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Reversible expansion of gallium-stabilized δ-plutonium

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Abstract

It is shown that the transient expansion of plutonium–gallium alloys observed both in the lattice parameter as well as in the dimension of a sample held at ambient temperature can be explained by assuming incipient precipitation of Pu_3Ga. However, this ordered ζ′-phase is also subject to radiation-induced disordering. As a result, the gallium-stabilized δ-phase, being metastable at ambient temperature, is driven towards thermodynamic equilibrium by radiation-enhanced diffusion of gallium and at the same time reverted back to its metastable state by radiation-induced disordering. A steady state is reached in which only a modest fraction of the gallium present is arranged in ordered ζ′-phase regions.
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1. Introduction

As a consequence of the radioactive decay, small dimensional changes occur in plutonium. Several manifestations of these dimensional changes have been reported. First, Chebotarev and Utkina [1] showed that at ambient temperatures the lattice parameter of gallium-stabilized δ-Pu increases and attains a new value after about 2–3 years. The relative change in lattice parameter is larger the higher the gallium content. This change can be reversed by heating the material to a temperature of 150 °C [2] or higher. After returning to ambient temperature, the lattice parameter increases again to the same characteristic saturation value. These reversible dimensional changes have been detected by X-ray diffraction as well as by measuring directly the elongation of specimens with time [3]. Curiously, the relative lattice parameter changes appear to be twice to three times larger than the relative length changes. The present paper presents an explanation and a qualitative theory for these reversible dimensional changes.

We note that irreversible dimensional changes occur also as a result of the accumulation of helium from α-decay and from the formation of bubbles. While helium bubbles expand the external volume of the material that contains them, they change its lattice parameter by a negligible amount, as shown in the Appendix. The radioactive decay of the various plutonium isotopes produces other actinide daughter products, namely Am, U, and Np. As

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recently shown by Wolfer et al. [4], these actinide daughter products also change the lattice parameter of δ-phase plutonium, but permanently or in an irreversible manner.

The experimental observations regarding the reversible changes of lattice parameter and specimen length are reviewed in Section 2. Next, we show in Section 3 that these observations can be explained by the incipient nucleation of Pu_3Ga precipitates, the ζ′-phase, and we show that this yields a simple relationship between length and lattice parameter changes that is in agreement with measured results. The precipitation of the ζ′-phase does not progress very far, however, and a qualitative theoretical treatment for the termination process is provided in Section 4.

2. Review of the observations

The gallium-stabilized δ-phase of plutonium has a face-centered cubic (fcc) crystal structure at ambient temperatures. The lattice parameter for this phase decreases markedly with increasing gallium content [5] as shown in Fig. 1. This tendency of gallium to induce smaller specific volumes is also evident in the compound Pu_3Ga, the ζ-phase, whose lattice parameter of $a_\xi = 0.44907\,\text{nm}$ [6] is also displayed in Fig. 1. We disregard the slight tetragonal distortion of this phase at ambient temperatures, where it is referred to as ζ′-phase, and instead approximate it with the ideal fcc structure that this compound assumes at higher temperatures. In the disordered solid solution range of the binary alloy Pu–Ga, the lattice parameter can be described by a linear relationship

$$a_\delta(x) = a_0 + \beta \cdot x = [0.4641 - 0.08794 \cdot x]\ \text{nm}, \qquad (1)$$

where x is the atomic fraction of gallium. This represents a linear fit to the lattice parameter measurements of Ellinger et al. [5] and is shown as the solid line in Fig. 1.

Even though the linear relationship (1) represents an excellent fit, it does not imply that Vegard's rule applies, as the slope is much larger (by a factor of 2.4) than predicted by this rule.

