

X-ray photoemission study of Ce-pnictides

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All the Ce pnictides crystallize in the NaCl structure with lattice constant increasing systematically from CeN to CeBi. Since Ce has the largest $4f$ -orbital radius in the entire lanthanide series, it is quite interesting to follow the evolution of this level as the distance between the Ce atoms is varied. The core levels and the valence-band region of CeN, CeP, CeAs, and CeSb have been studied by high-resolution x-ray photoemission spectroscopy. The $4d$ and $3d$ core-level spectra of Ce show clearly that the $4f$ state remains strictly localized in all compounds. In CeN a superposition of lines corresponding to two valences is found which reveals the intermediate valence character of this compound. In the valence-band spectrum, the $4f$ level is found to be pinned at the Fermi level and superimposed on the $5d$ states. The extended valence states originating from the anion p states are located at higher binding energies. In the compounds of heavier rare-earth elements the $4f$ state moves away from the Fermi level and gradually overlaps in energy with p states, so that the probability for interatomic Auger processes in the photoemission final state increases rapidly. The natural width of the $4f$ peak is already 0.8 eV in CeP, and becomes so large in CeAs and CeSb that this line can no longer be unambiguously identified in the other valence-band structure. Finally, it can be concluded from the similarity of the $4d$ spectrum of metallic Ce and CeN that the $4f$ electron remains localized in the α phase of this metal.

I. INTRODUCTION

The rare-earth monopnictides have generated many experimental and theoretical investigations in recent years. The magnetic and thermal properties of this class of compounds are particularly interesting,¹ though not completely understood. One of the main difficulties in the experimental study of rare-earth monopnictides is certainly the preparation of homogeneous, stoichiometric, and, as far as possible, single-crystal samples of useful dimensions. Since many physical properties show a marked dependence on deviation from ideal chemical composition or on lattice imperfections, more effort should be devoted to a better characterization of samples used in such measurements.

X-ray photoemission spectroscopy (XPS) yields information about the overall energy distribution of the occupied electronic states, which is not expected to depend critically upon small deviations from crystal perfection. One should be careful, however, when dealing with intermediate valences that can arise or be stabilized by small amounts of impurity. The surface sensitivity of XPS can furthermore generate serious problems in the study of solids with unstable valence, because even in the best vacuum the equilibrium state of a clean surface might be structurally and electronically different from that of the bulk.² In spite of such

uncertainties, which cannot always be completely eliminated, the Ce monopnictides represent a very interesting subject for an XPS study. All of the compounds of this series have the NaCl structure. Their lattice constants at room temperature increase roughly linearly from CeP (5.94 Å) to CeBi (6.50 Å), offering the opportunity to follow the evolution of the $4f^1$ level as a function of the interatomic separation. CeN is somewhat unusual in that its lattice constant of 5.019 Å is much smaller than the value of 5.24 Å expected by extrapolation from the monopnictides of the neighboring light rare-earth elements. Furthermore CeN is a gold-colored metal whereas the other compounds have the appearance of semiconductors or semimetals. This break in the properties of the Ce monopnictides which occurs for CeN, is attributable to a modification of the electronic structure involving the $4f$ level.³ A similar situation is encountered in the α -phase of metallic Ce. We believe that the present photoemission study yields an unambiguous picture of the density of the occupied states in these compounds.

II. XPS IN RARE-EARTH STUDIES

It was recognized early that low-energy ultraviolet photoemission spectroscopy (UPS) is usually unsuitable for the study of $4f$ levels because of

