A High-Pressure Structure in Curium Linked to Magnetism

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Curium lies at the center of the actinide series and has a half-filled shell with seven $5f$ electrons spatially residing inside its radon core. As a function of pressure, curium exhibits five distinct crystallographic phases up to 100 gigapascals, of which all but one are also found in the preceding element, americium. We describe here a structure in curium, Cm III, with monoclinic symmetry, space group $C2/c$, found at intermediate pressures (between 37 and 56 gigapascals). Ab initio electronic structure calculations agree with the observed sequence of structures and establish that it is the spin polarization of curium’s $5f$ electrons that stabilizes Cm III. The results reveal that curium is one of a few elements that has a lattice structure stabilized by magnetism.

The contribution of various factors in the electronic structure of a material to the bonding in its solid phase is at the heart of materials science and is a subject of extensive experimental and theoretical interest. It is well known that, when approaching the center of the actinide ($5f$) series of elements, a marked change occurs in the elemental volumes. The atomic volume of americium (Am) is almost 50% larger than that for the preceding element plutonium (Pu) (Fig. 1). The lighter actinides (Pa to Pu) have smaller atomic volumes and itinerant $5f$ states that participate in the (metallic) bonding and thus contribute to the cohesive properties of the solid. However, the $5f$ states are also capable of spin-polarization and hence magnetism. When the $5f$ bands are broad, as in the itinerant metals (Pa to Pu), there is an absence of magnetic correlations (1, 2). However, for heavier actinide elements (Am and beyond), there is no $5f$ bonding, and magnetic correlations give rise to local moments, as found in the analogous $4f$ elements. Of particular interest with these heavier actinides is whether applied pressure can bring about the delocalization (a change of character from localized to itinerant) of their $5f$ electrons, and, if so, what are the consequent crystallographic, electronic, and magnetic structures?

In the periodic table, iron and cobalt are unique in the sense that the magnetic interactions between individual electron states determine their crystal structures (3–5). Given that the magnetic correlations are between $f$ electron states in the actinides, we may ask whether such magnetic interactions can influence the sequence of crystal structures.

There are fundamental differences in the pressure-volume relationships of the light (6, 7) and heavy actinide metals (Fig. 1). Under compression, the relative volume changes with pressure for $\alpha$-uranium (the room-temperature–stable form of uranium metal) (7) are clearly different from those for either Am or curium (Cm). We have investigated in detail the case of Am (8, 9), where four crystal structures are found to exist between ambient pressure and 100 GPa. The delocalization of the $5f$ electrons of Am by pressure occurs in two stages, with the progressive formation of two lower symmetry structures, a face-centered orthorhombic Am III and a primitive orthorhombic structure, Am IV; the transition to each is accompanied by an abrupt decrease in the relative atomic volume. The formation of the Am IV structure (space group, $Pmna$), which was subsequently confirmed by theory (10), is now recognized as an important high-pressure structure for $f$ electron metals.

In Cm, the $5f$ half-filled orbital provides a stabilizing effect. Consequently, forcing its $5f$ electrons to participate in its bonding requires higher pressures than in the case of Am. At ambient pressure, only the $6d$ $7s$ states of these elements are involved in their metallic bonding (2). With the application of pressure, the double hexagonal close packed (dhcp) form of Cm ($Fd\overline{6} McCoy$, Cm I) converts to a face-centered cubic (fcc) structure ($Fm\overline{3}m$, Cm II) at 17(2) GPa. This transformation requires little energy and reflects an increase in the $d$ character of the bonding. There is a smooth transition between the Cm I and Cm II phases (Fig. 1), indicating that each phase has a comparable bulk modulus. This same transition occurs in Am, but at a lower pressure (6 GPa) (8, 9).

Previous work (11, 12) has identified the initial dhcp-fcc transition and also reported a phase transition above 40 GPa, but was unable to determine the correct structure. Given the pressure behavior of Am, one could have anticipated finding a structure similar to the Am III structure ($Fddd$) after the Cm II phase. However, our synchrotron radiation data show unambiguously that the Cm III phase is not $Fddd$ as found for Am III. Before looking in detail at this Cm III phase, we will discuss the higher pressure phases of Cm.

Increasing the pressure above 56(4) GPa results in a third phase transition (Cm III to Cm IV), and this phase can indeed be identified with the $Fddd$ structure as found for Am III. A smooth transition is observed between the Cm III and Cm IV phases. Above 95(5) GPa, the fourth phase transition (Cm IV to Cm V) is observed and yields a $Pmna$ phase, which was previously identified for the Am IV structure. The $Fddd$ to $Pmna$ (Cm IV to Cm V) transition is accompanied by an ~11.7% volume collapse, whereas the Cm II to Cm III transition, the collapse is ~4.5%. These abrupt volume changes signify the stepwise delocalization of the $5f$ electrons and their subsequent participation in the metallic bonding. In Am, the total collapse of ~9% for two transitions is smaller than that for Cm, but in both elements the collapses occur in two stages. The appearance of the $Fddd$ and $Pmna$ forms for Am (8, 9) and Cm at higher pressures is a clear indication that the $5f$ delocalization process favors these structures.
The puzzle, however, remains the formation of the Cm III phase. This phase, starting at \( \sim 37 \text{ GPa} \) and extending to \( 56 \text{ GPa} \), has a monoclinic structure with the space group \( C2/c \). A Rietveld fit of the Cm III data for this phase is shown in Fig. 2 at 45 GPa. This structure has not previously been reported for any element with \( f \) electrons.

