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LETTER TO THE EDITOR

Delocalisation of 5f electrons in berkelium–californium alloys under pressure

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Abstract. The high-pressure structural behaviour of two berkelium–californium alloys was studied up to about 47 GPa. The alloys had been formed through the ingrowth of ²⁴⁹Cf into ²⁴⁹Bk by β^- decay. The berkelium-rich alloy (about 35% Cf) exhibited the same phases as pure berkelium metal, the californium-rich alloy (about 60% Cf) the same phases as pure californium. An approximately linear increase of transition pressures with californium content was observed. The results are compared with data obtained previously for the high-pressure behaviour of the pure americium, curium, berkelium and californium metals. As in the pure metals, the transformation of the alloys to the alpha-uranium-type structure, accompanied by a sudden volume decrease, is interpreted as the onset of 5f electron itinerancy.

The actinide metals americium (Benedict *et al* 1985b), curium (Benedict *et al* 1985a, Haire *et al* 1985), berkelium (Benedict *et al* 1984, Haire *et al* 1984) and californium (Peterson *et al* 1983, Benedict *et al* 1984) have been investigated under high pressure. Previous studies of americium metal under pressure have been published by other research groups (Roof *et al* 1980, Akella *et al* 1980). These four actinide metals exhibit the double hexagonal close-packed (DHCP) structure at normal pressure and room temperature and transform to a cubic close-packed (CCP) structure with the application of sufficient pressure. At still higher pressures they exhibit an α -uranium-type orthorhombic structure. This latter transition is accompanied by a volume discontinuity. The formation of a lower symmetry structure with a simultaneous discontinuity in volume is considered to reflect the onset of 5f electron itinerancy (Johansson *et al* 1981). Among these four metals, Cm was found to have a particular behaviour (higher transition pressures and greater decrease in volume upon delocalisation) related to its half-filled 5f electron shell (Benedict *et al* 1985a). In addition, Am and Cf metals under sufficient pressure exhibit an 'intermediate' phase between the CCP and the α -uranium phases, but such a phase has not been observed in Cm and Bk metals under pressure.

Studies of these heavy actinide elements under pressure to date have been limited to the pure metals, from which the variation of phase transition pressures, volume change upon delocalisation and compressibilities with atomic number could be deduced. Additional studies of binary alloys of each two neighbouring elements under pressure will allow

completion of the systematics of the behaviour of these metals under pressure. Thus the variation of the above properties can be determined on a more refined atomic number scale. For example, one can expect to obtain more detailed information on the reasons for the behaviour of curium (Benedict *et al* 1985a, Haire *et al* 1985) under pressure by studying binary alloys of curium with each of its neighbours, americium and berkelium.

As a first step in a systematic study of the pressure behaviour of interactinide alloys, we report here the results of high-pressure x-ray diffraction work on $\text{Bk}_{1-x}\text{Cf}_x$ alloys at two compositions: $x = 0.35$ (Bk rich) and $x = 0.60$ (Cf rich). These alloys were formed from ^{249}Bk metal by the β^- decay of ^{249}Bk into ^{249}Cf ($t_{1/2} = 325$ days). Since the alloying element californium is formed on an atomic scale at randomly distributed lattice sites, these $\text{Bk}_{1-x}\text{Cf}_x$ alloys gave us the opportunity to study truly homogeneous solid solutions. It is difficult to obtain true homogeneity by the usual alloying procedures such as melting and sintering.