their low photoelectric cross section near threshold. At 50 eV the $4f$ cross section has already increased dramatically.⁴ This energy range is accessible with resonance line sources or synchrotron radiation, but it corresponds to the highest surface sensitivity which occurs at kinetic energies between 30 and 200 eV. If one is chiefly interested in bulk properties, photons of higher energies are more suitable, and XPS remains the best technique for studying $4f$ electrons in the rare-earth elements. In this case, the valence states, which have comparable binding energies, usually have smaller cross sections than the $4f$ electrons, but not so small that they would be obscured by the $4f$ response. Since the effective $4f$ intra-atomic correlation energy U_{eff} is very large (6–10 eV), the energy of the $4f$ level is a discrete function of the number of electrons. The corresponding photoelectron peaks normally appear a few eV below the Fermi level, whose position is determined by the filling of the valence states. The spectra resulting from the emission of one $4f$ electron generally contain many separate lines which account for the parent terms of the initial ground state. This is now well understood^{5,6} and is commonly used as a tool for determining the initial $4f$ configuration. Ce contains, at most, one $4f$ electron so that only a single peak is expected in its photoemission spectrum. On the other hand, the creation of a hole in a core shell other than the $4f$ gives rise to a set of final states corresponding to the multiplet coupling of this hole with the incomplete $4f$ shell. (It has spherical symmetry only if the occupation is 7 or 14.) This effect is particularly spectacular for the $4d$ subshell, which has the same principal quantum number as the $4f$. It is weaker in the case of a $3d$ hole, because of the smaller $3d$ - $4f$ coupling. The $3d$ XPS spectra consist essentially of two spin-orbit peaks. However, strong "satellites lines" of a different origin are often observed. They are related to the screening mechanism of the deep hole and are also indirectly due to the presence of the incomplete localized $4f$ shell near E_F .⁷

III. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUES

The method of sample preparation is, in principle, the same in all cases. The crucial problem is to determine the optimum conditions for each particular compound. First, a prereaction is performed between the elements, then crystals are grown in sealed tungsten or molybdenum crucibles at temperatures above 2000°C. Depending upon the temperature and its distribution along the crucible, recrystallization may occur directly in the pellet, or the material may sublime, resulting in

crystal growth at the cold end of the crucible. In some cases the samples were subsequently annealed for a few weeks at constant temperature. The quality of the compounds obtained by this method is rather unpredictable¹ even if one keeps all the conditions under strict control. However, we do believe that the information extracted from our XPS results is not seriously influenced by the imperfections of the crystals. In the case of CeN, which is the most critical compound of this series, we have checked that different samples yield identical results.

For XPS measurements, the samples were clamped or glued to the holder, keeping the exposure to air as short as possible, and in the case of CeN working in an atmosphere of dry Ar. Clean surfaces were produced *in situ*, either by cleaving the crystal or by abrading the surface with a tungsten brush or an Al_2O_3 file. The usual core-level control spectra were repeated at regular intervals to ensure that signals originating from surface contamination were making only insignificant contributions to the spectra. Two different XPS instruments, both with monochromatized Al $K\alpha$ radiation were used: for CeN and CeP, a modified AEI spectrometer⁸ with a total instrumental FWHM slightly better than 0.3 eV, and for CeAs and CeSb a Hewlett-Packard spectrometer with a FWHM of 0.55 eV. The difference in the resolution used for the different compounds is not likely to result in misleading interpretations, because the best resolution is only useful in the valence bands of CeN and maybe CeP. In the other cases, the natural width of the excited states is expected to dominate the broadening of the structures. The binding-energy scales are always referred to the Fermi level, which is defined by the kinetic energy where it is observed in the valence-band spectrum of a Au film evaporated on the top of the sample. No charging effect was detected in these compounds which are in no sense of the work good insulators, so that this calibration procedure is expected to be reliable and accurate.

IV. DEEP CORE LEVELS

The photoexcitation of $3d$ core levels in Ce produces relatively simple spectra, as previously mentioned. In the upper part of Fig. 1 the spectrum of LaSb is shown for reference, because in La the $4f$ levels are empty. The two main peaks, which are undoubtedly due to the spin-orbit splitting of the $3d$ level, have a rather unusual shape. The high-binding-energy side of photoelectron lines can be distorted by intrinsic effects involving final states containing some excitation, or by extrinsic energy losses of the photoelectrons as

