup> ions.<sup>11</sup>

At about 9 eV a double-peaked very broad structure is observed in Fig. 2. A fit with Lorentz oscillators gives us an oscillator strength of about  $f = 0.45$ , a value typical for a  $p \rightarrow d$  transition, which we expect at about this energy and which is in agreement with the band-structure calculation.<sup>19</sup> We then can assume that the two peaks correspond to transitions into the 10*Dq* crystal-field-split *d* conduction band. In the CaF<sub>2</sub> crystal structure the *d* band is split into a lower-lying, double-degenerate 5*d<sub>g</sub>* and a higher-lying, triple-degenerate 5*d<sub>2g</sub>* band. The crystal-field splitting 10*Dq* taken from Fig. 2 amounts to about 2 eV. This value can be compared with a crystal-field splitting of 2.8 eV in UO<sub>2</sub>,<sup>22</sup> having the same crystal structure. However, in the uranium compound the *d* band is made up of 6*d* wave functions, in contrast to the 5*d* ones in the cerium compound. Since 6*d* wave functions are much further from the ion core than 5*d* wave functions they are much more susceptible to the crystal field, thus explaining the larger splitting in UO<sub>2</sub> compared with the one in CeO<sub>2</sub>. The total density of states of CeO<sub>2</sub> is sketched in Fig. 5, where the position of the Fermi energy is definitely below the empty 4*f* states, the exact position depending on imperfections of the lattice.

The Kramers-Kronig transformation permits us to calculate the optical dielectric constant  $\epsilon_{\text{opt}}$  via the integration of the electronic transitions above about 2 eV. The value obtained is 4.7 and this number will be used in the discussion of the phonon properties of CeO<sub>2</sub>.

The infrared spectrum shows a region of high reflectivity which clearly must be associated with polar lattice vibrations. We analyzed this structure in terms of one damped harmonic oscillator.<sup>23</sup> The real and imagi-

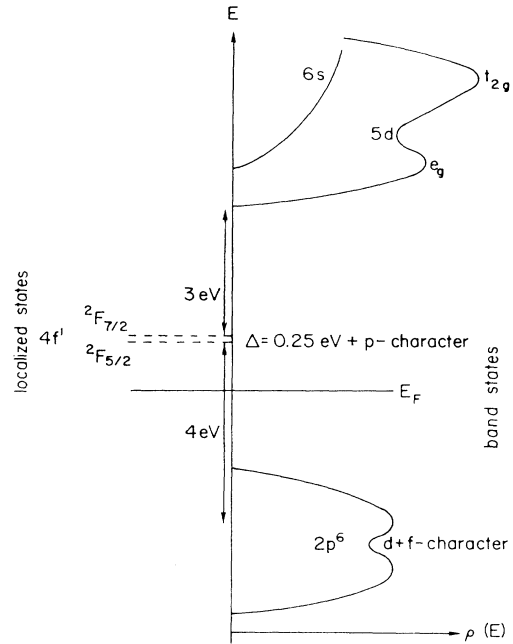


FIG. 5. Sketch of the electronic density of states of CeO<sub>2</sub>.

nary parts of the dielectric constant  $\epsilon(\omega)$  are defined as

$$\begin{aligned} \epsilon_1 &= n^2 - k^2 \\ &= \epsilon_{\text{opt}} + \frac{(\epsilon_{\text{stat}} - \epsilon_{\text{opt}})[1 - (\omega/\omega_{\text{TO}})]^2}{[1 - (\omega/\omega_{\text{TO}})^2]^2 + (\omega/\omega_{\text{TO}})^2(\gamma/\omega_{\text{TO}})^2}, \\ \epsilon_2 &= 2nk = \frac{(\epsilon_{\text{stat}} - \epsilon_{\text{opt}})(\gamma/\omega_{\text{TO}})(\omega/\omega_{\text{TO}})}{[1 - (\omega/\omega_{\text{TO}})^2]^2 + (\omega/\omega_{\text{TO}})^2(\gamma/\omega_{\text{TO}})^2}, \end{aligned}$$

where the characteristic frequency  $\omega_{\text{TO}}$  is associated with the transverse-optical frequency of the  $T_{1u}$  mode,  $\epsilon_{\text{stat}}$  is the low-frequency dielectric constant,  $\epsilon_{\text{opt}}$  is the high-frequency dielectric constant, and  $\gamma$  is a damping term. From the Lyddane-Sachs-Teller relation it is possible to also obtain  $\omega_{\text{LO}}$ , the longitudinal-optical-phonon frequency. We have fitted the data with a self-consistent computer program. The results of the analysis yield the values shown in Table I. Some caution should be exercised in dealing with  $\gamma$  since this parameter depends on an accurate measurement of the maximum reflectivity, but in our crystals a small uncertainty may result from surface effects. In an ideal crystal  $\gamma$  would be very small. In a real crystal the major contribution to  $\gamma$  is generally attributed to mechanical anharmonicity. However, the frequencies  $\omega_{\text{TO}}$  and  $\omega_{\text{LO}}$  are well defined and one can do very interesting calculations concerning the ionicity from

TABLE I. Results of the phonon-mode analysis.

