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A NEW ALLOTROPIC FORM OF CERIUM DUE TO ITS TRANSITION UNDER PRESSURE TO THE TETRAVALENT STATE*

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An x-ray structural analysis on cerium under pressure was made in order to investigate its valence behavior in the metallic state. A new form, α'-Ce, always fcc but strongly collapsed, was found to exist at pressures higher than 50 kbar. It was deduced that Ce is tetravalent in the α' form. The atomic radius of Ce^{IV} was calculated, and the probable values of the valency in γ-Ce and α-Ce are also estimated.

Till now four allotropic forms of cerium have been known: a bcc δ phase, a dhcp β phase, a fcc γ phase, and a fcc α phase.[1] The first-order $\gamma-\alpha$ transition, that occurs at 116°K and 1 atm or at 7670 atm and 298°K,[2] has been studied by several authors[3] and appeared due to a change in electronic configuration of cerium: Gschneidner and Smoluchowski,[4] from a critical review of the results, concluded that the most reliable values of the valence of cerium in the γ and α modifications are, respectively, 3.06 ± 0.06 and 3.67 ± 0.09. At the time they could not find any evidence to support the existence of a tetravalent state in metallic cerium. Recently Wittig,[5] investigating the electric properties of cerium under pressure, found at pressures higher than 50 kbar a new superconducting phase of cerium of unknown structure.

In order to extend the knowledge on the allotropy of cerium, a structural investigation has been carried out between about 7 and 100 kbar at room temperature by means of a high pressure x-ray camera (Model XKB-100), supplied by the Materials Research Corporation, using Mo $K_{\alpha\beta}$ radiation. The cerium used was a high-purity metal (99.95%) obtained by electrolysis. The calibration of the pressure was made using NaCl and Ag as markers and referring to their known compressibility data.[6,7] The accuracy in pressure measurements was ±1 kbar. The uncertainty in the lattice-parameter values was ±0.01 Å.

The experimental results, reported in Table I and Fig. 1, show that the α-Ce phase exists at room temperature between 7.6 and 50 kbar. In this pressure range the lattice constant decreases continuously, as pressure increases, from 4.85 to 4.73 Å.

At 50 kbar the fcc cell of α-Ce undergoes a drastic drop of 4.37% in volume: Its lattice constant varies discontinuously from 4.73 to 4.66 Å without any change in structure. The new fcc α'-Ce "collapsed" form appears to exist up to the highest pressure reached in this work (82.5 kbar) with a pressure-independent lattice parameter. All attempts to observe this phase in metastable conditions at pressures less than 50 kbar were unsuccessful with our exposure time of 12 h.

The first-order $\alpha \rightarrow \alpha'$ transition (like the γ

Table I. Experimental values of the lattice constant of cerium, at room temperature, as function of pressure, between 0 and 100 kbar.

Pressure[a] (kbar)	Lattice constant[b] (Å)	Pressure[a] (kbar)	Lattice constant[b] (Å)
Atmospheric pressure	5.16	54	4.66
10.5	4.82	56	4.66
11.5	4.83	62.5	4.66
14.5	4.81	63	4.66
15	4.82	67.5	4.66
21	4.79	70	4.65
26.5	4.78	71	4.66
36.5	4.75	72	4.66
46	4.73	74.5	4.66
49.5	4.73	78.5	4.66
49.5	4.66	82.5	4.66
53	4.67		

[a]All ±1 kbar.

[b]All ±0.01 Å.

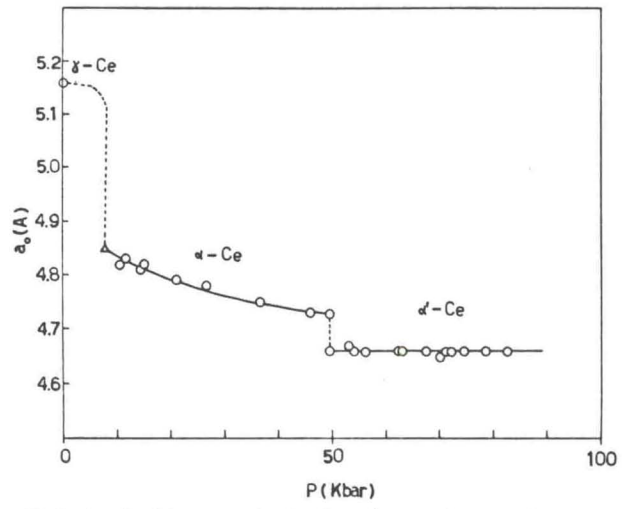

FIG. 1. Lattice constant of cerium, at room temperature, versus pressure. Open triangle, data reported in Ref. 4. Open circles, this work.

$\rightarrow \alpha$) can be interpreted only in terms of a change in the electronic configuration of cerium: The contraction in atomic volume determined in this work and the electric properties reported by Wittig[5] allow us to conclude that the valence of cerium must be less than 4 in the α phase and reaches the value 4 in the α' phase. This is also in very good accord with the theoretical predictions of Ratto, Coqblin, and Galleani d'Agliano.[8]

On the basis of this assumption the atomic radius of cerium in the tetravalent state has been calculated from the lattice constant of α'-Ce; its value is $r(\mathrm{Ce^{IV}}) = 1.648$ Å.

The metallic radii of cerium in the hypothetical trivalent state (deduced by interpolation from the behavior of the atomic radii of the trivalent rare earths versus atomic number) in the γ-Ce and α-Ce phases (which are isostructural with α'-Ce) are, respectively, $r(\mathrm{Ce^{III}}) = 1.846$ Å, $r_{\gamma\text{-Ce}} = 1.824$ Å, and $r_{\alpha\text{-Ce}} = 1.715$ Å.

Assuming a linear variation of the atomic radius versus valence between the two ends corresponding to $\mathrm{Ce^{III}}$ and $\mathrm{Ce^{IV}}$, one can deduce that the valency should be 3.11 in the γ phase and should become 3.67 at the $\gamma \rightarrow \alpha$ transition.

These results are in good agreement with those deduced through another method by Gschneidner and Smoluchowski.[4]

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ANOMALOUS NUCLEAR SPIN-LATTICE RELAXATION IN THE MIXED STATE OF SUPERCONDUCTING NIOBIUM

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The Nb^{93} spin-lattice relaxation time T_1 in the mixed state of niobium metal has been observed to depart at high temperatures from the temperature and field dependence predicted by the theory of gapless superconductivity. This anomaly indicates either a breakdown of the gapless theory or, more plausibly, the existence of a new relaxation mechanism at high temperatures.

The Nb^{93} nuclear spin-lattice relaxation time T_1 has been measured in the normal and superconducting states of niobium metal in the presence of an applied field. The measurements were undertaken to verify the "gapless" theory of elementary excitations recently reported.[1,2] At high temperatures T and correspondingly low applied fields H_e an anomalously fast relaxation appeared, although for low enough T the predicted dependence of T_1 on H_e and T was observed.

The measurements were made at constant H_e and variable T, and consisted of the usual observation by pulsed NMR of the longitudinal nuclear magnetization $M_z(t)$ at variable time t after an initial saturating train of rf pulses at the Larmor frequency ν_L. For $4.2 < T < 8$°K a variable-tem-