When Ga-stabilized δ-Pu samples are held at ambient temperature, the lattice parameter increases gradually with time and reaches a somewhat higher value, referred to as the saturation value. An example of the evolution of the lattice parameter is shown in Fig. 2 [7] for an alloy with 3.7 at.% Ga. As a function of the irradiation dose τ, given in displacements per atoms (dpa), the lattice parameter change can be fit to an exponential relationship

$$a_\delta(\tau) = 0.46086 + 0.00045 \cdot [1 - \exp(-\tau/0.0217)]\ \text{nm} \qquad (2)$$

and is shown by the dotted curve in Fig. 2. The saturation value for this particular alloy is

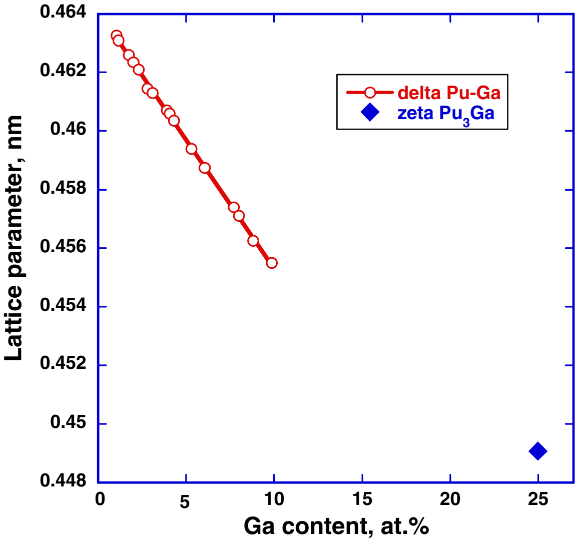

Fig. 1. Lattice parameters of Ga-stabilized δ-Pu as a function of the gallium concentration. The diamond symbol is the lattice parameter of Pu_3Ga, the ζ-phase.

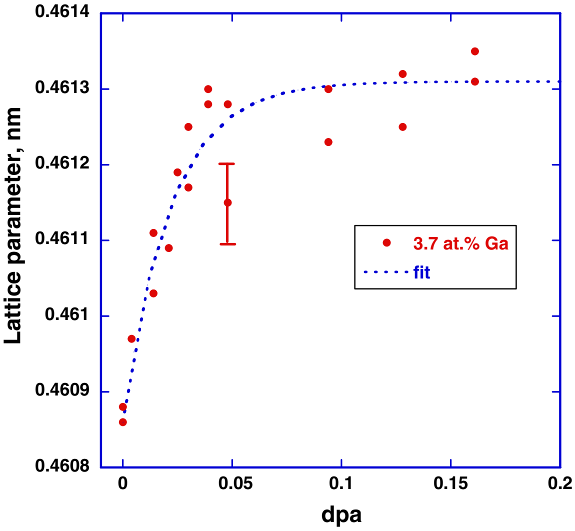

Fig. 2. Evolution of the lattice parameter in a homogenized Pu–Ga alloy with 3.7 at.% Ga. Errors for data points are similar to the one shown.

0.46131 ± 0.00004 nm, so the final relative change in lattice parameter is $\Delta a/a_\delta \approx 0.1\%$.

These final, reversible changes in lattice parameter increase with the gallium content as shown in Fig. 3 [1,7], which displays the results by Chebotarev and Utkina [1] reported in 1975, and the more recent results by Oudot [7]. As pointed out by Oudot [7], however, the increase of $\Delta a/a$ with gallium content is in part the result of the decline of the lattice parameter a_δ with gallium content. His results indicate that Δa may in fact be independent of the gallium content.

Length change measurements of plutonium specimens have also been reported recently, but only for alloys with gallium concentrations around 2 at.%. The results of one length measurement [3] is shown in Fig. 3. When compared with the changes in lattice parameter, length changes are found to be less by a factor of 2–3. This is opposite to what one would normally expect from radiation-induced generation and accumulation of lattice defects. For example, the formation of voids and helium bubbles will result in length increases, but little or no change in lattice parameter, as shown in the Appendix. One is therefore led to the conclusion that the reversible changes of lattice parameter and of length are not associated directly with the accumulation of radiation damage defects, as proposed earlier by Caturla et al. [9], but have a different origin.

