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Classification
Physics Abstracts
71.20+d — 78.70Dm

Short Communication

Anomalous behaviour of X-ray absorption observed on the highly correlated cerium nitride (CeN) compound

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(Received 29 July 1991, accepted in final form 29 July 1991)

Abstract. — In this study, we present recent X-ray Absorption Spectroscopy (XAS) results obtained on highly pure cerium nitride (CeN) compounds. CeN is the "archetype" of the strongly mixed-valent (MV) cerium compounds, where the ground state properties are governed by strong hybridization effects beween the 4f and the conduction electrons. We will show that, in clear contradistinction with earlier results, the $L_{III,II}$ absorption edges of cerium in CEN do not exhibit the two contributions usually observed in strong MV systems. Indeed, in all cases only one single white line is observed. This anomalous behaviour is related with similar results obtained recently on *in-situ* prepared CeN studied by both L_{III} absorption and Ce 2p X-ray photoemission (XPS). The possible influence of the presence of p conduction states to explain this anomalous behaviour is addressed.

Cerium nitride (CeN) is one of the archetypes of the cerium metallic compounds whose physical properties are driven by strong hybridization processes between the 4f and the conduction electrons. In this class of materials we found for instance the Mixed-Valence (MV) compounds, the Kondo-like systems and the heavy fermions materials. Since more than fifty years ago, CeN was known to present a 12% reduction in its unit-cell volume [1] which was historically taken as an evidence of a valence fluctuation from $Ce^{3+}\left(4f^15d^16s^2\right)$ to $Ce^{4+}\left(4f^05d^26s^2\right)$. The only comparable case is the γ-α transition which occurs under pressure on metallic cerium [2]. All the thermodynamical properties of CeN reflect this valence anomaly. The magnetic susceptibility is nearly temperature independent below room temperature with a $\chi_0 = 0.46 \times 10^{-3}$ emu/mole

(*) UM CNRS 380046.
(**) UA CNRS 155.
(***) UPR 209

[3,4] smaller than that of α-Ce ($\chi_0 = 0.53 \times 10^{-3}$ emu/mole). The transport properties, such as electrical resistivity and thermoelectricity, are also nearly temperature independent below room temperature, with a large increase at $T \geq 600$ K [3, 5] in coincidence with the thermal expansion [3, 4]. The compressibility at room temperature was found to be 10% larger than that of the normal REN compounds (LaN, PrN etc...) [4]. Finally, the electronic coefficient of the low temperature specific heat, $\gamma = 8.3$ mJ/mole K^2 [6], turns out also to be smaller than that of α-Ce [2]. The ratio $\chi_0/\gamma = 0.06$ emu K^2/J is found within the values observed in other instable Valent Ce compounds. For all these reasons, CeN was labelled as a MV compound. However, we must emphasize that this denomination may be confusing in the case of cerium compounds where hybridization between the 4f and the conduction electrons is really important (the 4f, 5d, 6s etc... electrons form a band with a width (W) in the eV range). We are really in a highly correlated situation, where $W \approx U$ (U is the Coulomb repulsion between the electrons), which is obviously the most complicated situation one can encounter in solid state physics. Such a situation should not be confused with the usual mixed-valence regime where integer valence state are distributed on different crystallographic sites and even with homogeneous MV compounds like those obtained with heavy RE elements (e.g. SmB_6) where hybrydization between the electrons is believed to be one or two orders of magnitude less than in the Ce compounds.