An illustration of the different structures observed in Cm is given in Fig. 3. In comparison to the Am III or Cm IV (\( Fdd\bar{d} \)) structures, the Cm III (\( C2/c \)) structure is composed of slightly distorted (rectangularly distorted) close-packed hexagonal planes, but in contrast to the (\( Fdd\bar{d} \)) structure, it has a stacking arrangement that reduces the symmetry to monoclinic.

The isothermal bulk modulus (\( B_0 \)) and its pressure derivative (\( B'_0 \)) for Cm were determined from experimental data for the Cm I and Cm II low-pressure phases (localized \( f \) electrons) by fitting the experimental data to the Birch-Murnaghan (13) and Vinet (14) equations of state. Values of 36.5(3) GPa for \( B_0 \) and 4.6(2) for \( B'_0 \) were obtained with both equations. The inset of Fig. 1 shows the atomic volumes of the actinide metals at ambient pressure plotted together with their bulk moduli (6–9, 15–17).

In an attempt to understand the stability of the unusual Cm III structure with its lower \( C2/c \) symmetry, we performed calculations using the full potential linear muffin-tin orbital (FPLMTO) method (18–20), in which basis functions, electron densities, and potentials are calculated without geometrical approximations. These quantities were expanded in spherical waves (with a cut-off maximum orbital angular momentum of 6) inside non-overlapping spheres surrounding the atomic sites (muffin-tin spheres) and in a Fourier series in the interstitial region between the spheres. Total energy calculations were performed with two magnetic configurations, ferromagnetic (FM) and antiferromagnetic (AFM), as a function of volume. The calculations show that the AFM configuration is always lower in energy compared to the FM configuration for all structures. For example, for the Cm III structure, the difference in energy between the AFM and FM configurations at a volume of 16 \( \text{A}^3 \) per atom (where Cm III is the stable phase) is around 30 milli-rydberg (mRy) per atom in favor of the AFM configuration. Total energy differences for different magnetic configurations over a wide volume range are shown in fig. S2. Furthermore, the calculations also show that the correct structural sequence can only be obtained if we treat all the structures in the AFM configuration.

Calculated total energy differences between the various structures using Cm II as the reference structure are shown in Fig. 4. The Cm III phase is theoretically stable between 17 and 15 \( \text{A}^3 \), whereas experimentally it is found between 19.6 and 17.2 \( \text{A}^3 \). In all cases, the theoretically derived critical volumes are smaller than those observed experimentally, but this is a general problem probably associated with the simulation of the core states. However, the relative sequence of phase transitions is reproduced. More importantly, the Cm III structure without magnetic correlations is not the favored crystal structure. By comparing enthalpies, we calculated the transition pressures for Cm III and found good agreement with those determined experimentally (table S1).

The calculated magnetic moment for the Cm I phase in the AFM state starts at almost 7 Bohr magnetons (\( \mu_B \)), as expected for the half-filled shell and full spin polarization, and in agreement with experiments at ambient pressure (21). Theoretically, as the volume is decreased, the moment decreases gradually and disappears at the Cm IV to Cm V phase transition, when the \( 5f \) electrons are completely delocalized. In the Cm III phase, the calculated AFM moment decreases from 5 to 4 \( \mu_B \) as the pressure is increased. Experiments give the magnetic moment of Cm as a function of pressure have not been reported.

The experiments presented here on Cm, a pivotal element at the center of the \( 5f \) actinide series, have shown that it exhibits a complex sequence of phase transitions up to 100 GPa (1 Mbar). As expected, given the immediate proximity between Am and Cm in the periodic table and that, under high pressures, both will reach states with fully delocalized (itinerant) \( 5f \) behavior, the sequences of phase transitions as a function of pressure in Am (8, 9) and Cm are similar. However, Cm exhibits an additional intermediate phase, Cm III, a monoclinic \( C2/c \) structure, that occurs before the \( 5f \) states become...
The magnetic correlations in Cm are very strong in contrast to Am in which the spin (S) electrons cancel (S = −L = 3, thus J = L + S = 0 in Russell-Saunders coupling) and there is no magnetic moment. We thus find that the magnetic correlation energy in AFM Cm plays a crucial role in establishing its structural characteristics and, in particular, in leading to the stabilization of the Cm III structure.

In only two known cases, iron and cobalt, the magnetic phenomenon on an element as a function of volume (3–5). The reason is that magnetic interactions are on the scale of meV, whereas structural stabilities are on the scale of eV, although at phase transitions these differences are in the meV range. Now we have found a third element, curium, which has a half-filled shell of 5f electrons, where this magnetic phenomenon is again observed and where the magnetic correlations of f electrons determine the crystal structure. The nature of the interactions and the associated crystal structure of Cm III suggest that such effects may become prevalent in other f elements at small atomic volumes.