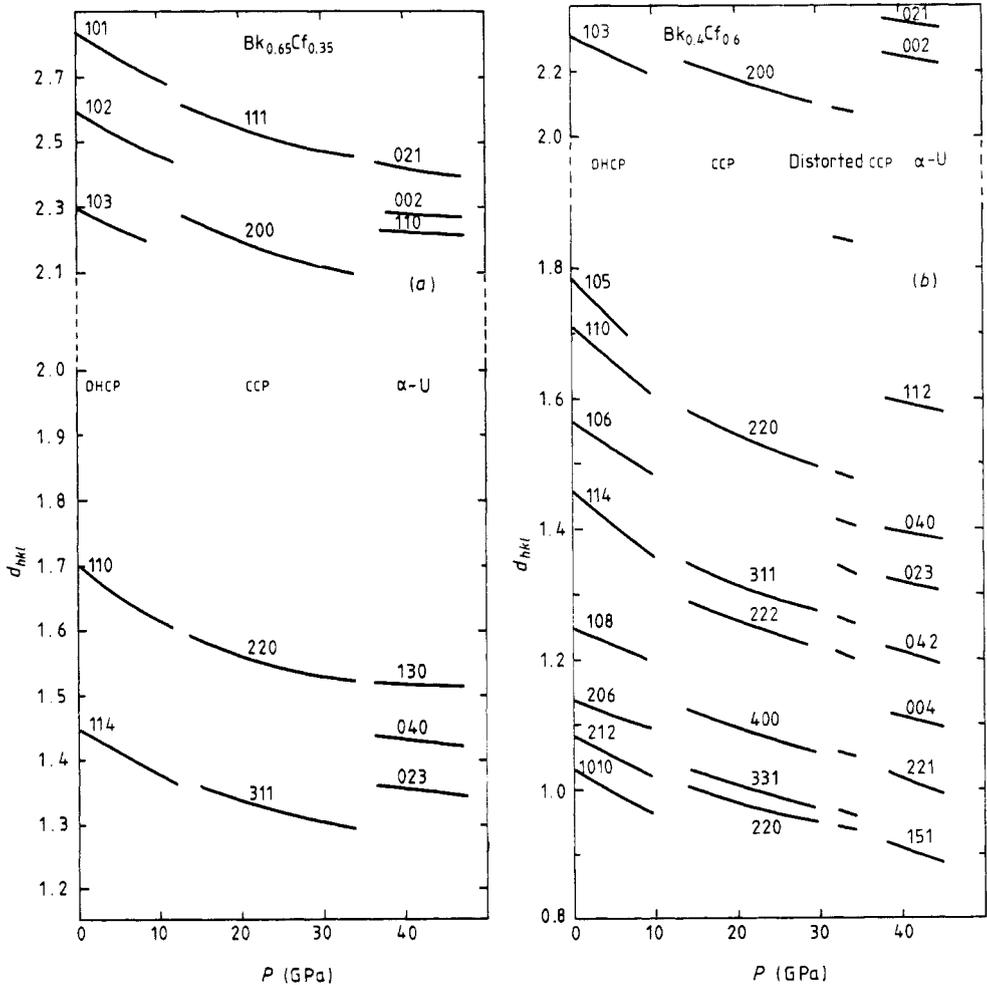


Figure 1. Variation with pressure of interplanar distances in $\text{Bk}_{1-x}\text{Cf}_x$. (a) $x = 0.35$, Bragg angle = 5° ; (b) $x = 0.60$, Bragg angle = 7° . The Miller indices hkl are indicated.

The initial berkelium metal samples were prepared at the Oak Ridge National Laboratory; details of the method of preparation have been published elsewhere (Haire 1982). A Syassen-Holzappel-type diamond anvil cell was used for obtaining diffraction data at high pressure; silicone oil served as the pressure-transmitting medium. The pressure was measured by the ruby fluorescence technique (Mao *et al* 1978). The diffraction measurements were made at room temperature using the high-pressure x-ray diffraction facility of the European Institute for Transuranium Elements in an energy-dispersive mode with a fixed Bragg angle of 5° or 7° (Benedict and Dufour 1984). Maximum pressures reached in these experiments were 47 GPa for $\text{Bk}_{0.65}\text{Cf}_{0.35}$ and 46.5 GPa for $\text{Bk}_{0.40}\text{Cf}_{0.60}$.

In figures 1(a) and (b) the interplanar distances in each alloy are plotted as a function of pressure. Up to 12 GPa all the diffraction lines were indexed in the DHCP structure. The volumes obtained at normal (1 atm) pressure (111.75 \AA^3 for the alloy with $x=0.35$ and 110.86 \AA^3 for the one with $x=0.60$) are in accord with the volumes known for the pure metals. The DHCP \rightarrow CCP transition occurred without a discontinuity in volume (figures 2(a) and (b)). The transition pressures, 12 GPa for the alloy with $x=0.35$ and 14 GPa for the one with $x=0.60$, are intermediate between those obtained for the DHCP \rightarrow CCP transition in Bk (10 GPa) and Cf (17 GPa) metals (figure 3). As for the pure actinide metals (Benedict *et al* 1985a), this transition can be correlated to the variation in d-electron occupancy (for references, see Benedict *et al* 1985a).

At pressures higher than 34 GPa, a new crystallographic phase appeared in both alloys. This phase remained stable up to the highest pressures attained and was indexed on the basis of an α -uranium-type orthorhombic structure. Accompanying this transition we

