THE STRUCTURE AND THERMAL EXPANSION

OF δ- AND η-PLUTONIUM

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Based on the increase in the covalent component of a bond with reduction in temperature in crystalline modifications of uranium, neptunium and plutonium, a new idea is put forward for the structure of δ- and η-plutonium. The crystalline structure of these modifications is considered as the result of a comparatively small deviation from the ideal face-centered lattice under the action of four covalent bonds. This idea makes it possible to explain a number of anomalous properties of δ- and η-plutonium, in particular the negative values of the volume coefficient of thermal expansion and the high values of the atomic volume.

Introduction

The modifications of δ- and η-plutonium have certain specific properties not found in ordinary metals. Of these properties, the first which should be mentioned is the negative value of the volume coefficient of thermal expansion and the anomalously high atomic volume of these phases.

According to the existing data the δ-phase has a face-centered cubic lattice with parameter a = 4.637 Å (at 320°C), and an η-phase - a face-centered tetragonal lattice with parameters a = 4.701 Å and c = 4.489 Å (at 490°C). The density of these phases is 15.9 and 16.0 g/cm³, respectively, which is much less than the density of the high-temperature body-centered δ-phase (16.5 g/cm³).

In accordance with the data of [1] the mean value of the coefficient of thermal expansion of the δ-phase in the temperature range 320-440°C is equal to \(-8.6 \times 10^{-6}\), and the coefficient of thermal expansion of the η-phase in the various axes has the following values:

\[
\alpha_a = (305 \pm 35) \times 10^{-6} \quad \text{according to the data of [1];}
\]
\[
\alpha_c = (-659 \pm 67) \times 10^{-6}
\]
\[
\alpha_a = (444.8 \pm 12) \times 10^{-6}
\]
\[
\alpha_c = (-1063.5 \pm 18.2) \times 10^{-6}
\]

In a number of papers, attempts have been made to explain the unusual properties of these phases. In particular, in [3] it was suggested that due to the small difference in energy levels of the 5f- and 6d- electrons in plutonium, two forms of the atoms could exist simultaneously with a different electron structure and with different dimensions respectively.

With increase in temperature, the number of atoms with a smaller diameter increases due to a reduction in the number of atoms of larger diameter, which leads to a negative value of the coefficient of thermal expansion. The tetragonal nature of the η-plutonium lattice, according to this concept, is due to the formation of an ordered structure of these two forms of atoms.

An attempt was made in [4] to explain the negative coefficient of thermal expansion of δ-plutonium by the possibility of sharp increase in density of the states in the region at the top of the filled part of the Brillouin zone. However, most authors consider that a satisfactory explanation of the mechanism of the anomalous thermal expansion of δ- and η-plutonium is yet to be found.
In a paper by one of the present authors [5] it was shown that the anisotropy of the thermal expansion of a number of modifications of uranium, neptunium and plutonium is due to a weakening of the four covalent bonds with increase in temperature and their uneven distribution in the various crystallographic directions. The weakening of the covalent bonds means that the minimum interatomic distance \( d_{\text{min}} \) on transition to higher temperature modifications increases abruptly and the difference \( d_m - d_{\text{min}} \) decreases accordingly until it is equal to zero in the higher temperature modification (in the body-centered cubic lattice). The values of \( d_{\text{min}} \) for a number of neptunium and plutonium phases are given in the table.

The Value of \( d_{\text{min}} \) for Some Phases of Neptunium and Plutonium

<table>
<thead>
<tr>
<th>Element</th>
<th>Phase</th>
<th>( d_{\text{min}}, \text{Å} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Np</td>
<td>( \alpha )</td>
<td>2.62</td>
</tr>
<tr>
<td></td>
<td>( \beta )</td>
<td>2.79</td>
</tr>
<tr>
<td></td>
<td>( \gamma )</td>
<td>3.03</td>
</tr>
<tr>
<td>Pu</td>
<td>( \alpha )</td>
<td>2.52 - 2.73</td>
</tr>
<tr>
<td></td>
<td>( \beta )</td>
<td>( -2.7^* )</td>
</tr>
<tr>
<td></td>
<td>( \gamma )</td>
<td>3.05</td>
</tr>
<tr>
<td></td>
<td>( \epsilon )</td>
<td>3.15</td>
</tr>
</tbody>
</table>

*An approximate value from [6].

