First observation of Ce volume collapse in CeN

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On the occasion of the 80th anniversary of the first observation of Ce volume collapse in CeN a remembrance of the implications of that transcendent event is presented, along with a review of the knowledge of Ce physical properties available at that time. Coincident anniversary corresponds to the first proposal for Ce as a mix valence element, motivating to briefly review how the valence instability of Ce was investigated since that time.

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I. 2017 - 80th anniversary of the first observation of Ce volume collapse in CeN

In Volume XXV, p.129 (1937), of the "Rendiconti Accademia Nazionale dei Lincei", a report on the crystal structure of rare earth nitrides (REN, RE = La, Ce, Pr and Nd) was presented. There, the authors, Aldo Inadelli and Erico Botti of the Institute of Chemistry of the University of Genova (Italy), informed that "The lattice parameter of CeN presents a strange anomaly" in comparison to the linear decrease of the other REN compounds. As it can be seen in Fig. 1, the lattice parameter 'a' of the NaCl-type structure of CeN (a = 5.011 Å) "... is much lower than that of the neighbor compound with Pr (a = 5.155 Å) and also to that of [pure] face centered cubic Ce (a = 5.141 Å)". This reduction of the lattice parameter in CeN is about 4% of the value extracted from the interpolation between the respective LaN (a = 5.275 Å) and PrN lattice parameters, as depicted in Fig. 1.

To verify such unexpected collapse of the CeN volume, the authors mention that "For security, many photograms were performed on different CeN samples, trying to change as much as possible the [compound]formation conditions, always with the same result." They recognize that "The abnormal behavior of Ce is difficult to explain because the CeN compound does not present different characteristic with other compounds". However, they remark that the only ascertained difference [with the neighboring LaN] is that the heat of formation seems to be larger.

This observation is backed by the fact that a large volume contraction (∆V_f) respect to the volume of elementary components in the compound formation process corresponds to a large heat of formation (∆H_f) because ∆H_f ∝ ∆V_f [1]. This feature is illustrated in Fig. 2 where ∆H_f is plotted as a function of the Electrostatic Energy E_φ = qφ [3], being φ ∝ qZ/r = exp(-λ/r) the electrostatic potential including the Thomas-Fermi screening factor: exp(-λ/r). The ∆H_f values for CeN and Zr^{4+}N are taken from Ref. [5]. From Fig. 2 it becomes clear that the extra ∆H_f observed in CeN is related to the shift of the Ce^{3+} valence ν = 3 in the pure metal towards ν = 4, reaching a value of ν = 3.7. Nowadays, the extraordinary volume contraction or large ∆H_f of CeN compared with LaN and PrN can be understood taking into account the transference (or delocalization) of the 4f^3-Ce electron to the electronic band, which is related to the drastic change of valence.

II. What was known before 1937 concerning Ce and Ce-alloys properties

In its elemental form, Ce was first isolated by Carl G. Mosander at the Chemical Laboratory of the Caroline Medical Institute, Stockholm, in 1839 [6] while identifying the major components of mischmetal alloys [7].
An early report on Ce alloys with transition elements (Fe, Co and Ni) appeared 1903 by Auerton Welsbach [5]. According the author, "the property of giving off sharp sparks with a hard object on the basis of the iron alloys of cerium is also peculiar to its alloys with cobalt, nickel and manganese". Shortly after, 1904, W. Muthmann and H. Beck [9] published their studies on the heat of formation of Ce-Mg alloys. These thermochemical studies are followed by those performed on CeN by J. Lipzki in 1909 [10].

Two extensive articles on Ce-Sn and Ce-Al alloys containing the early phase diagrams of these binary systems were published by Rudolf Vogel, from the Chemical Physics Institute of the University of Göttingen, in 1911 [11], see Fig. 3 and 1912 [12] respectively. These papers contain a detailed description of the samples preparation procedure.