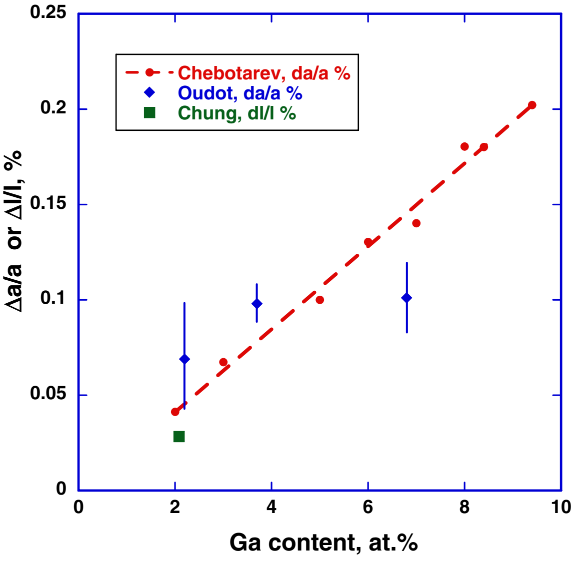

Fig. 3. Saturation values for lattice parameter and length increases of δ-phase Pu–Ga alloys as a function of gallium content.

3. Incipient precipitation of the ζ′-phase

It is known [8,14] that Ga-stabilized δ-Pu is in fact thermodynamically stable only at temperatures above about 100 °C. Fig. 4 shows the phase diagram [8] for Pu–Ga alloys with Ga contents up to 10 at.%. At ambient temperatures and gallium concentrations between 2 and 9 at.%, the δ-phase is retained in a metastable state, and should eventually transform according to the reaction

$$(1-x)\mathrm{Pu}(\delta) + x\mathrm{Ga} \Rightarrow (1-4x)\mathrm{Pu}(\alpha) + x\mathrm{Pu_3Ga}. \tag{3}$$

That it does not transform is attributed to the fact that diffusion of substitutional gallium is too sluggish for the reaction (3) to proceed to completion and to achieve the thermodynamic equilibrium state. In this latter state, practically all gallium should be contained in $\mathrm{Pu_3Ga}$ precipitates, and the depleted matrix should then transform to the α-phase. It is further known that at cryogenic temperatures the departure from thermodynamic equilibrium can become so large that the transformation to the α-phase is driven to proceed via a diffusionless, martensitic transformation [10–14]. However, since gallium remains within the α-structure, it is not in its true equilibrium state, but in a state supersaturated with gallium. This martensitic phase designated as the α′-phase [13] is yet another, but less metastable phase than is the Ga-stabilized δ-phase [14].

At ambient temperatures then, the available pathway for transformation is for gallium to first form the ζ′-phase, which is a slightly tetragonally

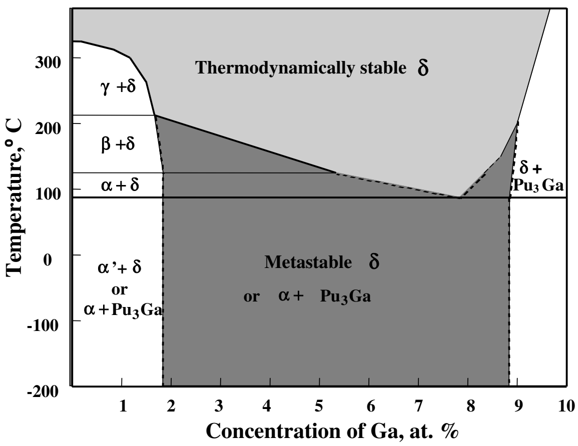

Fig. 4. The phase diagram of Ga-stabilized δ-phase alloys [8].

distorted version of the face-centered cubic structure of Pu_3Ga (the ζ-phase), and when the δ-phase is sufficiently depleted of gallium, to transform subsequently to the α-phase. As mentioned already, thermally activated diffusion is insufficient, but radiation-enhanced diffusion is taking place, as vacancies are created by radiation damage and are able to migrate at ambient temperatures. In an alloy with 2 at.% of Ga distributed randomly, the average distance between Ga atoms is only 2.88 a_δ, where a_δ is the lattice parameter. Within the ζ-phase, the distance between Ga atoms is exactly equal to the lattice parameter a_ζ of this phase. Therefore, long-range diffusion is not required for ordered regions to form in which the local Ga concentration reaches 25 at.%. It is these regions that we shall call incipient ζ′-precipitates. These small nuclei of Pu_3Ga will subsequently be destroyed again by radiation-induced disordering, as further discussed in the next section. As a result, radiation-enhanced diffusion and radiation-induced disordering (RID) are two counter-acting processes that in the final analysis limit the extent of gallium ordering or incipient precipitation, and that prevent the metastable δ-phase from transforming.