In the last ten years, the use of high-energy spectroscopies like X-ray photoemission (XPS) and/or X-ray absorption (XAS) has been generalized to the study of these strongly correlated materials, although the interpretation of the results given by such techniques ask severe questions due to the complicated many-body problem which, in principle, governs the final state properties and may obscure the ground state properties of the system (see for instance Ref. [7] and the Refs. herein). The controversy was rough and is not yet finished, but due to a considerable effort both in theory [8-10] and in a systematic experimental approach [11, 12], some general conclusions can be given:

i) Due to the attractive potential of the core-hole created by the phototoabsorption process the final states of both XPS and XAS are made of two main resonances separated roughly by the Coulomb interaction between the core-hole and the f states ($U_{cf} \approx 10$ eV). In the case of XPS, an extra shake-down structure $\left(4f^2\right)$ is clearly seen on the low energy side of the Ce 3d core level spectra (see Ref. [9]).

ii) The intensity one can measure in both channels (i.e. those associated to $4f^1(5d6s)^3$ and $4f^0(5d6s)^4$ configurations *in the final state*) can be correlated with the admixture of these states in the ground-state as soon as the hybridization between the 4f electrons and the conduction electrons (V_{kf}) is explicitly taken into account [8] yielding thus a correct estimate of the 4f occupation number (n_f) in the ground-state.

iii) A fundamental difference exists between the XPS and XAS process in that sense that, for XAS the photoelectron contributes directly to the screening of the core-hole (adiabatic approximation limit), whereas in XPS, due to its high kinetic energy, the photoelectron cannot screen this core-hole (Sudden approximation limit). This is the main reason why the theory for XAS is not yet clear [10]. Therefore even if, so far, no spectacular effect has been reported concerning the possible breakdown of the sudden approximation, one has to be cautious when comparing XPS and XAS experiments.

The anomalous properties of CeN prompted spectroscopists to its study. It was one of the very first MV system where different 4f configurations were evidenced in core-levels XPS [13]; subsequent works by the same group were devoted to the electronic stucture of CeN films and single crystals as revealed by UPS (Ultra-Violet Photoemeission Spectroscopy) and BIS (Bremstrahlung Isochromat Spectroscopy) [14]. All these studies may be consistently interpreted within the Gunnarson-Schönhammer theory [8] mentioned above with a n_f value of 0.85. XAS experi-

ments on CeN, performed at the cerium L_{III} edge [15], were also reported and were, at first sight, in complete agreement with the XPS and BIS data. However, the sample quality used in these XAS studies was recently questioned [12], mainly because of the high oxygen reactivity of CeN. This statement motivated us to reinvestigate carefully the absorption spectra of CeN and to compare them to those of integer valent compounds like PrN and LaN.

The RE nitrides were prepared via elemental synthesis, heating the RE metals at about 2000 K in a tantalum resistance furnace, under an atmosphere of pure and dry nitrogen. The starting metals were Ce and Pr (99.9% purity). The actual composition of the samples was controlled by chemical analysis, the nitrogen content was determined with the Kjeldahl method. All samples were controlled by X-ray diffraction in order to confirm the existence of a single phase with the NaCl structure. The lattice constants we found (a = 5.020 Å for CeN, a = 5.165 Å for PrN) are in perfect agreement with the results given in the literature. The XAS experiments were performed at LURE (Orsay) on the EXAFS II station using the synchrotron radiation delivered by the DCI storage ring which was operated at 1.8 GeV and 300 mA. We use Si(311) crystals to monochromatize the X-ray beam and mirrors were used in order to reject higher order harmonics. The experimental resolution is estimated to be 1 eV at the cerium edges.

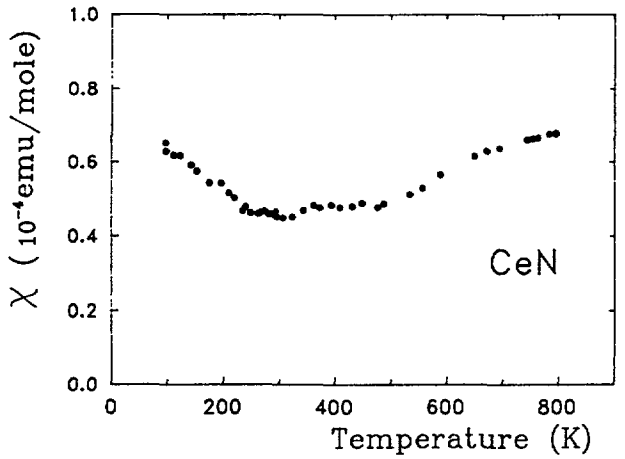

Fig. 1. — Temperature behaviour of the magnetic susceptibility of CeN.