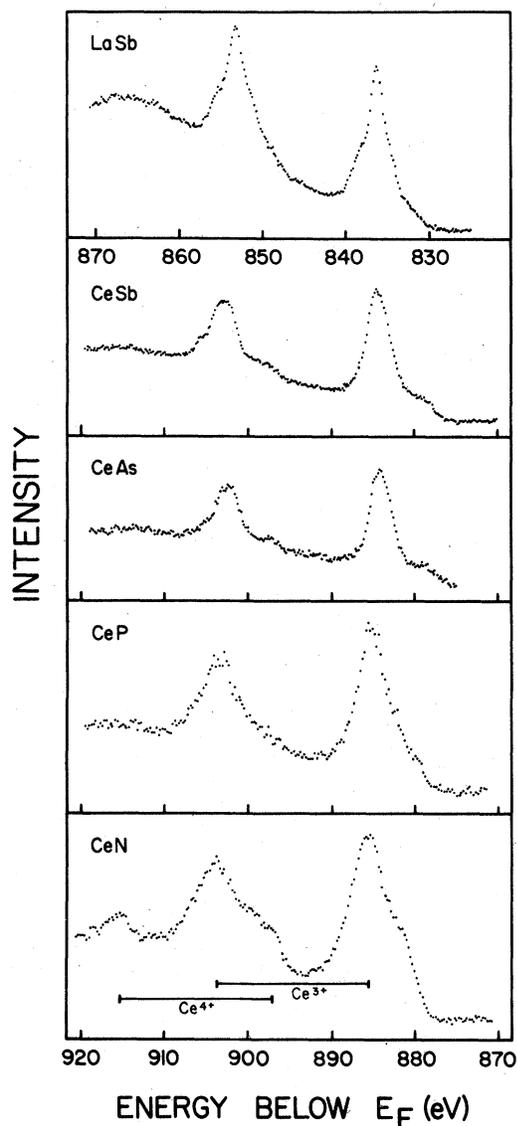


FIG. 1. XPS spectra of the $3d$ core levels of LaSb and Ce pnictides.

they traverse the sample. In LaSb, the shoulder at a binding energy slightly larger than the main line is probably due to an energy loss. This superposition is consistent with the location of the main valence-band peak 2 eV below E_F (Fig. 3). The low-energy side of the lines is far from Lorentzian and contains a non-negligible contribution corresponding to a final state containing one $4f$ electron. This unusual situation, encountered in elements at the beginning of the rare-earth series, is attributable to the fact that the first unoccupied $4f$ level lies not far above E_F . This orbital is localized and, even in metals, keeps its quasiautomic

character, so that the interaction with an empty core level is poorly screened by valence electrons. In the presence of a $3d$ hole, this empty $4f$ state is pulled down, and can even be expected to lie below E_F in metallic La and Ce. The filling of this $4f$ state offers a final state of lower energy than that produced by the screening by valence electrons. This exceptional situation gives rise to interesting resonance phenomena which have already been observed and discussed in different spectroscopies.⁹⁻¹² For the purpose of this study it is sufficient to recognize that a $3d$ spectrum containing these two main peaks corresponds to a trivalent Ce atom. This is true for all spectra of Fig. 1, except for CeN, where two additional peaks appear with exactly the same spin-orbit splitting, but shifted to higher binding energies by 11 eV. In fact, this corresponds to a very particular chemical shift. The Ce atoms in CeN all have the same chemical environment, so that one has to assume that the ground-state electronic configuration is generated by a resonance between two distinct configurations. The conditions for such valence fluctuations are more easily fulfilled in Ce where the $4f^1$ level is expected to be located in the vicinity of E_F . In this case, the trivalent configuration $4f^1$ and the tetravalent configuration $4f^0 5d^1$ have comparable energy so that a mixed configuration is allowed. In a temporal picture,⁵ photoemission yields an instantaneous picture of the electronic structure, so that the final-state spectra contain a superposition of the lines corresponding to the two configurations involved in the initial state. The large shift in energy must be ascribed to a major modification of the outer shielding when an electron is transferred from a localized $4f$ orbital to a more extended $5d$ orbital.