References and Notes

20. Materials and methods are available as Supporting Material on Science Online.
On-Wire Lithography

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We report a high-throughput procedure for lithographically processing one-dimensional nanowires. This procedure, termed on-wire lithography, combines advances in template-directed synthesis of nanowires with electrochemical deposition and wet-chemical etching and allows routine fabrication of face-to-face disk arrays and gap structures in the range of five to several hundred nanometers. We studied the transport properties of 13-nanometer gaps with and without nanoscopic amounts of conducting polymers deposited within by dip-pen nanolithography.

Despite their many attributes and capabilities, nanolithographic techniques such as electron-beam lithography, dip-pen nanolithography (DPN), focused ion-beam lithography, and nanoimprint lithography are limited with respect to throughput, materials compatibility, resolution, and cost (1). For example, the field of nanoelectronics depends on the ability to fabricate and functionalize electrode gaps less than 20 nm wide for precise electrical measurements on nanomaterials. Fabricating such structures is far from routine and often involves low-yielding, imprecise, and difficult-to-control procedures such as break-junction techniques and gap narrowing by electroplating (2–6). Here, we present a relatively high-throughput procedure for lithographically processing nanowires that allows us to control gap size down to the 5-nm length scale. This procedure, termed on-wire lithography (OWL), combines advances in template-directed synthesis of nanowires with electrochemical deposition and wet-chemical etching and allows the routine fabrication of architectures that would be difficult, if not impossible, to make with any known lithographic methodology (Scheme 1).

OWL is based on the idea that one can make segmented nanowires consisting of at least two types of materials, one that is susceptible and one that is resistant to wet-chemical etching. For proof of concept, we used Au-Ag and Au-Ni. We first describe the process involving Au-Ni nanowires. These materials can be electrochemically deposited in porous alumina templates (pore diameter = 360 nm) in a controlled fashion from suitable plating solutions through well-established methods (Scheme 1) (7–11). The length of each segment can be tailored by controlling the charge passed during the electrodeposition process (fig. S1). They are released from the template by dissolution of the template through literature procedures (12).

The nanowire aqueous suspension was cast on a glass microscope slide, pretreated with piranha solution to make it hydrophilic, and allowed to dry in a desiccator. A layer of silica (50 nm) was deposited on the nanowire-coated substrate by plasma-enhanced chemical vapor deposition (13). The substrate was immersed in ethanol and sonicated (VWR Ultrasonic Cleaner, MODEL 50T) for 1 min, which resulted in the release of the wires (fig. S2).

The final step of the OWL process involves the selective wet-chemical etching of the Ni segments. The Ni can be removed from the wires by treating them with concentrated HNO₃ for 1 hour to generate nanowire structures with gaps precisely controlled by the length of the original Ni segments (Scheme 1).

We also prepared similar structures using Ag as the sacrificial segment material and an Au/Ti bilayer (40 nm/10 nm) deposited by thermal evaporation as the segment-bridging layer instead of silica. In this case, the Ag was removed by treating the wires with an etching solution consisting of methanol, 30% ammonium hydroxide, and 30% hydrogen peroxide (4:1:1 v/v/v) for 1 hour.

Using the OWL procedure, we prepared nanowires with designed gaps of 5, 25, 40, 50, 70, 100, 140, and 210 nm (Fig. 1). The physical dimensions and block compositions of the nanowires, before and after etching, were determined by field-emission scanning electron microscopy (FESEM) and energy-dispersive x-ray spectroscopy (fig. S3), respectively. Structures made of Au and Ag before coating with Au/Ti and wet-chemical etching exhibit a bright contrast for the Ag regions and a dark contrast for the Ag regions (Fig. 1A). Etching then creates the notched structures (Fig. 1B). The average length of the wires (±SD) is 4.5 ± 0.25 μm, and each wire exhibits two notches measuring 210 ± 10 nm, two measuring 140 ± 8 nm, and two measuring 70 ± 5 nm (Fig. 1B). The diameter of each wire is 360 ± 20 nm. Certain views show the Au/Ti backing, which bridges the notched regions on these structures (Fig. 1B, inset). Structures with gaps sizes of less than 100 nm can be routinely generated with OWL. To demonstrate this capability, we used OWL to prepare wires with 25-, 50-, and 100-nm gaps (Fig. 1C).

We observed similar results with the use of Ni as the sacrificial segment and silica as the bridging material. To demonstrate that OWL can make repeating structures consisting of regular 40-nm gaps, we made nanowire structures with 22 40-nm Ni segments and 23 40-nm Au segments (Fig. 1D). After coating with silica and subsequent removal of the Ni blocks, face-to-face disk arrays with 40-nm gaps were generated (Fig. 1E). The statistical

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Supporting Online Material
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Materials and Methods
Figs. S1 and S2
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References and Notes
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Editor's Summary