The magnetic susceptibility of CeN, in the temperature range from 100-800 K, is reported in figure 1 and well agrees with previous published data [3, 4]. The increase of the magnetic susceptibility at low temperature may be due to the presence of a few percent trivalent cerium impurities resulting either from stoichiometry defects or from a slight contamination of the sample. On the other hand the temperature behaviour between 600 and 800 K traduces simply the small change in n_f as deduced from thermal expansion and electrical resistivity measurements. A good test of the sample quality can be made by taking benefit of the high sensitivity of X-ray near edge structures (XANES) to the presence of any traces of impurities and particularly to that of oxides. In the case of CeN this point, as we shall see later, is of special interest because any trace of CeO_2 will make an extra contribution to the $L_{III,II,I}$ absorption edges which falsifies the n_f value which may be deduced from the XAS experiments. According to Natoli's rule [16] which simply states that the XANES oscillations may be scaled in energy as: $(E - E_0) \cdot R^2$ = Cst (here E_0 is the

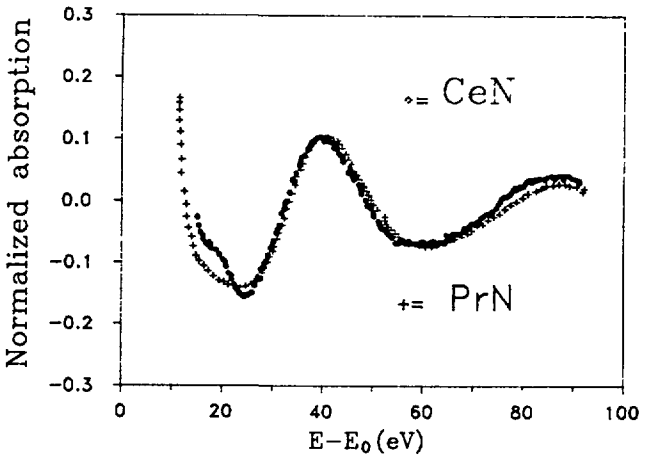

Fig. 2. — XANES of CeN and PrN (see text).

threshold energy and R is the lattice parameter of the compound), it is rather easy to compare the XANES of different compounds with the same crystal structures [17]. Figure 2 illustrates the XANES of CeN and PrN obtained after the L_{III} edges of Ce and Pr respectively (the energy scale for PrN has been expanded by the factor $(R_{CeN}/R_{PrN})^2 \approx 1.05$). The comparison between CeN and PrN is interesting because the reactivity of PrN to oxygen is much smaller than that of CeN, moreover these two compounds develop rather different oxides. We notice that, except a small deviation in the 20 eV range, both XANES structures match quite perfectly, particularly in the 40 eV range where we expect the main contribution of CeO_2. Thus we can safely conclude that our CeN sample is free of any type of impurities which may obscure the n_f determination. Similar conclusions can be extracted from the analysis of the EXAFS oscillations which are not detailed here.