Let us first evaluate the changes in lattice parameter and in specimen length due to the incipient precipitation of Pu_3Ga. If an atomic fraction Δx of gallium is extracted from the δ-phase and incorporated into precipitates of the ζ-phase, the lattice parameter of the δ-phase will change by

$$\Delta a = -\beta \cdot \Delta x = 0.8794 \cdot \Delta x, \tag{4}$$

according to Eq. (1). Note that Δx represents a loss of gallium in the δ-phase, enters therefore with a negative sign into Eq. (1) and leads to a positive Δa.

To obtain the change in volume of a specimen, we first note that the volume per atom of a Pu–Ga alloy, $\Omega_\delta(x)$, can be viewed as a function of the composition x. Then, if x_0 and x_f denote the initial and the final gallium compositions of the δ-phase, the relative change in volume of a sample will be

$$\frac{\Delta V}{\Omega_\delta(x_0)} = \frac{\Omega_\delta(x_f)}{\Omega_\delta(x_0)} - 1 + 4\left[\frac{\Omega_z}{\Omega_\delta(x_0)} - 1\right](x_0 - x_f) \approx 3\frac{\Delta l}{l_0} \tag{5}$$

and is very close to three times the relative length change. Here, $\Omega_\zeta = a_\zeta^3/4$ is the volume per atom in the compound Pu_3Ga and a_ζ is its lattice parameter.

In contrast, the relative lattice parameter change of the δ-phase is given by

$$3\frac{\Delta a}{a_\delta(x_0)} \approx \frac{\Omega_\delta(x_f)}{\Omega_\delta(x_0)} - 1 = \frac{a_\delta^3(x_f)}{a_\delta^3(x_0)} - 1. \tag{6}$$

With the above equations we can derive the following relationship between the lattice parameter change in the δ-phase and the length change of the sample

$$\frac{\Delta a}{a_\delta(x_0)} = \frac{\Delta l}{l_0}\left[1 - \frac{4a_\delta(x_0)}{3\beta}\left(\frac{a_\zeta^3}{a_\delta^3(x_0)} - 1\right)\right]^{-1}. \tag{7}$$

Evaluation of the proportionality factor between length and lattice parameter changes gives the results shown in Fig. 5. Here, a lattice parameter of $a_\zeta = 0.44907$ nm is used for the ζ′-phase. We see that the relative lattice parameter increase of the δ-phase is up to 2.4 times larger than the relative length change, the precise factor depends on the initial gallium content of the alloy.

The relative change in the gallium content within the matrix δ-phase can be determined from the equation

$$-\frac{\Delta x}{x_0} = \frac{\Delta a}{0.8794 x_0} = 0.109 \pm 0.017. \tag{8}$$

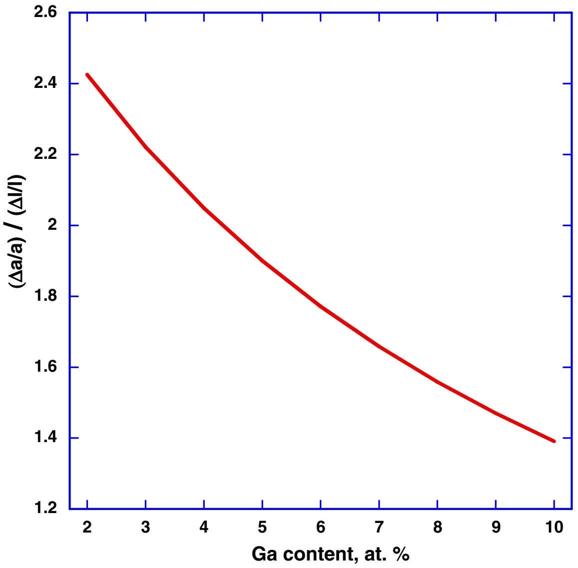

Fig. 5. The ratio of the relative increases of lattice parameter and length as a function of the gallium content of δ-phase Pu–Ga alloys.

