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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2017.

I. 2017 - 80th anniversary of the first

observation of Ce volume collapse in CeN

In Volume XXV, p.129 (1937), of the “Rendi-

conti 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 com-

pound 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 charac-

teristic than 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 vol-

ume 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 plot

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 La3+N,

CeN and Zr4+N are taken from Ref. [5]. From

Fig. 2 it becomes clear that the extra ∆H_f ob-

served in CeN is related to the shift of the Ce3+

valence ν = 3 in the pure metal towards ν = 4,

reaching a value of ν ≈ 3.7.

Nowadays, the extraordinary volume contrac-

tion or large ∆H_f of CeN compared with LaN and

PrN can be understood taking into account the

transference (or delocalization) of the 4f^1-Ce elec-

tron 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 mayor components

of mischmetal alloys [7].
An early report on Ce alloys with transition elements (Fe, Co and Ni) appeared 1903 by Auerton Welsbach [8]. 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 [γ - 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

There is a work on elastic properties of heavy elements by P. W. Bridgman, reported in 1927 with the title "The compressibility and pressure coefficient of ten elements" [14]. This is the first observation of the \( \gamma - \alpha \) transition at room temperature performed through electoresistance measurements, see the 300 K isotherm in Fig. 4.

In 1932 the existence of a cubic allotropic Ce phase was confirmed by Von Laurence L. Quill, at the University of Göttingen (Germany) [16]. The author confirms that "Ce still continuous crystallizing, according to A.W. Hill, in face-centered-cubic", and remarks that "Ce shows a higher compressibility than La and Pr.", see Fig. 5. The Ce lattice parameters reported in its different allotropic phases are: i) for the hexagonal structure \( a = 3.65 \, \text{Å} \) and \( c = 5.96 \, \text{Å} \), with a ratio \( c/a = 1.633 \) and ii) for the cubic structure \( a = 5.12 \, \text{Å} \).
FIG. 4. (Color online) Phase diagram of pure Cerium under hydrostatic pressure, after [17]. Dashed line indicates ambient temperature.

FIG. 5. (Color online) Comparison of pure Ce compressibility with the neighboring rare earth elements, data from Ref.[15].

FIG. 6. Inverse susceptibility of Ce metal showing an hysteretic trajectory between 100 and 200 K.

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 α 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 (≈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 Ce$^{4+}$ ion has no magnetic moment whereas the Ce$^{3+}$ ion has 2.56$\mu_B$ magnetons". According to the formula $\mu_{eff} = 2.84(\chi * T)$ they report the following effective moments $\mu_{eff}$ for Ce metal at three temperatures: at 90 K: $\mu_{eff} = 1.80\mu_B$, at 195 K: $\mu_{eff} = 2.23\mu_B$ and at 291 K: $\mu_{eff} = 2.34\mu_B$. 

FIG. 7. (Color online) Electrical resistivity of pure Ce as a function of temperature showing different hysteresis cycles when starting from stabilized dhcp-$\beta$ or fcc-$\gamma$ 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].

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].
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 dworn 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 \(a = 4.84 \pm 0.03 \text{ Å} \), yielding an over-all volume change at this pressure of 16.5%," as it is shown in Fig. 10.

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 promotional 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 \(\gamma - \text{Ce} \) 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. 11b. Then, "The mechanism for the transition to \(\alpha - \text{Ce} \) 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\(_6\),
the contribution of each kind of electronic orbital interaction the Gschneidner criterion [32] used to evaluate allization (or fusion) process. For such calculating electronic configurations of the ligand band can be projected into the three formers. By analyzing the relationship between crystal and electronic configurations 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 [32] 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 L1III and L1 X-ray Absorption (XAS) edges measurements [33]. While the L1III showed an extremely narrow ‘white-line’, the L1 one displayed a double maximum in agreement with the extreme mixed valence thermodynamic evidences (specific heat, susceptibility, resistivity and thermal expansion [34]. Furthermore the Ce-volume collapse was revealed by the L1III-XANES themselves. The conclusion was that the electron band has a ‘pure-p’ character and therefore the (2p → ϵ d) electronic transition, corresponding to the L1III absorption, is not allowed. On the contrary, the Lf edge related to the (2s → ϵ 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 4f1 electron transference from the Ce3+ configuration to a ligand-band hole like in CePd2 [35]. In this compound, the measured Sommerfeld coefficient: \(\gamma(CePd_2) = 9.8 \text{mJ/molK}^2\) 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: \(Z_i * Vol, \approx 153 \text{Å}^3\), where Vol, is the volume of the Ce-cell extracted from the respective 3+ or 4+ metallic radius [36].

\[\text{V. CONCLUSIONS}\]

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".
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