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Electronic Structure of CeN Studied by X-Ray-Photoemission Spectroscopy

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The core levels and the valence-band region of CeN have been studied by x-ray photoemission. Clear evidence is found that Ce has a mixed valence between 3 and 4 in this compound. A comparison of the $4d$ spectra of the Ce pnictides and of pure Ce at different temperatures leads to the conclusion that the α phase of this metal corresponds very likely to an intermediate valence.

In many respects Ce shows quite exceptional properties, both in the pure metal and in compounds. These properties are related to the fact that Ce is the first element of the lanthanide series; its $4f$ shell is occupied by at most one single electron which has the largest orbital radius of the whole series and is expected to be very weakly bound. It is not well established today whether the peculiar behavior of Ce, which manifests itself in anomalous changes of the lattice constants, has to be attributed to a delocalization of the $4f$ states forming a band or to an intermediate valence arising from an interplay of $4f$ states with $5d$ states.

The $\gamma \rightarrow \alpha$ transition in pure metallic Ce provides apparently one of the clearest examples of a transition driven by a configuration modification in the outermost electronic levels. The magnetic and lattice constant data¹ can be explained in a promotion model by a valence change from 3.0 to 3.7, which should be clearly reflected by photoemission spectra. Unfortunately the hydrostatic pressure required to produce the α phase at low temperature cannot be realized at the pres-

ent time in the existing photoelectron spectrometers. The available spectra^{2,3} correspond to the trivalent γ phase (with only a low concentration of α phase for cooled samples). Until now it has not been possible to locate by photoemission the energy position of the occupied $4f$ level in γ -Ce. An attempt has been made to analyze the x-ray-photoemission spectroscopy (XPS) spectra of the valence bands of La, Ce, and their aluminum alloys. An ingenious but questionable manipulation of the data places the $4f$ states 0.5 eV below the Fermi energy.⁴

In the XPS spectra of Ce halides, the position of the $4f$ level could be determined by comparison with La halides.⁵ In CeF_3 , only an isolated peak above the valence states is observed. In the available spectra of Ce pnictides (CeAs , CeSb) the situation is again quite confusing.⁶ No characteristic $4f$ structure is found, although it is established that these compounds are trivalent at room temperature. Magnetic data might provide indications of a valence modification at low temperatures.⁷ In addition, CeP shows an anomalous volume contraction at a pressure of 100 kbar,⁸

which is a further indication that this compound is not far from a valence instability under normal conditions. Among the Ce pnictides, CeN is known to behave anomalously. The lattice constant is 5.019 Å at room temperature but an interpolation between the values LaN, PrN, and NdN yields a hypothetical lattice constant of 5.24 Å for pure trivalent CeN. Assuming that a change of 0.48 Å takes place in a complete transition from trivalent to tetravalent CeN,¹ one can expect at room temperature a valence of 3.46. The magnetic properties, however, do not provide a straightforward confirmation of this situation.⁹

We have undertaken an XPS study of this exceptional compound with the hope that it will also help us to understand the electronic structure of the other Ce pnictides and of the pure metal. In a first step, CeN was prepared by direct reaction of turnings from Ce metal with purified nitrogen ($p = 1.5$ atm) in an open Mo crucible at 2000°C. Single crystals were grown by sublimation in a sealed W crucible at 2200°C ($\Delta T = 85^\circ\text{C}$). A chemical analysis showed a few-percent excess of Ce metal. The samples were clamped to the holder and transferred into the spectrometer without leaving a dry atmosphere of Ar. A pure Al₂O₃ file and a tungsten brush were used to scratch the surface. The vacuum could be maintained in the low 10^{-11} -Torr range during the cleaning procedure, and the measurements which were performed in a high-resolution XPS instrument are described elsewhere.¹⁰

The XPS spectra of the core levels of Ce are expected to reflect the mixed valence in CeN. Figure 1 shows the Ce 4*d* spectra of the pure metal and of CeN. At room temperature, the configuration of metallic Ce is trivalent and the spectrum shows the multiplets arising from the interaction of the 4*d* hole with the 4*f* electron. Similar 4*d* spectra have also been obtained in the trivalent compounds CeSb and CeAs.⁶ For the low-temperature measurement, Ce films were evaporated on clean thorium cooled at liquid-nitrogen temperature. This procedure is supposed to favor the formation of the α phase. The only difference in the low-temperature spectrum is the appearance of two new peaks at approximately 10 eV below the main structures. They correspond to the fraction of tetravalent α -Ce formed in the film. Similar peaks have already been observed in Ce and CeTh alloys at low temperature.³ From an interpolation between La and Lu,¹¹ one obtains for Ce a spin-orbit splitting of 3.36 eV, in good agreement with the value of 3.2 eV measured in