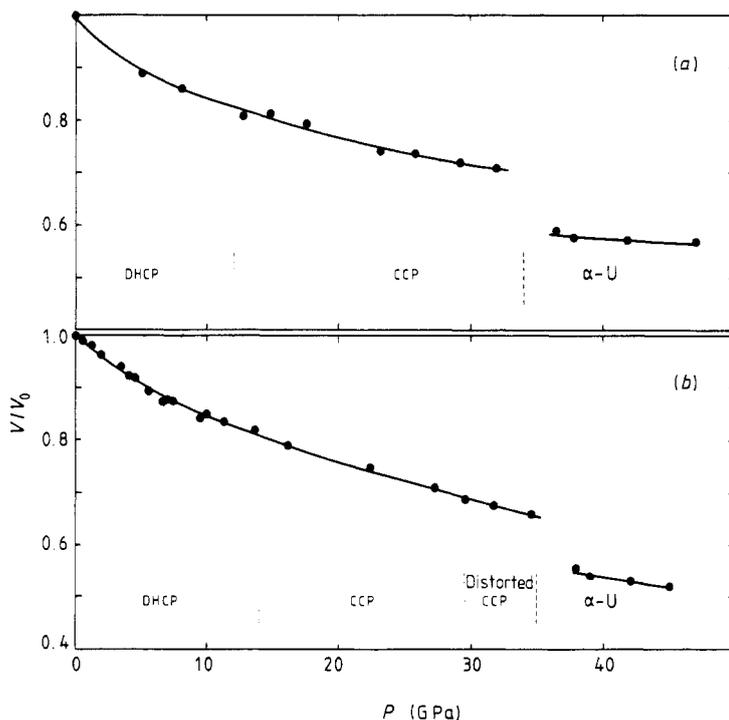


Figure 2. Unit cell volumes of $\text{Bk}_{1-x}\text{Cf}_x$ alloys as a function of applied pressure: (a) $\text{Bk}_{0.65}\text{Cf}_{0.35}$, $\Delta V/V \sim 16\%$; (b) $\text{Bk}_{0.40}\text{Cf}_{0.60}$, $\Delta V/V \sim 15\%$.

observed a sudden decrease in volume. As with the pure transplutonium metals, this transition to a lower symmetry structure, accompanied by a discontinuity in volume, is related to 5f electron delocalisation. The $\Delta V/V$ at the delocalisation transition observed for both alloys ($\sim 16\%$ and $\sim 15\%$) is comparable with those obtained for Bk ($\sim 12\%$) and Cf ($\sim 16\%$) metals. The pressures at which delocalisation takes place (34 GPa for the alloy with $x=0.35$ and 35 GPa for the one with $x=0.60$) are also intermediate between those determined for Bk (32 GPa) and Cf (41 GPa) metals alone.

Another objective of this study was to determine if an additional structural phase forms in the Bk–Cf alloys between the CCP and the α -uranium phases. Such a phase has been found in Cf metal but not in Bk metal (Benedict *et al* 1984). The absence of this 'intermediate' phase in Bk metal was confirmed by recent work of the present authors, where its range of possible existence was investigated in small pressure steps. In the Cf-rich alloy, we observed, in both series of experiments performed, this 'intermediate' phase (figure 1(b)) that we have indexed as the distorted CCP (trigonal) structure determined by Vohra *et al* (1984) for trivalent rare-earth metals. But the pressure at which this phase first appeared differed in the two series (20 as opposed to 29 GPa), although the pressures at which the other phase transitions took place remained about the same. This discrepancy could be accounted for if the distorted CCP structure represents only a slight deformation of the CCP structure such that the two phases are nearly thermodynamically equivalent. If so, the actual transition pressure can be strongly influenced by the homogeneity of the applied

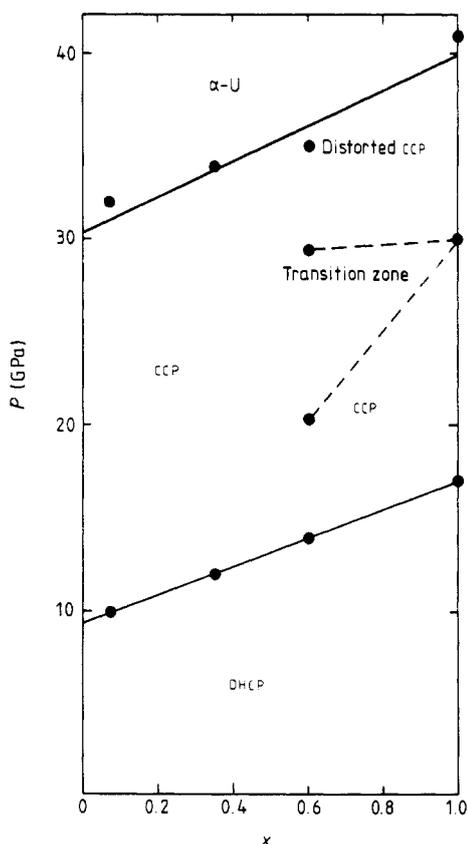


Figure 3. Transition pressures as a function of concentration of Cf in $Bk_{1-x}Cf_x$ alloys formed by the β^- decay of ^{249}Bk .

Table 1. Transition pressures, volume decreases and relative volumes upon delocalisation, and bulk moduli for americium, curium, berkelium (containing ~7% Cf), berkelium–californium alloys and californium. The data stem from the references at the end of the paper, with the exception of the two bulk moduli indicated.

