Structure of Cerium Metal at High Pressure*

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The high-pressure form of cerium metal stable above 56 kbar is found to be orthorhombic with the α-uranium type of structure. The effective metallic radius and the observed compressibility correspond to full tetravalency for cerium. A second, metastable form of cerium metal with a monoclinic structure has also been observed above 60 kbar.

A number of investigators have observed a phase change $\alpha \rightleftarrows \alpha'$ in cerium metal. The transition pressure as determined from resistance measurements has been reported to be 60–65 kbar,[1] 50 kbar,[2] and 56 kbar.[3] It is assumed in the present paper that the most recent value of 56 kbar is correct for high-purity metal. According to Wittig[2] the α' phase is superconducting below 1.7°K.

We have taken numerous *in situ* x-ray diffraction patterns of various cerium metal preparations of high purity up to about 110 kbar. The diffraction patterns were obtained with diamond-anvil screw-loaded equipment of the Bassett type,[4] using filtered Mo $K\alpha$ radiation. The analysis of the patterns proved to be difficult because of large hysteresis effects and the coexistence of two or more phases. We can report the following preliminary results for our studies.

We have observed the γ and α phases in metastable coexistence at 8 and 14 kbar where the pressures are deduced from the lattice constants and known compressibility of γ-Ce. The lattice constant of α-Ce was found to be 4.832 ± 0.004 Å and 4.801 ± 0.004 Å at 14 kbar. Single-phase patterns of α-Ce with lattice constants down to 4.629 ± 0.004 Å were observed, and it was assumed that this value corresponds to the pressure of 56 kbar. Accordingly one finds an average value of $K = (2.6 \pm 0.2) \times 10^{-6}$ cm^2/kg for the compressibility of α-Ce.

At least two high-pressure forms of cerium, α' and α'', have been observed. α'-Ce is orthorhombic, C centered, with four atoms per unit cell. At 66 kbar the cell dimensions (accuracy of ± 0.01 Å) are $a = 3.06$ Å, $b = 6.01$ Å, $c = 5.23$ Å. The structure of α'-Ce is that of α-U. α'-Ce was observed in coexistence with α-Ce at pressures as low as 43 kbar and as high as 62 kbar, the pressures being deduced from the observed lattice constants and compressibility of α-Ce. The volume contraction of α'-Ce from 43 and 62 kbar corresponds to a compressibility of $K = (1.5 \pm 0.3) \times 10^{-6}$ cm^2/kg.

α''-Ce is monoclinic, body centered, with two atoms per unit cell of dimensions $a = 4.79 \pm 0.02$ Å, $b = 3.20 \pm 0.01$ Å, $c = 3.18 \pm 0.01$ Å, $\beta = 92.1 \pm 0.2°$ at 56 kbar. The structure is a distorted cubic close-packed atomic arrangement. Samples containing the α'' and α phases (as well as the α' phase) have been found in the 51–62-kbar range. Above 62 kbar the diffraction patterns show the presence of the α' and α'' phases. However, the relative proportion of the two phases varies widely and depends upon the rate at which the pressure was increased. We believe that α''-Ce is a metastable phase formed by a second-order reversible transformation from the α phase at about 60 kbar. Above this pressure α''-Ce changes irreversibly to α'-Ce, but the transition is very sluggish.

Franceschi and Olcese[5] have reported that α'-Ce is cubic, face centered, with a lattice constant $a = 4.66 \pm 0.01$ Å which remains unchanged from 50 to 80 kbar. We find that the lattice constant of α-Ce decreases uniformly with increasing pressure from 4.832 ± 0.004 Å at 8 kbar to 4.606 ± 0.004 Å at 62 kbar. It seems thus that Franceschi and Olcese observed only α-Ce and that the pressure in their experiments did not exceed 48 kbar. McWhan[6] suggested that α'-Ce is hexagonal with $a = 3.16 \pm 0.01$ Å, $c = 5.20 \pm 0.02$ Å at about 65 kbar; but the agreement between observed and calculated spacings is poor. However, the McWhan data are in excellent agreement with the orthorhombic structure for α'-Ce described above.

The metallic radii (as defined in terms of the experimental atomic volumes[7]) of the various forms of cerium metal adjusted to room pressure and temperature are 1.824 Å for γ-Ce, 1.719 Å for α-Ce, and 1.675 Å for α'-Ce. However, at the transition pressure of 56 kbar the difference in size is much smaller, with an effective metallic radius of 1.636 Å for α-Ce and 1.627 Å for α'-Ce. We find that the atomic volume is the same (within experimental error) for the α' and α'' phases.

The experimental value of the cerium radius in α'-Ce is nearly identical with the value obtained for tetravalent cerium metal by extrapolation from the $3d$ and $4d$ series[7] and suggests the complete absence of localized $4f$ electrons in α'-Ce.

As far as we can tell from the diffraction intensities, the single positional parameter in the α'-Ce structure has the same value as the α-U structure. Thus each metal atom forms four short bonds, all directed within one hemisphere. However, the metallic radius of uranium in α-U is much smaller than of cerium in α'-Ce because uranium is hexavalent[7] and cerium tetravalent in these metal structures.

The occurrence of the unusual metal structures for the low-temperature forms of uranium, neptunium, and plutonium, and now for α'-Ce, suggests a correlation with admixture of f character in the valence-electron band structure. However, we can offer no reasonable explanation why α'-Ce with four valence electrons and α-U with six valence electrons are isostructural.

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Surface Electronic Structure via Generalized Wannier Functions

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A method which represents surface electronic structure exactly in terms of local functions is tested by applying it to a one-dimensional surface potential. A single four-parameter variational calculation yields continuum and surface-state wave functions for an entire perturbed band. Comparison with exact solutions obtained independently indicates that the calculation is quite accurate.

There is ample experimental evidence that the effects of a surface on the electronic properties of a solid, while locally strong, are rapidly damped so that such observables as charge densities and local densities of states quickly revert to their bulk values.[1] This suggests an inherent advantage in a description of the electronic structure in terms of local functions as opposed to a description in terms of wave functions, since the local description may more easily exploit the local nature of the surface perturbation. The generalized-Wannier-function concept recently introduced by Kohn and Onffroy[2,3] describes the electronic structure exactly in terms of local functions *which may be calculated directly without first calculating wave functions.* We report here the first test of this new concept and method as a practical tool for calculating the electronic structure of solid surfaces.

Generalized Wannier functions (GWF's) are the counterparts for crystals with defects of the familiar Wannier functions of perfect crystals. They are atomiclike functions localized about the lattice sites of the system and represent an alternative basis for the description of the electronic structure of the defect problem. A single set of GWF's is sufficient to describe an entire perturbed band, and only those GWF's near the de-