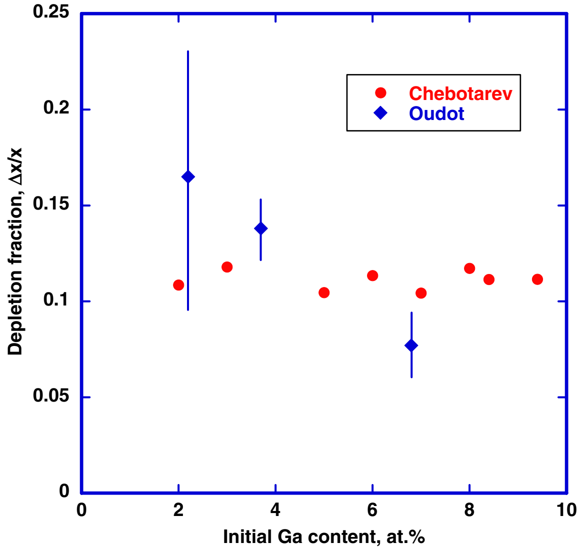

Fig. 6. The fraction of gallium removed from solution and incorporated in ζ'-phase precipitates for δ-phase Pu–Ga alloys of different composition.

The numerical value given is obtained with the experimental values for the lattice parameter changes as displayed in Fig. 3. The individual gallium depletion fractions are shown in Fig. 6, and it is appears that their average is about 11% and independent of the initial gallium content. In other words, 11% of the initially present gallium becomes eventually incorporated into small ζ'-nuclei. But what terminates this micro-precipitation of gallium, and why is it limited to such a relatively small fraction? Before addressing this question, let us first explain why the lattice parameter change can be reversed upon heating.

When gallium-stabilized material is heated to temperatures at or above about 200 °C, the δ-phase becomes thermodynamically stable for gallium concentrations between 1.9 and 8.9 at.% according to the phase diagram shown in Fig. 4. Hence, gallium tied up in incipient ζ'-precipitates goes back into solution, thereby restoring the initial lattice parameter and the initial length.

4. Limit of gallium precipitation

We have argued up to now that radiation-enhanced diffusion makes it possible for gallium to migrate and to start the precipitation reaction for the equilibrium ζ'-phase. The ζ'-structure is an ordered compound with a slightly distorted $L1_2$ crystal lattice [6]. It is well known that ion-bombardment [15] of other $L1_2$ compounds, such as Cu_3Au, Ni_3Al, and Ni_3Mn, results in disordering. At low temperatures, prolonged ion bombardment either results in the amorphization or in the disordering of ordered alloys. Radiation-induced amorphization occurs in intermetallic compounds that preserve their order up to their melting points. In contrast, ordered alloys that can also be disordered by heating above a certain temperature, T_{Ord}, that is lower than their melting point, undergo radiation-induced disordering (RID) when subject to ion bombardment at temperatures below T_{Ord}. Pu_3Ga is an ordered alloy that has the characteristics for RID, and the radioactive α-decay of plutonium provides the ion bombardment in the form of 85 keV uranium ions.

The displacement dose, τ_{RID}, required to reduce the order parameter to $1/e$ of its maximum value of one has been determined for some alloys. Guinan et al. [16] found a value of $\tau_{\mathrm{RID}} = 0.025$ dpa for Cu_3Au, Kirk and Blewitt [17] obtained $\tau_{\mathrm{RID}} = 0.077$ dpa for Ni_3Mn, and Howe and Rainville [18] measured a $\tau_{\mathrm{RID}} = 0.1$ dpa for Zr_3Al.

We therefore conjecture that while self-irradiation of plutonium facilitates the diffusion of gallium and its precipitation of the ζ'-phase, it also destroys this phase by RID. A simple quantitative model of this conjecture can be constructed as follows.