The $4d$ spectra shown in Fig. 2 yield a still more convincing demonstration of the mixed valence in CeN. Starting again from LaSb, the La $4d$ spectrum shows simply the two $4d_{3/2}$ and $4d_{5/2}$ lines separated by $\delta = 2.9$ eV. In the Ce compounds the features of the $4d$ spectra are greatly modified by the presence of the $4f$ electron. The $4d^9 4f^1$ multiplet structure has been calculated by Signorelli and Hayes,¹³ and is in agreement with experimental data which are similar in all cases, including insulators and metals. This allows us to use $4d$ spectra to characterize the $4f$ configuration. In CeN, this sequence of multiplets is also easily recognized, even if they are not as well separated as in the other spectra. The two new peaks around 120 eV clearly do not belong to the $4f^1$ configuration but to the $4f^0$ configuration previously identified in LaSb. As expected, the spin-orbit splitting is slightly larger for Ce ($\delta = 3.3$ eV) than for La ($\delta = 2.9$ eV). These $4d$ spectra yield a straightforward

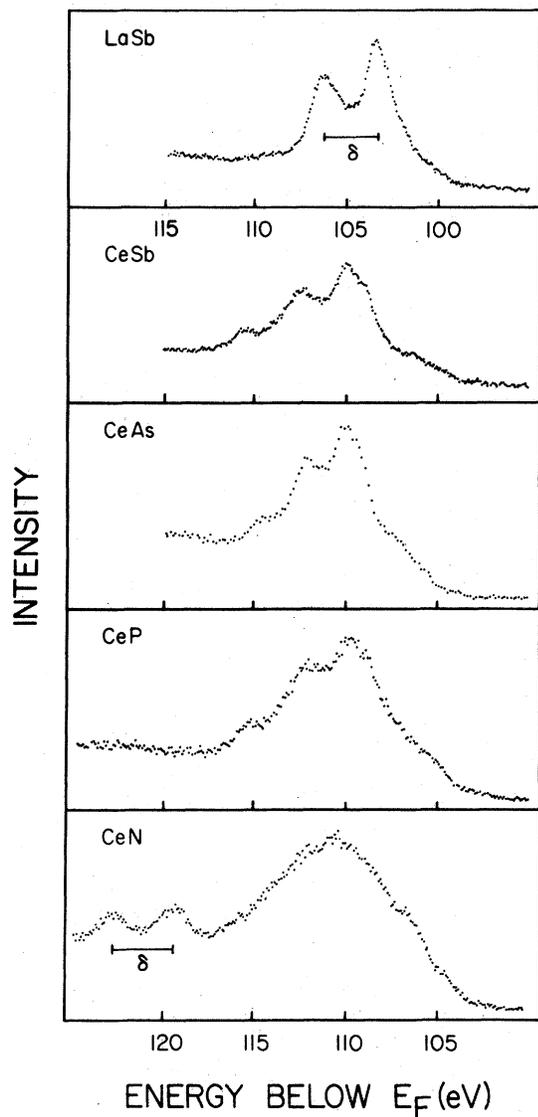


FIG. 2. Same as Fig. 1, but for the $4d$ core levels.

ward example of the power of XPS in determining the initial state $4f$ configuration.

V. VALENCE-BAND SPECTRA

Ce occurs most often in the trivalent state. Consequently, one expects the Ce monpnictides to be semiconductors or semimetals, and the valence states to have largely anion p -state character. This picture is clearly oversimplified, and strong s - p - d hybridization certainly occurs in this band. Nevertheless, for reason of simplicity, we shall retain the same p -band, without implying a purely ionic model. Since CeN has a mixed valence between 3 and 4, as demonstrated by the core-level spectra, a state of f and d symmetry must be pre-