	<i>P</i> (GPa)				$\Delta V/V$ upon delocalisation	V/V_0 at onset of delocalisation	B_0 (GPa) in the DDCP phase
	DHCP → CCP	CCP → Distorted CCP	Delocalisation				
Am	9.5	13.5	23	~6%	~67%	45	
Cm	23	—	43	~21%	~53%	37†	
Bk	9–10	—	32	~12%	~54%	52†	
Bk _{0.65} Cf _{0.35}	12	—	34	~16%	~59%	47	
Bk _{0.40} Cf _{0.60}	14	20–29	35	~15%	~55%	47	
Cf	17	~30	41	~16%	~53%	50	

† Based on recent unpublished work by the present authors.

pressure. In the Bk-rich alloy this 'intermediate' phase was not observed (figure 1(a)), in accord with its absence in Bk metal alone. It appears that a relatively large proportion of Cf is required to stabilise this phase.

The relative volumes V/V_0 at delocalisation, when the α -uranium structure is first observed, are about 59% for the composition $x=0.35$ and about 55% for the Cf-rich alloy. These values are similar to the values obtained for Cm, Bk and Cf metals. For Am, on the basis of a new experiment (Benedict *et al* 1985b), we propose that delocalisation occurs only when the α -uranium phase appears, which occurs at a relative volume of about 67%, noticeably larger than the values above.

For both Bk-Cf alloys the variation with pressure of the relative volume of the DHCP phase has been fitted to the Murnaghan and Birch first-order equations of state. There was excellent agreement between the two equations of state. The same bulk modulus (47 GPa) was obtained for both alloy compositions. This value is in accord with other bulk moduli reported for the trivalent lanthanide and transplutonium metals (see table 1).

The present results are summarised in table 1 and compared with those reported for Am, Cm, Bk and Cf metals. We observe continuity between Bk and Cf for the transition

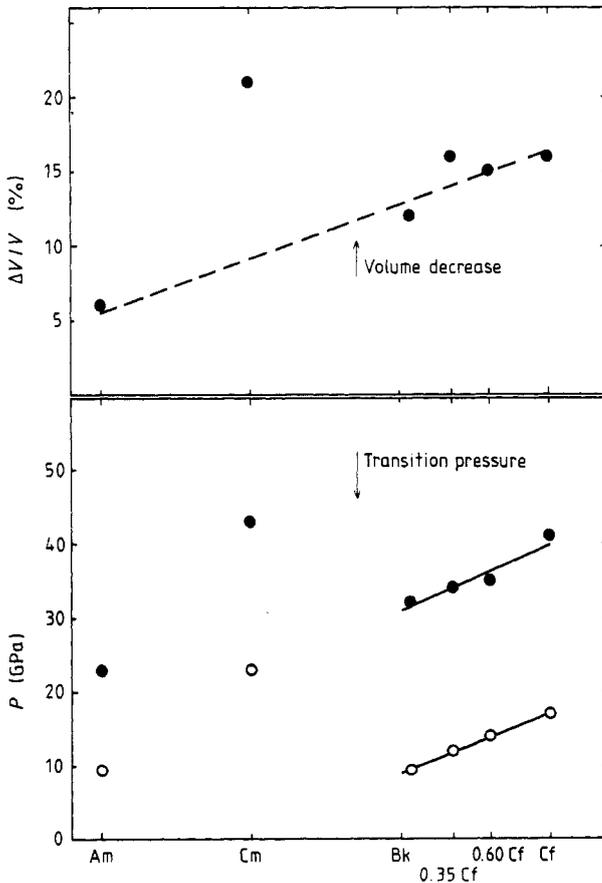


Figure 4. Pressures of the DHCP \rightarrow CCP (○) and the delocalisation (●) transitions, and volume decreases accompanying delocalisation, for metals from $Z=95$ to $Z=98$. Fractional atomic numbers have been assigned to the Bk-Cf alloys.

pressures, the relative volume and the volume decrease upon delocalisation and for the bulk modulus. The variations of transition pressures and of volume changes upon delocalisation through the series Am to Cf, including the Bk–Cf alloys which can be considered as having non-integral atomic numbers, are shown in figure 4. With the exception of Cm, a continuous increase of transition pressures and of volume changes with Z is observed, as indicated for example by the broken line in the $\Delta V/V$ plot. The data for curium underscore its particular situation caused by its half-filled 5f electron shell. The existence of an 'intermediate' phase between the ccp and the α -uranium phases indexed with a distorted ccp (trigonal) structure in Cf metal, in the Cf-rich alloy here and in Am metal is not yet very well understood. Further investigations on other actinide alloys (for example Am–Cm alloys) would provide valuable information toward resolution of this problem and also clarification of the particular behaviour of Cm metal under pressure.

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