Damping coefficient $\gamma$ (eV)	Phonon frequencies		Dielectric constants		Effective charge
	TO (eV)	LO (eV)	$\epsilon_{\text{stat}}$	$\epsilon_{\text{opt}}$	
0.008	0.027	0.074	35.3	4.7	2.48

them. One convenient approach to define the degree of polar character in an ionic crystal is based on the concept of an effective ionic charge  $e^*$ , which can be defined from a classical treatment of the dielectric polarization due to lattice vibrations. The well-known Szigeti expression for a microscopic effective charge provides<sup>23,24</sup>

$$e^*/e = \frac{3\omega_{\text{TO}}}{(\epsilon_{\text{opt}} + 2)e} \left( \frac{\epsilon_{\text{stat}} - \epsilon_{\text{opt}}}{4\pi} \right)^{1/2} \left( \frac{\mu}{N} \right)^{1/2} \\ = 2.48 .$$

Here  $N$  is the number of dipoles per unit volume and  $\mu$  is the reduced mass. Assuming  $N$  equal to the number of cerium ions  $N = 25.3 \times 10^{21} \text{ cm}^{-3}$  and  $\mu = 26.05$  (we considered a dipole formed by one positive Ce ion and two negative oxygen ions), we obtained a value for the effective charge of 2.48 (Table I). If we compare this result with the band-structure calculations<sup>19</sup> we realize that it is in excellent agreement with the muffin-tin charge of cerium, though somewhat larger than the reanalyzed charge. To analyze our data we made a very simple model assuming non-overlapping ions. For an insulator this may be quite a good approximation. However, the value of the effective charge of the metal ion is not four but only 2.48. We have to ascribe this discrepancy to partial covalent bonding as argued also in Ref. 19. In  $\text{UO}_2$ , having the same crystal structure as  $\text{CeO}_2$ , the effective charge has been found to be 2.33.<sup>22</sup> Thus our method provides a direct measurement of the degree of covalency or ionicity and we can clearly state and prove by experiment that  $\text{CeO}_2$  is a covalent insulator and not of intermediate valence.

Then, where is the problem with the interpretation of high-energy, especially core-level, spectroscopy? One aspect is the shake-up and shake-down process in  $4f$  states, already mentioned in the Introduction. The creation of a core hole will necessarily lead to a renormalization of outer electron states, especially the  $4f$  states. Empty  $4f$  states can thus be pulled below the Fermi level, which could be interpreted as a partial occupation of the initial state. In an early core-level XPS experiment this effect has been clearly recognized.<sup>25</sup>

A second aspect is the covalency of a  $4f$  compound, such as, e.g.,  $\text{CeO}_2$ . Covalency means that metal wave functions are found in nominal anion bands and vice versa. In the case of a  $4f$  compound  $f$  and  $d$  wave functions are found in the  $p$  valence band of oxygen and there is  $p$  character in the  $4f$  states. This does not mean that empty  $4f$  states are now partially occupied. More simply this can be proven by looking at another oxide, e.g.,  $\text{ZnO}$ : the  $4s$  band of Zn is empty and the  $2p$  band of oxygen is full; however, the  $s$  band, due to covalency, has some  $p$  character and the  $p$  band some  $s$  character.  $\text{ZnO}$  is still an *insulator* at low temperatures. The partial  $f$  and  $d$  character in the valence  $p$  band of  $\text{CeO}_2$  has been calculated by Koelling *et al.*<sup>19</sup>