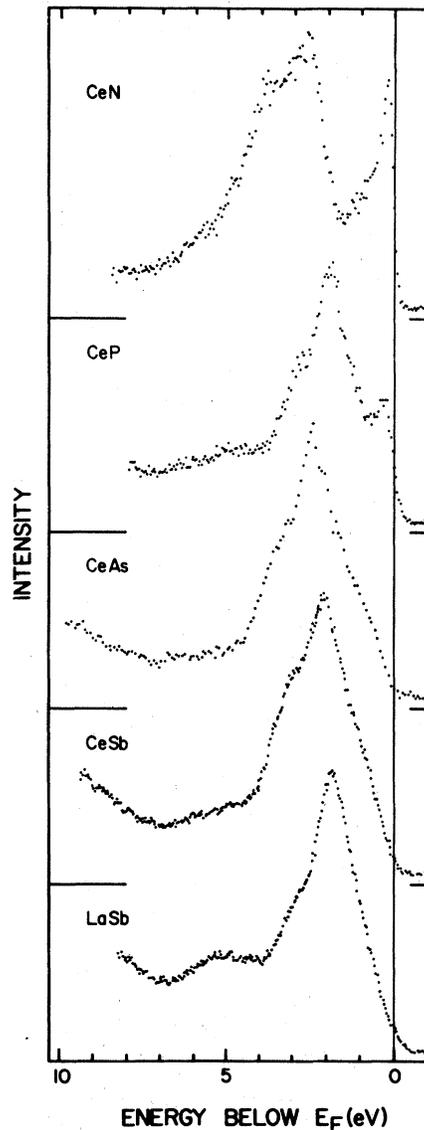


FIG. 3. XPS spectra of the valence-band region of Ce pnictides and LaSb.

sent at E_F . This situation can easily be recognized in the CeN valence-band spectrum of Fig. 3, which shows an exceptionally narrow $4f$ peak pinned at E_F and superimposed on a broader $5d$ band. The valence band of extended states, which is located at higher binding energies, is relatively broad and shows a marked splitting around 3–4 eV. This situation can be explained by the increase of the attractive potential resulting from the partial delocalization of the $4f$ electron into d states. The metallic character of CeN is determined by the simultaneous presence of occupied $4f$ and $5d$ states at E_F .

The valence-band spectrum of CeP shows many similarities with that of CeN, but it corresponds

in fact to a rather different physical situation. Ce in this compound has a stable trivalent configuration and the XPS peak centered at 0.4 eV represents a singly occupied $4f$ orbital. The valence-band- $4f$ separation has decreased relative to CeN. A superficial inspection of the valence-band spectrum of CeP would lead to the conclusion that this compound is metallic because of the high intensity observed E_F . In fact, the extrapolation of the main band of extended valence states shows that it does not make any contribution at E_F but overlaps slightly in energy with the localized $4f$ states. XPS investigations on other rare-earth compounds have shown¹⁴ that the lifetime of $4f$ holes is drastically shortened by interatomic Auger processes when the hole-state binding energy is located within the valence band. This broadening mechanism appears clearly in the comparison of the $4f$ peaks in CeN and CeP. In the first case, the position of the peak at E_F allows no Auger transition. As a result it is so narrow that the observed width is mainly determined by the instrumental resolution. In the second case, a shift of 0.4 eV already results in a sizable width, estimated to be 0.8 eV. The intensity found at the Fermi level of CeP corresponds simply to the low-binding-energy tail of the $4f$ line, due to its exceptionally small (0.4 eV) separation from E_F . We conclude, therefore, that CeP is very likely a semimetal. In the heavier rare-earth pnictides, the $4f$ level moves further away from E_F , penetrating into regions of higher density of states. The probability for filling the $4f$ photohole by Auger processes increases very fast, and in CeAs the $4f$ spectrum is already so broad that it can no longer be clearly distinguished from the valence band. It generates a shoulder around 1–2 eV below E_F but no accurate binding-energy value can be ascribed to it. The valence-band spectrum of LaSb, shown at the bottom of Fig. 3, is really very similar to that of CeSb, demonstrating that the $4f$ peak is too broad to make a discernible contribution to the valence band. Fortunately the core-level spectra can be used to prove that one localized $4f$ orbital in CeAs and CeSb is occupied, otherwise their valence-band spectra could lead to an erroneous conclusion.