For the phases of \( \delta \)- and \( \eta \)-plutonium, the value of \( d_{\text{min}} \) is 3.28 and 3.25 Å respectively. A comparison with the data of the table shows that these values of \( d_{\text{min}} \) are much higher than those for the highest temperature modification – \( \epsilon \)-plutonium. This lack of correspondence in the value of \( d_{\text{min}} \) for \( \delta \)- and \( \eta \)-plutonium contradicts the above considered regularity. Hence it follows that the structure of these phases is actually more complex. If we assume that the four covalent bonds appearing in plutonium in the \( \alpha \)- and \( \gamma \)-modifications also occur in the \( \delta \)- and \( \eta \)-modifications, where \( d_{\text{min}} \) corresponding to these bonds lie within the limits between these values of \( d_{\text{min}} \) for \( \gamma \)- and \( \epsilon \)-phases (between 3.05 and 3.15Å) then it is possible to explain not only qualitatively but in the first approximation quantitatively the anomalous character of the thermal expansion of \( \delta \)- and \( \eta \)-plutonium. The anomalously high value of the atomic volume and a number of other properties of these phases can also be explained.

Since the structures of the \( \delta \)- and \( \eta \)-plutonium are considered as the result of distortion of an ideal tightly packed structure under the action of the covalent bond forces, the analysis should start with the higher temperature modifications – the \( \eta \)-phase, in which these bonds should appear more weakly.

**Structure and Thermal Expansion of \( \eta \)-Plutonium**

It is well known that a body-centered cubic lattice with a parameter \( a_{bc} \) can be considered as a tetragonal face-centered lattice with parameters \( a_{ft} \) and \( c_{ft} \) and a ratio of the axes \( c_{ft}/a_{ft} = 0.707 \). The deformation of this face-centered cell, accompanied by approach of the ratio of axes \( c_{ft}/a_{ft} \) to unity, will be a transition from a body-centered to a face-centered cubic lattice. On transition to the latter the initial body-centered cubic lattice changes to a body-centered tetragonal lattice with ratio of axes \( c_{bt}/a_{bt} = 1.41 \).

The volumes of the initial and final cells will be respectively

\[
V_{bc} = a_{bc}^3; \quad V_{bt} = a_{bt}^2 c_{bt} = \sqrt{2} a_{bt}^3.
\]

If we assume in the first approximation that the volume of the unit cell does not change during transformation, i.e. we neglect the change in degree of compactness of the packing, then \( a_{bc} = \sqrt{2} a_{bt} \). Hence it follows that

\[
a_{bt} = \frac{a_{bc}}{\sqrt{2}} = 0.89a_{bc}; \quad c_{bt} = \sqrt{2} a_{bt} = 1.26a_{bc}.
\]

Therefore, for complete conversion of the body-centered cubic cell to a face-centered cell it is essential to have expansion of the initial cell along the z-axis by 26% and compression along the x- and y-axes by 11%. In accordance with this ratio the increases in axes \( \Delta c / \Delta a = -0.26 / 0.11 = -2.4 \). If the transformation stopped at some intermediate stage, then the values of \( \Delta c \) and \( \Delta a \) respectively decrease.

This transformation of the lattice can be accomplished by displacement of the atoms under the action of four covalent bonds. A crystallographic analysis shows that the tetragonal deformation of a body-centered cubic lattice can be accomplished in two ways, schematically shown in Fig. 1. In the first case (see Fig. 1, a) of four atoms at the centers of the unit cells, two atoms are displaced upwards (the + sign) and two others downwards (the - sign). As a result of these displacements, the atoms under consideration approach the four atoms of the upper or lower bases of the cell and open the hole which is formed by them. A tetragonal structure of the \( \beta \)-neptunium type then forms with a ratio of axes \( c / a < 1 \).