The essential result obtained in this letter is shown in figure 3 where the L_{III} absorption edges of Ce and Pr, respectively in CeN and PrN, are reported. We notice that both edges exhibit a single "white-line" resonance due to direct $2p_{3/2} \rightarrow 5d$ transitions, this resonance is even sharper in CeN than in PrN, and thus indicates *that both compounds seem to be trivalent* as long as we refer only to these XAS results. Indeed, the n_f value we extract from the L_{III} edge of Ce in CeN is thus exactly 1, as indicated by the fit shown in figure 3a (the small bump located at 5737 eV, i.e. 13 eV above the edge is due to a multiple scattering process and cannot be related with a $4f^0$ channel), instead of 0.85 as suggested from the XPS, UPS and BIS experiments mentioned above. Thus we have here clear evidence that both techniques may give rather different conclusions concerning the ground state properties of highly correlated materials. To our knowledge, this is the first time that such a huge effect is observed in the case of Ce MV compounds, usually the n_f value extracted from $L_{III,II}$ edge spectroscopy is even slightly *lower* ($\approx$ 5-10%) than that obtained from XPS on the core levels. Another interesting result is reported in figure 4, where the L_I edge of Ce in CeN is shown: in this case where $2s \rightarrow \varepsilon p$ transitions are involved (ε means that the transition occurs between s and p hybridized states built by the 2p states of N and the 6p states of Ce), we notice clearly the presence of the "$4f^0$" final state at 6574 eV, the solid line is a fit of the data assuming an n_f value of 0.82 which is in good agreement with the photoemission results. Let us notice, in figure 4, the existence of a shoulder located at 6551 eV, whose origin is not yet clear. It may be due either to the signature of a $4f^2$ channel in the final state (i.e. a shake-down process due to

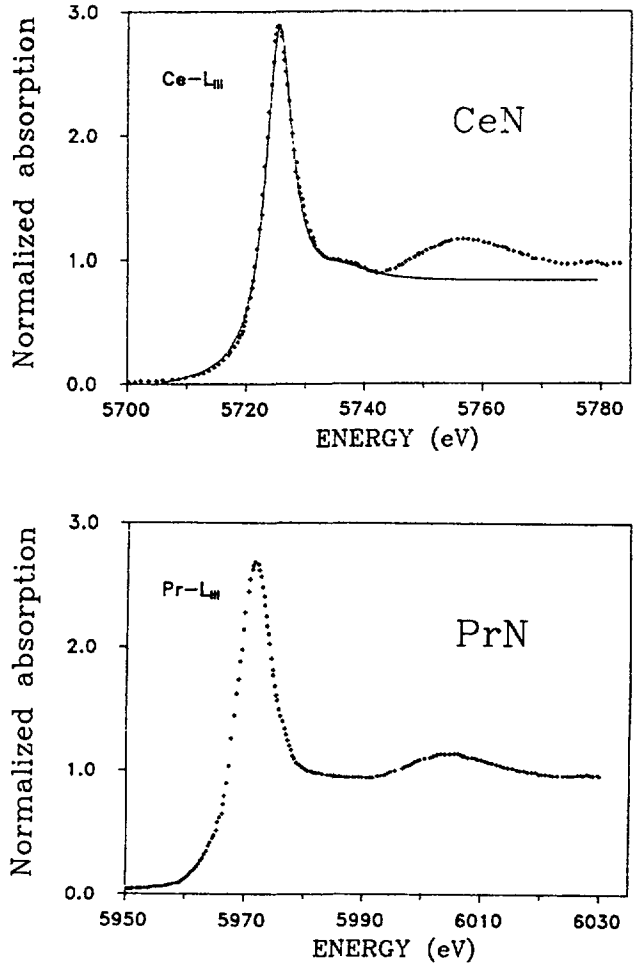

Fig. 3. — L_{III} absorption edge of Ce in CeN (a) and of Pr in PrN (b). The solid line in figure 3a is the result of a fit assuming $n_f \approx 1$ (see text).

hybridization) or to some problem related with the stoichiometry of the sample. Nevertheless we have to conclude that the screening mechanisms of the Ce 3d core hole by a 2p or a 5d electron are rather different which result in different final states for the absorption process. Recently, we reported the results of XPS and XAS experiments performed at the same (2p) core-level, on *in-situ* prepared CeN samples [18], these results are in good agreement with those obtained here for a bulk material and confirm completely that the final states of XPS and XAS (on the $L_{III,II}$ Ce edges) are indeed different.