A. Cerium properties as pure metal, at ambient conditions

In the crystal structure study performed by Albert W. Hull, from General Electric Res.Lab. in 1921 [13], he reports that "Cerium shows the same structure as Ti and Zr [hex] with axial ratio 1.62" and "The side of the elementary triangle is 3.65 Å and height 5.96 Å.". However, he notices that "There is present also a face centered cubic [\(\gamma\) - fcc] form, with side of cube 5.12 Å giving the same density as the hexagonal form. Cerium thus appears to be composed of a mixture of the hexagonal and cubic forms of close-packed.", see Ce metal phase diagram in Fig. 4 at ambient pressure.

B. Ce properties as a function of temperature

The first study on the magnetic properties of pure Ce were published in 1934 by M.F. Trombe
to the French Academy of Sciences in a work presented by M.P. Weiss under the title "Propriétés magnétiques du Ce, du La et du Nd à diverses températures" [18]. The author reports that "At low temperature, Ce possesses complex magnetic properties: i) at 99 K its magnetization coefficient drops from \(3.8 \times 10^{-6}\) (under \(H = 3\) kGs) to \(3.9 \times 10^{-6}\) (under \(H = 7\) kGs). ii) It seems to have two states, with different temperatures for heating and cooling, see Fig. 6.

One decade later 1944 a new research on the "Range of existence and properties of the allotropic states of metallic cerium" studied through thermal expansion measurements was published by F. Trombe and M. Foex [19]. They mention that the Ce-\(\alpha\) state, which has previously been defined by its thermomagnetic anomaly was studied by dilatometry and that "It can be shown that the magnetic variation almost coincides with an exceptionally great anomaly of expansion which amounts to 10% in volume." Their measurements show that "... during contraction (decreasing temperature) the expansion coefficient has a maximum at -164°C (109.3 K) whereas, with increasing temperature, the maximum is reached at -98°C (175.4 K). The maxima of the magnetic anomaly have been found at -163°C (108.4 K) and -100°C (177.4 K) respectively". These results support the Ce-magnetic phase diagram presented in Fig. 4.

The mentioned magnetic and dilatometric behavior were then confirmed by electrical conductivity measurements, which indicate that "The electrical conductivity tests were made with a 99.6% pure Ce, ..., cooled to low temperature, where it passes into the \(\alpha\) state, shows an electrical anomaly at -186 (87.4 K) and -98 (175.4 K), respectively. Fig. 7[20] represents those results.

New results on pressure effects investigated by P.W. Bridgman in 1948 were quoted by A.W. Lawson [25]. Those results indicate an over-all contraction in volume of 16.5% at 15,000 atmospheres (\(\approx 15\) kbar) [22]. This contraction is illustrated in Fig. 8 as the evolution of Ce-lattice parameter with pressure.
III. VALENCE INSTABILITIES

IV. 80th anniversary of the report on valence instabilities in lanthanid elements

Another relevant anniversary corresponds to the review article by Von W. Klemm and H. Bommer in 1937 [24]. This work was addressed to the volume contraction of the lanthanide series as a function of the atomic number, Fig. 9-left, and their different electronic configurations at ambient conditions, Fig. 9-right. As it can be seen in Fig. 9-left Eu and Yb strongly expand their atomic volumes by reaching their divalent (2+) configurations. On the contrary, Ce atoms slightly reduces its volume respect to the other lanthanides as it increases its valence. On the right side of Fig. 9 a collection of extreme deviations from the trivalent (3+) states of the RE element is presented where also Sm is included into the 2+ tendency whereas Pr and Tb into the 4+ direction. Noteworthy is the name of ‘Cassiopeium’ for present Lu and the number ‘61’ to identify Promethium not yet isolated at that time.

A. Ce as a ’static mix’ of 3+/4+ electronic configurations

In chapter 3 of Ref. [24] under the title ”Rare Earth metals ionic moments” the authors state the ”For Ce, from the atomic volumetric curve we conclude that there are both three and tetra valent ions. This assumption is magnetically easy to test since the Ce3+ ion has no magnetic moment whereas the Ce4+ ion has 2.56µB magnetons”. According to the formula $\mu_{\text{eff}} = 2.84/\chi * T$ they report the following effective moments $\mu_{\text{eff}}$ for Ce metal at three temperatures: at 90 K: $\mu_{\text{eff}} = 1.80\mu_B$; at 195 K: $\mu_{\text{eff}} = 2.23\mu_B$ and at 291 K: $\mu_{\text{eff}} = 2.34\mu_B$. 

