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STUDIES OF CALIFORNIUM METAL AT HIGH PRESSURE BY X-RAY DIFFRACTION*

John H. Burns

Transuranium Research Laboratory, Oak Ridge National Laboratory, Oak Ridge, TN.

and

J. R. Peterson

Department of Chemistry, University of Tennessee, Knoxville and Transuranium Research Laboratory, Oak Ridge National Laboratory, Oak Ridge, TN., U.S.A.

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ABSTRACT

The behavior of the crystal structure of californium metal under various pressures up to 140 kbars has been studied by use of a diamond-anvil type of miniature X-ray diffraction camera. Ten-microgram samples were encapsulated in aluminum foil, which also served as an internal standard for pressure determination. The phase transitions in cerium metal were produced and identified as a test of the apparatus and technique.

Californium metal samples in the low-density face-centered cubic form (a_o = 5.75 Å) and in the high-density face-centered cubic form (a_o = 4.96 Å) were each subjected to high pressure, but no transition was observed from one phase to the other. On release of the pressure, the lattice constant returned to its original value. Approximate values of the compressibility were obtained; they are about equal at 7×10^{-7} cm^2/kg.

Introduction

Among the metals of the lanthanide series of elements, Ce is unique in exhibiting an isostructural phase transition at about 7 kbars and room temperature. This transition also occurs at higher temperatures and pressures until a critical point is reached at about 20 kbars and 600 K; above this point the transition is continuous (see, e.g., Gempel, et al., 1972). Many theories have been advanced to explain this phenomenon. Some indicate a valence change while others do not, but they all involve interaction of the 4f and conduction electrons.

Phase studies of Cf metal by Noé and Peterson (1976) present what appears to be an analogous case; namely, there exists two face-centered cubic (f.c.c.) phases of widely different lattice dimensions which can be interconverted by proper thermal treatment. Metallic radii derived for these two forms are in good agreement with values predicted by Zachariasen (1973) for divalent and trivalent metals. A still more dense double-hexagonal close packed (d.h.c.p.) modification was observed but never isolated as a pure phase. In ionic compounds Cf is known to exhibit valences of 2, 3, and 4; hence it is reasonable to expect that these metallic phases represent two or more different valences (Zachariasen, 1973, 1976). The three lighter transplutonium elements each exhibit only two crystalline forms: f.c.c. and d.h.c.p.

Thus we have carried out a study of Cf metal under pressure to further examine its phase behavior, with the expectation of producing an isostructural phase transition between the f.c.c. forms.

Experimental Details

The samples of ^{249}Cf metal used in this study were those prepared previously by Noé and Peterson (1976) and used in their phase studies at atmospheric pressure. These samples were made by high-temperature reduction of CfF_3 with Li metal, followed by quenching to room temperature. Samples prepared above ≈725 C, when quenched, had the f.c.c. form with a_o = 5.75 Å ("divalent"), and those prepared between ≈600 and ≈725 C, when quenched, had another f.c.c. structure with a_o = 4.94 Å ("trivalent"). (The d.h.c.p. form was observed after annealing the lower-temperature f.c.c. form, but was found only in a mixture with it.) Four different samples were studied under pressure. They are described in the previous work, but we shall label them here as (1) "divalent" Cf, (2) "trivalent" Cf, (3) a mixture of two f.c.c. phases with lattice parameters near the trivalent value, and (4) a sample previously annealed in quartz and suspected of being an oxide.

For x-ray diffraction measurements a miniature camera equipped with diamond anvils (Bassett, et al., 1967) was used. An inconel gasket was used between the diamonds to prevent extrusion of the samples. Molybdenum K_α (λ = 0.7107 Å) x-rays were generated by a Jarrell-Ash microfocus unit. Two holes in the film cassette provided fiducial dots for correcting for film shrinkage, and the film radius was calibrated by x-ray diffraction studies with ThO_2. Known phase transitions in AgI and Ce metal were reproduced to check the apparatus and technique.

Loading of each Cf metal sample into the diamond press of the x-ray camera was done in an inert-atmosphere box and observed through a microscope. A tiny cup of Al foil was placed on the diamond anvil in the opening in the inconel gasket. The particle of Cf having a diameter of about 0.01 cm was

placed into the cup and covered with a disc of Al foil. The opposing diamond was then screwed into place and the pressure applied. The result was to encapsulate the Cf in a can of Al. The press and its contents were all removed from the box for x-ray study. This arrangement provided radioactive containment for the α-emitting ^{249}Cf, exclusion of air to prevent oxidation of this active metal, and an internal probe of the pressure by means of the Al x-ray diffraction pattern.

Each sample, stored in a quartz capillary at room temperature since its previous study, was examined by conventional Debeye-Scherrer techniques before insertion into the high-pressure device. Then there followed a series of x-ray exposures (18-24 hrs) with the sample at successively higher pressures; afterwards the pressure was reduced and further exposures were made.

The powder-diffraction patterns were measured with a steel scale provided with a 0.05 mm precision vernier. Equivalent lines on both sides of the beam hole were measured and converted to interplanar spacings by use of calibration and film-shrinkage factors. Only lines in the forward-scattering direction were recorded, but this includes spacings to less than 1 A when Mo radiation is used. The Cf lines generally were broader than found in the usual method: this may result from the irradiated sample being spread over a pressure gradient between the diamonds. The pressure was determined by measurement of the Al lines and use of the compression curve given by Roy and Steward (1969). All patterns were taken at room temperature.

Results and Discussion

In Table I are summarized the quantities involved in the measurements and the approximate values for the compressibility which were derived. The most

TABLE I

Sample	Starting a_o (Å)	Highest Pressure (kbars)	Compressibility, K. (cm^2/kg)
Divalent	5.750	127	7.3×10^{-7}
Trivalent	4.956	54	6.7×10^{-7}
Intermediate Mixture	5.043 4.966	125	7.3×10^{-7}
Oxide	5.602	144	4.8×10^{-7}

significant result, in view of the aim of this study, was the failure of the "divalent" Cf to convert to the "trivalent" form under high pressure. Indeed, on release of the pressure the lattice constant returned to its original value. The measured compressibility of the denser Cf phase is reasonable by comparison with previous measurements of actinide elements up through Am (see Stephens, et al., 1968) and extrapolation by analogy to the lanthanide metals. The "divalent" Cf phase, however, shows about the same compressibility as the other phases; this is not expected since in the lanthanide series Eu and Yb have compressibilities 2 or 3 times that of their trivalent neighbors (Rosen, 1969).

The findings presented here are preliminary because they result from a limited number of measurements on necessarily scarce quantities of this exotic element. On this micro scale of chemistry, impurities can have a significant effect; and while these samples were well characterized by x-ray diffraction, they were not subjected to elemental analysis. Further measurements will be made as new and larger samples become available. We have begun similar measurements on Cm in which we expect to produce the f.c.c. to d.h.c.p. transformation by application of pressure.

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