In order to show how the reactivity of CeN to oxidation is a crucial problem, we report in figure 5 the evolution of the L_{III} Ce edges in CeN as a function of time. We see that if the sample is not protected seriously for oxidation, all the possible values of n_f may be obtained in the range from 1 to 0.65 (we have just to wait enough between two experiments!). For instance the spectrum labelled 2 in figure 5 corresponds to an n_f value of 0.85. To our opinion this explains the previous XAS results reported for CeN. Obviously such an explanation is ruled out for the XPS results

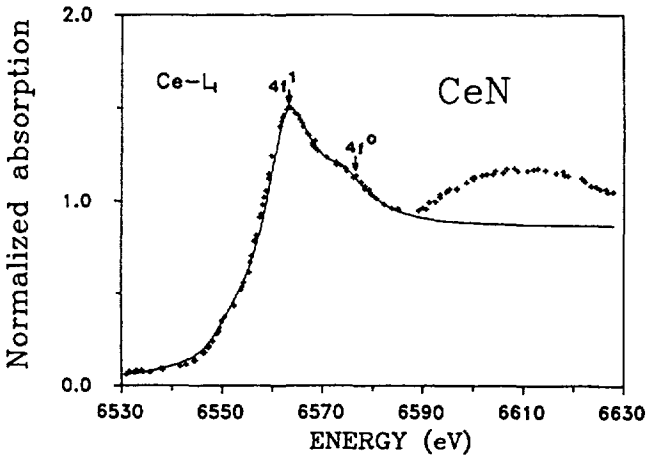

Fig. 4. — L_I absorption of Ce in CeN. The solid line is the results of a fit assuming $n_f = 0.82$.

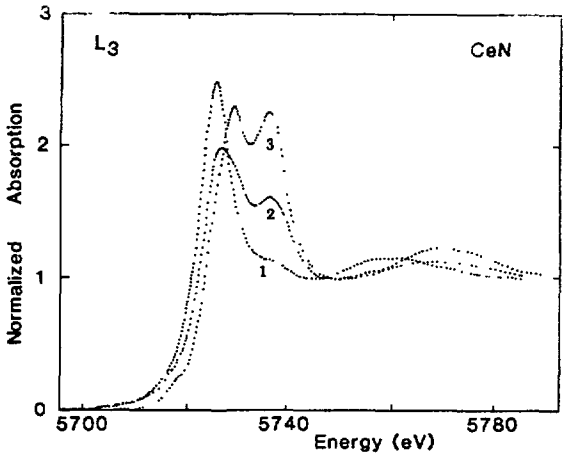

Fig. 5. — L_{III} absorption edge of Ce in CeN: 1) taken immediately after preparation; 2) taken after 30 minutes without protection from air; 3) taken after 2 hours without protection from air.

which have been performed under ultra high vacuum conditions.

Now we want just to stress some important points concerning the possible origin of the discrepancy between XAS (on the $L_{III,II}$ edges) and XPS. It is not fortuitous that we observe this effect on a material like CeN, where the conduction electrons are essentially of p character (this is well shown in figure 4 by the resonance we can observe at the Ce L_I edge in CeN and which are due to direct $2s \rightarrow \varepsilon p$ transitions), whereas in other MV intermetallic cerium compounds like $CePd_3$, $CeNi_2$, $CeNi_5$, $CeCo_2$, $CeCo_5$ etc... these conduction electrons are of d character and such an effect seems to be never observed. Because in XAS the photoelectron itself interacts strongly with all the other conduction electrons (breakdown of the sudden approximation) it is necessary to take these interactions properly into account in the final state of the absorption process, and such interactions may be rather different for p and/or d electrons. This is discussed

in details in our previous paper [18]. Finally, we want just to mention that CeN should not be an exception and that other examples may be found, particularly in the cerium highly correlated systems in which sp elements (B, Be, Sn etc...) are present e.g. CeB_4, $CeBe_{13}$ [19] or even $CeSn_3$. We believe that in such systems, like as in CeN, the XAS experiments involving "d" final states cannot be used to deduce directly the number of occupation of the 4f shell (n_f).

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