VI. DISCUSSION AND CONCLUSION

As far as we know the density of states of the outer levels of these compounds have not been calculated. One can expect, however, that all trivalent rare-earth monpnictides crystallizing in the NaCl structure will have similar densities of states except for the $4f$ level. Hasegawa and Yanase¹⁵ have computed the energy band structures of the Gd pnictides using an augmented plane wave

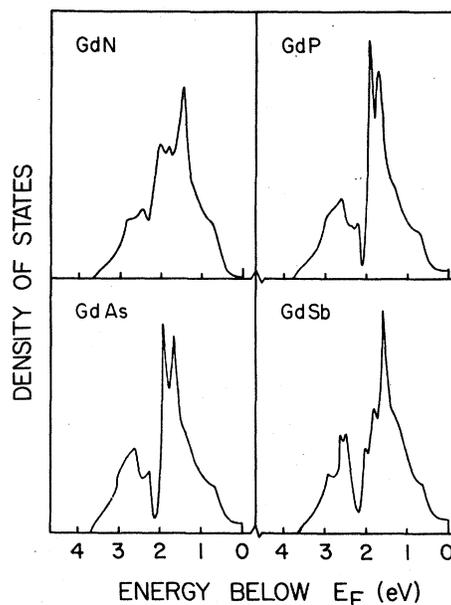


FIG. 4. Occupied part of the densities of states of the Gd pnictides computed by Hasegawa and Yanase (Ref. 15).

method. Gd is a particularly simple case because of its spherically symmetric $4f^7$ shell, which does not overlap in energy with valence states and can legitimately be considered as a core level. The occupied part of the bands computed by these authors is reproduced in Fig. 4. With the exception of GdN, all these densities of states show very similar features. Taking into account the broadening due to the lifetime and to the instrumental resolution, with XPS one can expect to observe a main peak with a sharp maximum between 1 and 2 eV, followed at higher binding energies by a shoulder. The total bandwidth remains close to 3.6 eV for all compounds. The XPS spectrum of GdP shown in Fig. 5 gives a good indication of the reliability of the computation of Hasegawa *et al.* The agreement is extremely good, except for a shift of the experimental spectrum of less than 1 eV. The increasing intensity beyond 5 eV corresponds to the tail of the $4f^7$ peak which is located at 8.6 eV, but was not included in the calculation. There is little point to attempt to decide here whether GdN is really a metal or not. The experimental spectrum does show a weak Fermi edge, in agreement with the calculation, but one has to bear in mind the great difficulty of producing these compounds without a deviation from the ideal stoichiometry which is likely to produce states at E_F . Setting aside the presence of the $4f$ line and the position of E_F , great similarities are found between the extended states in the XPS spectra of CeP and GdP. We believe that these similarities will persist for the whole

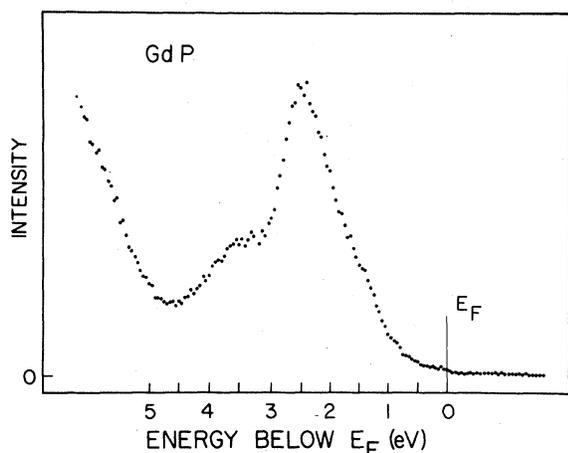


FIG. 5. XPS spectrum of the valence band of GdP.

series, so that the comparison between the calculations of Hasegawa *et al.* and the present measurements is expected to be valuable. In fact, detailed earlier investigations of the valence-band region of R-Sb (Ref. 16) and especially of GdSb confirm these conclusions. The overall agreement with respect to the bands origination from *p* states is very encouraging and even the CeN spectrum which is rather different from the other spectra is well predicted by the calculated density of states of GdN.