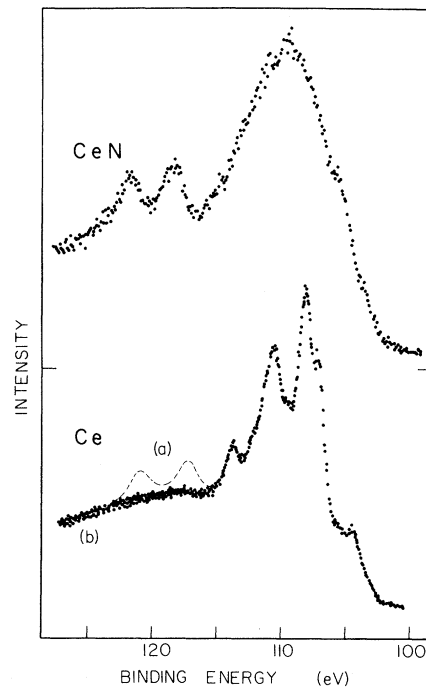


FIG. 1. XPS spectrum of the Ce 4*d* level in CeN and metallic Ce: *a*, at liquid-nitrogen temperatures; *b*, at room temperature.

the spectrum¹² of CeF₄ and the present value of 3.3 eV. The same 4*d* peaks corresponding to the Ce⁴⁺ configuration are found in the spectrum of CeN (Fig. 1), demonstrating the mixed valence of this compound. The energy shift between the barycenters of the structures corresponding to Ce³⁺ and Ce⁴⁺ is roughly 10 eV, in agreement with the observation made for Sm²⁺ and Sm³⁺.¹³ The Ce³⁺ 4*d* spectrum is broader than in pure trivalent solids. This is possibly explained by a significant metal excess at the surface, which brings an intensity contribution shifted by approximately 1.2 eV. For the same reason the intensities of these structures cannot be used to determine the ratio of Ce³⁺ and Ce⁴⁺ in CeN. In Fig. 2, besides shakeup satellites¹² and a broadening due to a Ce excess, the 3*d* spectrum shows clearly a superposition of spin-orbit-split peaks corresponding to the two initial configurations. A slightly larger separation of 11.1 eV is found for this deeper shell. The 3*d* spectrum of CeSb accounts only for a trivalent configuration.⁶ This analysis of the core-level spectra demonstrates unambiguously the mixed valence in CeN.

The spectrum of the outermost levels reproduced in Fig. 3 yields further evidence of the mixed valence. The broad structures between 2

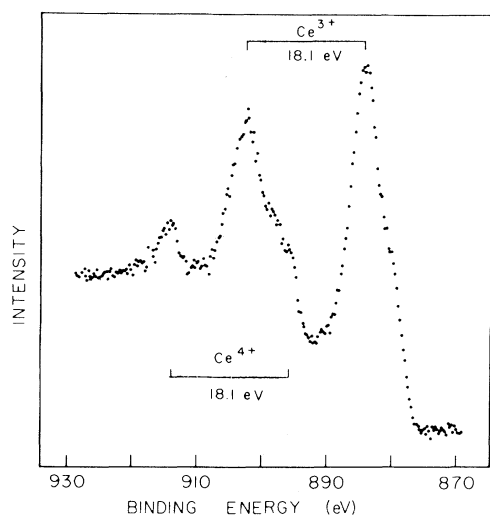


FIG. 2. XPS spectrum of the Ce 3d level in CeN.

and 6 eV correspond to the $2p$ band of nitrogen whereas the very narrow peak pinned at E_F is due to the additional electron of Ce, fluctuating between d and f symmetry. We believe that the $4f$ feature is superimposed on the spectrum of the d states, forming a band which might extend over 2–3 eV below E_F . The excess of metal brings also s contribution in this region but it cannot account for the narrow peak which has a base width of 0.5 eV. The correlation energy U for the $4f$ electrons in Ce is surely larger than 1 eV so that a model based on the formation of a band of delocalized $4f$ states¹⁴ seems inappropriate in this case. The valence-band spectra of CeAs and CeSb show that these compounds are semimetallic.⁶ The $4f$ states, surprisingly, do not appear as peaks and cannot even be located unambiguously. This apparent absence of $4f$ states seems at first in contradiction with the spectrum of CeN. It has been shown, however, that the lifetime broadening can become very important in nearly empty $4f$ shells as a consequence of interatomic Auger processes.¹⁵ In CeN, the $4f$ level being pinned at E_F , the Auger processes are energetically forbidden. This is not the case for the other Ce pnictides in which the $4f$ electron is probably located a few eV below E_F . The decrease of the ionic character from N to Bi is also expected to enhance interatomic Auger processes. CeP might be an intermediate case with observable $4f$ states not far below E_F .