FIG. 7. (Color online) Electrical resistivity of pure Ce as a function of temperature showing different hysteresis cycles when starting from stabilized dhcp-β or fcc-γ phases, after [20].

FIG. 8. Lattice parameters of different allotropic Ce metallic phases: $a_0$ [Å], as a function of pressure [kbar] after [23].

FIG. 9. (Color online) (left) Volume contraction of the lanthanide series as a function of the atomic number. (right) Lanthanides valencies at ambient conditions, after [24].

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After having extracted this temperature dependence of the effective magnetic moments, they propose a description of their results based in a mixing valence picture: "... that's why the actual moments lie between the two limit values. The values closer to Ce$^{3+}$ are at higher the temperature. According to the mixing rule (valid only as a first approach), from the observed susceptibility values the ratio between Ce$^{4+}$ and Ce$^{3+}$ ions is: i) both charges are similar at 90 K; at 195 K Ce$^{3+}$ ions amounts to 70%, and to 84% at room temperature." as it is shown in Fig. 10.

B. Cerium electronic configuration instability

At the end of the following decade the early concepts on the possible Cerium electronic instability were known by different authors. One of them in 1949 by A.W. Lawson and T-Y Tang [25] indicates that "Powder patterns, taken at approximately 15 kbar, reveal that the high pressure modification of the ambient pressure FCC lattice is also FCC!. The new structure possesses a lattice constant $a = 4.84 \pm 0.03\ \AA$, yielding an over-all volume change at this pressure of 16.5%." These values remind those from Bridgman in 1948 [22].

The microscopic origin of such a volume collapse is then proposed "as a result of stimulating conversations with our colleague, W.H. Zachariasen, we propose the following simple model: ... Ce, which is the first atom in the periodic table to permit the existence of a 4f electron, when condensed exhibits the tendency to become perverted from a 3-valent to a 4-valent state."

This breaking through idea refers to an electronic transition: "Apparently, the application of 12 kbar of pressure is sufficient to evoke this transformation and the 4f electron is literally squeezed into a 5d state."

Quite simultaneously (in 1950) a similar electronic effect proposed by Linus Pauling is quoted by A.F. Schuch and J.H. Sturdivant [26] indicating that in 1944 [19] "... Trombe and Foex observed a transition at 109 K accompanied by a 10% volume decrease and a decrease in magnetic susceptibility, Prof. Linus Pauling suggested to us in 1946 that this transition is caused by the promotion of a 4f electron to a bound-forming orbital." One may appreciate that in the late 40's more quantum mechanic pictures emerged in the attempt to understand the Ce-valence dilemma.

C. Coqblin-Blandin model

The well known Coqblin-Blandin model (1968 [27]) was a qualitative improvement to the knowledge of the microscopic mechanism of Ce magnetic properties. An illustrative summary of this model is provided in a chapter of the "Handbook of Phys. and Chem. of Rare Earths" dedicated to "Cerium" [28].

This model is described as "One consequence of the promotinal idea is that it implies the localized 4f state in Ce is close in energy to the Fermi level and therefore should also be coincident with the conduction band, see Fig. 11a. Their feeling was that "... under these conditions the 4f state should mix or hybridize with the conduction band states to form a 4f virtual bound state". This basic idea clearly reminds the earlier proposition by Zachariasen-Pauling mentioned in Section III-B.

Concerning the allotropic phases of Ce metal: "In $\gamma \rightarrow \alpha$ Ce the occurrence of localized moments could be described as arising from a spin and orbital magnetic 4f virtual bond state lying about 0.1 ev below the fermi level and having half-width of around 0.02 ev, see Fig. 11a. Then, "The mechanism for the transition to $\alpha \rightarrow \gamma$ Ge was believed to arise from a cooperative interaction between a number of volume dependent terms in their free energy expression", as depicted in Fig. 11a.