The study of the Ce core levels has demonstrated unambiguously that the 4*f* level remains strictly localized. From its position at the Fermi level in CeN, it moves toward higher binding energies when the anion atomic number increases. This effect is connected with the lattice constants which increase continuously from CeP to CeSb. With pressure (100 kbar) it is still possible to induce an isostructural phase transition in CeP (see Ref. 17) with a large volume contraction of ~8%. The position of

the 4*f*¹ level found in our spectrum 0.4 eV below *E_F* confirms that this transition involves a discontinuous valence change from 3+ toward 4+. It seems reasonable that 100 kbar is sufficient to shift the relative 4*f* electron binding energy by 0.4 eV, so that it reaches *E_F* and generates a mixed-valence phase of CeP. The high-pressure phase of CeP is therefore expected to have an electronic structure quite similar to that observed in CeN. In the other Ce pnictides, the 4*f* electron being more tightly bound, this type of transition would in principle still occur at higher pressure, but has not yet been observed.

The nature of the low-pressure $\gamma \rightarrow \alpha$ transition in metallic Ce has been quite often studied and two models have been proposed. In one, the γ -phase valence of 3.0 is changed to 3.7 in the α phase¹⁸ in which the 4*f* electron spends part of its time in a 5*d* orbital. In the other,¹⁹ the occupation of the 4*f* states remains integral through the transition but a delocalization occurs in the more dense α phase so that a 4*f* band is formed. The XPS 4*d* spectrum of the metal in the α phase is very similar to that of CeN,³ whereas it shows only the multiplets corresponding to Ce³⁺ in the γ phase. We therefore conclude that the 4*f* orbital of metallic Ce always retains its localized character and does not form a "band" in the usual sense. In this respect Ce can not be considered as a precursor of the light actinides which are known to form hybridized 5*f* bands.

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¹F. Hullinger and H. R. Ott, *Z. Phys. B* **29**, 47 (1978).

²G. K. Wertheim and G. Creelius, *Phys. Rev. Lett.* **40**, 813 (1978).

³Y. Baer and Ch. Zürcher, *Phys. Rev. Lett.* **39**, 956 (1977).

⁴D. E. Eastman and M. Kuznietz, *Phys. Rev. Lett.* **26**, 846 (1971).

⁵P. A. Cox, *Struct. Bonding (Berlin)* **24**, 59 (1975).

⁶M. Campagna, G. Wertheim, and Y. Baer, in *Topics in Applied Physics* (Springer, Berlin, 1979), Vol. 27.

⁷G. Wertheim and M. Campagna, *Solid State Commun.* **25**, (1978).

⁸Y. Baer, G. Busch, and P. Cohn, *Rev. Sci. Instrum.* **46**, 466 (1975).

⁹M. B. Chamberlain, A. F. Burr, and R. J. Liefeld,

Phys. Rev. A **9**, 663 (1974).

¹⁰J. M. Mariot and R. C. Karnatak, *J. Phys. F* **4**, L223, (1974).

¹¹J. Kanski, P. O. Nilsson, and I. Curelaru, *J. Phys. F* **6**, 1073 (1976).

¹²G. Wendin and K. Nuroh, *Phys. Rev. Lett.* **39**, 48 (1977).

¹³A. J. Signorelli and R. G. Hayes, *Phys. Rev. B* **8**, 81 (1973).

¹⁴J. N. Chazavie, M. Campagna, G. K. Wertheim, P. H. Schmidt, and Y. Yafet, *Phys. Rev. Lett.* **37**, 919 (1976).

¹⁵A. Hasegawa and A. Yanase, *J. Phys. Soc. Jpn.* **42**, 492 (1977).

¹⁶M. Campagna, E. Bucher, G. K. Wertheim, D. N. E. Buchanan, and L. D. Longinotti, in *Proceedings of the*

11th Rare Earths Conference, October 7-10, 1974,
Traverse City, Michigan (unpublished); M. Campagna
and G. K. Wertheim (unpublished).

¹⁷A. Jayaraman, W. Lowe, L. D. Longinotti, and E.

Bucher, Phys. Rev. Lett. 36, 366 (1976).

¹⁸K. A. Gschneidner and R. Smolochowski, J. Less-
Common Met. 5, 374 (1963).

¹⁹B. Johansson, J. Phys. F 4, L169 (1974).