The present demonstration that in CeN the $4f$ states are localized and located at E_F is important for understanding the other Ce pnictides

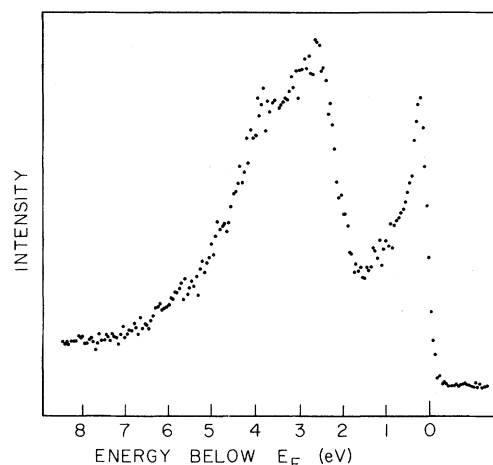


FIG. 3. XPS spectrum of the valence-band region of CeN.

which have larger lattice constants. It shows that the absence of this level from the spectra can be considered as an indirect proof that it is highly localized and has a sizable binding energy related to the Fermi level. For the pure metal, we have found signs which militate in the favor of the promotion model to explain the transition from the γ phase to the α phase. The fact that the $4d$ spectra of CeN and of metallic Ce at low temperature contain features of both configurations cannot be explained in a model keeping constant the $4f$ population and assuming the formation of a band. It remains, however, to be explained why the $4f$ electron, which must be immediately below E_F in γ -Ce, is not observed in photoemission. Lifetime broadening can hardly be invoked in this case but it might be a question of experimental resolution if the $4f$ peak is just located in a very steep increase of the d band at E_F . Further experimental efforts will be necessary to give a final answer to this puzzling question.

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Recombination Luminescence from "Hot" Carriers in Electron-Hole Droplets in Stressed Ge

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We have observed luminescence lines from "hot" free excitons and from recombination of "hot" electrons within electron-hole droplets in Ge under uniform $\langle 111 \rangle$ uniaxial stress. Our results suggest that both "hot" and "cold" electrons coexist in the same electron-hole droplets. We have also measured the total lifetime of the hot electrons, which is in good agreement with intervalley relaxation by electron-electron scattering.

Experimental studies¹⁻⁴ of electron-hole droplets (EHD) in Ge under uniform $\langle 111 \rangle$ uniaxial stress have been of considerable interest because of the simplifications in the band structure allow a stringent test of the theoretical calculations.⁵⁻⁷ Unstressed germanium has a fourfold-degenerate conduction band at the L points of the Brillouin zone and doubly degenerate valance band at the Γ point. Under $\langle 111 \rangle$ uniaxial stress, the conduction-band ellipsoid along the $\langle 111 \rangle$ axis shifts to lower energy; the other three to higher energy. Both previous theoretical and experimental studies suggested that intervalley scattering is sufficiently fast⁶; complete depopulation of electrons in the three up-shifted conduction-band ellipsoids would occur for a $\langle 111 \rangle$ uniaxial stress near 3 kg/mm²,^{1,4} corresponding to a splitting between conduction bands greater than the Fermi energy of electrons. In this Letter we report new experimental results which show that intervalley-scattering time is actually rather long, and significant population in the up-shifted conduction bands persists up to a stress of 9 kg/mm². This gives rise to the first observation of "hot" EHD luminescence line from "hot"-electron recombination

within electron-hole droplets. From the luminescence spectrum we have determined the densities of "hot" and "cold" electrons in the electron-hole droplets and the condensation energies of "hot" and "cold" free excitons (FE). We have also measured directly the total lifetime of the hot electrons, which agrees well with intervalley relaxation by electron-electron scattering.

The samples used in our experiments were rectangular solids ($12 \times 3 \times 3$ mm³) of ultrapure germanium. The samples were either chemically polished with Syton or mechanically polished and then etched in CP-4 solution. The samples were glued between two polished copper pistons. Two differently designed stress devices were used. In one device, the force was applied to the pistons by a push rod held in place by a pair of bellows; in the second device, the force was applied through two ball bearings. The purpose of the bellows and the ball bearings was to eliminate nonvertical forces. The Ge crystals were photoexcited by a focused continuous-wave Ar⁺-laser beam (5145 Å) in spectroscopic measurements and by a weakly focused (focal spot ≈ 1 mm²) 1- μ s pulsed dye-laser beam (6600 Å) in lifetime