D. Phenomenological models

Through measurements of magnetic, structural, transport and spectroscopic properties on RE compounds it has been established that nonmagnetic RE ions can be described as fluctuating in time between two electronic configurations [29]. In SmB$_6$,
SmS, YbAl₃, α-Ce, TmTe, and EuCu₂Si₂, each configuration is characterized by a different integral occupation of the 4f shell. In this "Inter-Configurational Fluctuations" (ICF) model, it is assumed that "...there are two distinct states of the rare earth atom and its environment, one with an integral number 'n' of electrons in the 4f shell, the other with 'n - 1' electrons in the 4f shell together with one delocalized electron in the environment". The energies of these two states are $E_n$ and $E_{n-1}$ respectively, and one defines $E_{ex} = E_n - E_{n-1}$. Thus "In each state $E_i$ the 4f shell is assumed to have a well defined angular momentum 'J' and a corresponding magnetic moment '$\mu_i$'". Although this model properly described the magnetic dependence of Yb, Eu and Sm compounds, it is not applicable to Ce ones because the energy difference between Ce³⁺ and Ce⁴⁺ electronic configurations is about 60kJ/mole > 2eV/mole.

Other phenomenological approaches to the valence instability of Cerium atoms were obtained analyzing the relationship between crystal and structures in binary compounds. A clear correlation was observed between cubic "fcc" structures and significant hybridization of Ce-4f states. In such symmetry p-orbitals and 4f ones have the same parity and three of them (among 7 f-orbitals) can be projected into the three formers. By analyzing electronic configurations of the ligand band it was found that the 'spdf' configuration may become the most energetically favored after the metallization (or fusion) process. For such computation the Gschneidner criterion used to evaluate the contribution of each kind of electronic orbital to the total cohesive energy was applied.

The most relevant example for the fcc-CeN. Its p-band character was recognized though an unexpected contradiction between $L_{III}$ and $L_I$ X-ray Absorption (XAS) edges measurements. While the $L_{III}$ showed an extremely narrow 'white-line', the $L_I$ one displayed a double maximum in agreement with the extreme mixed valence thermodynamic evidences (specific heat, susceptibility, resistivity and thermal expansion). Furthermore the Ce-volume collapse was revealed by the $L_{III}$-XANES themselves. The conclusion was that the electron band has a 'pure-p' character and therefore the $(2p \rightarrow \epsilon_d)$ electronic transition, corresponding to the $L_{III}$ absorption, is not allowed. On the contrary, the $L_I$ edge related to the $(2s \rightarrow \epsilon_p)$ transition occurs. This restriction of the XAS spectroscopy explains most of the contradictions between this technique and the thermodynamic determination of the Ce valence in CeX compounds with X = a semimetal of p-like character.

Another efficient mechanism to destabilize the valence of Ce-atoms is provided by a chemical-potential 'pressure' which drives the $4f^1$ electron transference from the Ce³⁺ configuration to a ligand-band hole like in CePd₇[35]. In this compound, the measured Sommerfeld coefficient: $\gamma(CePd_7) = 9.8 mJ/molK^2$ equals the value of single $\gamma(Pd)$ atom.

Notably, the Ce-volume collapse and the related change of valence ($Z_i = 3$ or 4) show a nearly constant relationship in the product: $Z_i*Vol_i \approx 153 Å^3$, where $Vol_i$ is the volume of the Ce-cell extracted from the respective 3⁺ or 4⁺ metallic radius.

V. CONCLUSIONS

The small spark of a Ceria stone that had lighted the darkness along centuries already triggered the process of the Ce valence transition. In the last century this valence instability was one of the outstanding subjects in international conferences addressed to the study of RE intermetallic compounds, that progressively revealed the physical richness of this mechanism. Its relevance was resumed in the statement by D.C. Koskenmaki and K. Gschneidner Jr. [28]: "In its elemental form Ce is the most fascinating member of the Periodic Table".

![FIG. 11. a) Localized 4f state close in energy to the Fermi level, b) 4f virtual bond state lying about 0.1 ev below the fermi level and having a half-width of around 0.02 ev, c) slightly occupied highly hybridized 4f level.](image)
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[7] Also quoted at The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science Vol. 23 (1943) p.152 as: C.G. Mosander, On the new metals, lanthanium and didymium, which are associated with cerium; and on erbium and terbium, new metals associated with yttria.