Generally speaking, one uses for the description of the ground state of a  $4f$  compound the Anderson Hamiltonian as introduced by Gunnarson-Schönhammer.<sup>13</sup>

$$H = \sum_{k,\sigma} E_k^c n_{k\sigma_c} + \sum_{k,\sigma} E_k^v n_{k\sigma_v} \\ + E_f \sum_{m,\sigma} n_{m\sigma} + U \sum'_{m,m',\sigma,\sigma'} n_{m\sigma} n_{m'\sigma'} \\ + a \sum_{k,m,\sigma_c} (V_{km_c} a_{k\sigma_c}^\dagger c_{m\sigma} + \text{H.c.}) \\ + b \sum_{k,m,\sigma_v} (V_{km_v} a_{k\sigma_v}^\dagger c_{m\sigma} + \text{H.c.})$$

with  $E_k$  the energy of a conduction electron,  $E_f$  the energy of an electron in the  $f$  level, and  $U$  the Coulomb repulsion between two  $f$  electrons.  $n_{m\sigma}$  is the operator of the  $4f$ -state occupation with azimuthal quantum number  $m$  and spin quantum number  $\sigma$ . The indices  $c$  and  $v$  stand for conduction and valence band, respectively. The coupling between a  $4f$  state and the conduction band is described by the third line, where  $a_{k\sigma_c}^\dagger$  is the creation operator of an electron in the conduction band and  $c_{m\sigma}$  is the annihilation operator of an electron in the  $4f$  level.  $V_{km_c}$  is the hybridization matrix element between the two states. The factor  $a$  in front of the third line is a number between zero and one. The Hamiltonian introduced by Ref. 13 ends here and uses  $a = 1$ , i.e., it uses only the hybridization between the  $4f$  states and a conduction band, usually of  $5d$  character. It thus describes intermediate valence. Because of covalency, and every compound has some degree of covalency, we have  $f$  character also in the valence band and another mixing matrix element  $V_{km_v}$  exists with the corresponding fourth line in the Hamiltonian, with a prefactor  $b = 1 - a$ . In general, more terms may exist when  $f$  character is found also in other bands. This is especially also true in intermetallic alloys where one generally does not speak of covalency. A distinction to intermediate valence is then necessary. There one has a mixing of two cation states ( $f$ - $d$ , not on the same ion), whereas in covalent compounds one has a mixing of cation and anion states, or in an alloy one has a mixing of cation and alloy partner states which has nothing to do with intermediate valence. *Intermediate valency is not covalency.*

The problem then rests with distinguishing between the third and the fourth line in the Hamiltonian or determining the factors  $a$  and  $b$ . This is not possible with XPS or core-level spectroscopy alone, which then cannot distinguish between intermediate valence and covalence. In Refs. 1 and 3–6 the fourth line has simply been neglected and as a consequence  $\text{CeO}_2$  has been claimed to be intermediate valence.

In Ref. 7 it has been assumed that the third line is absent, thus the  $4f$  level is empty, which has been concluded mainly on the basis of a BIS experiment, thus the material is covalent in agreement with band-structure calculations.<sup>19</sup> What one needs, however, is a measurement free of any assumptions. In our opinion this is given by the infrared measurements discussed above, where one clearly can see, within the precision of the experiment, whether the  $4f$  state is occupied or not.

Assuming now that a material is truly of intermediate valence, as, e.g.,  $\text{SmB}_6$  "gold"  $\text{SmS}$ ,  $\text{YbB}_{12}$ , or  $\text{TmSe}$ , all being compounds with a certain degree of covalency, or

YbCuAl and CePd<sub>3</sub>, having  $f$  character also in the non-rare-earth metal, it becomes clear that the determination of the factors  $a$  and  $b$  will be extremely difficult.

Instead one usually neglects the fourth line in the above Hamiltonian. In a first approximation this is legitimate for not being able to do better. However, one should then clearly realize that the determination of the degree of valence mixing is only precise to within, let us say 10%, and not within the second digit after the point.<sup>26</sup> We are not claiming that other methods to determine the degree of valence mixing are more precise, but that is the present state of the art.

### CONCLUSION

It can be said that hardly any other material has stimulated research in such a short time and produced so many papers with adverse view points than CeO<sub>2</sub>. On the other hand, with no other material has it been possible to such an extent to point to some problems of high-energy and

especially core-level spectroscopies regarding the occupation of  $f$  levels, and thus to determine the degree of valence mixing. It is clear that in doing so one must consider all bands in which  $f$  wave functions appear, and as a first and obvious case covalency is an important aspect. In the future the question should rather be addressed as to whether high-energy methods can add an important contribution to the determination of the degree of covalency and how it can distinguish (if at all) between intermediate valency and covalency. This point has been considered already in a paper on CeF<sub>4</sub>, another covalent insulator, also using XPS and core-level spectroscopy.<sup>27</sup>

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