Let us denote the fraction of gallium in the ζ'-phase as $\Delta x(\tau)$ at the dose τ , and the rate of gallium precipitation as P. The amount of gallium contained in the ζ'-phase can be described by the simple differential equation

$$\frac{\mathrm{d}[\Delta x(\tau)]}{\mathrm{d}\tau} = P - \frac{\Delta x(\tau)}{\tau_{\mathrm{RID}}^{\zeta}}. \tag{9}$$

The solution of this equation with the condition that $\Delta x(\infty) = (x_0 - x_f)$ is

$$\Delta x(\tau) = (x_0 - x_f)[1 - \exp(-\tau/\tau_{\mathrm{RID}}^{\zeta})]. \tag{10}$$

Since $\Delta x(\tau)$ is also proportional to the change in lattice parameter, its evolution also follows a dose dependence as given by the function in the square brackets. In fact, Oudot [7] used such a function to fit his data, an example of which is presented in Fig. 2 and in Eq. (2). The parameter $\tau_{\mathrm{RID}}^{\zeta}$ obtained from his data is 0.022 ± 0.003 dpa for alloys with 3.7 and 6.8 at.% of Ga, and 0.023 ± 0.013 dpa for an alloy with 2.2 at.%.

The rate of precipitation, P, can now be estimated from this simple model. When saturation is reached and $\Delta x(\tau)$ no longer changes, then Eqs. (8) and (9) give

$$P = (x_0 - x_f)/\tau_{\mathrm{RID}}^{\zeta} = (0.109 \pm 0.017)x_0/\tau_{\mathrm{RID}}^{\zeta} = (5 \pm 1.5)x_0 \text{ dpa}^{-1}. \qquad (11)$$

The precipitation rate is therefore found to be proportional to the gallium content in this model.

However, an alternate conclusion may be reached. Oudot's measurements [7] suggest that the lattice parameter expansion may be a constant, namely $\Delta a \approx 0.00045$ nm. This means then a constant value for the gallium depletion, namely $\Delta x(\infty) \approx 0.005$ or 0.5%, and a constant precipitation rate of $P = 0.23 \text{ dpa}^{-1}$, independent of the gallium content. Intermediate cases between these two extremes are also conceivable, and additional data from experiments in progress should enable us to improve the model presented here.

5. Discussion

The peculiar observation first reported by Chebotarev and Utkina [1], namely that gallium-stabilized, δ-phase plutonium alloys experience a small expansion of their lattice parameters, can be satisfactorily explained with the conjecture that a small fraction of the gallium is segregated or precipitated into the ζ′-phase. It is necessary to invoke two well-known radiation effects for this precipitation process: radiation-enhanced diffusion of gallium at ambient temperature, and radiation-induced disordering of the ζ′-phase. Both these effects are concurrent, and a steady state is eventually reached when the rate of precipitation is balanced by the rate of disordering. The dose required to reach this balance is of the same magnitude as the dose needed to disorder other inter-metallic $L1_2$ compounds by external ion bombardment.

The conjecture also leads to a natural explanation why the lattice parameter increase is significantly larger than the dimensional increase. The gallium depletion of the δ-phase increases its lattice parameter and its dimension equally, but the two-phase composite (consisting of the δ-phase matrix and ζ′-phase precipitates) possesses a net dimension which is smaller.

Finally, it trivially follows from this conjecture that lattice parameter and dimension can be reset to their initial values by heating up the alloy to a temperature within the domain of the phase diagram where the δ-phase Pu–Ga alloys are thermodynamically stable. The ζ′-phase precipitates dissolve in this domain and gallium returns to the δ-phase.

A consequence of the perpetual re-precipitation and subsequent RID is that the ζ′-phase inclusions or gallium ordered regions will never grow to large sizes sufficient for their detection by X-ray diffraction, at least not for alloys with gallium contents of a few atomic per cent. The density of these small regions or precipitates cannot be reliably estimated because the radiation-enhanced diffusion coefficient is unknown. Other experimental techniques have been contemplated, such as EXAFS studies and TEM observations. The former have been discussed recently [14], and a particular careful study was performed by Allen et al. [19]. The EXAFS results indicate that the Ga–Pu bond length in the disordered δ-phase is 0.317 nm, which is about equal to the same bond length in the ζ′-phase. Hence, EXAFS experiments cannot distinguish the ζ′-phase from the gallium containing δ-phase. If the gallium ordered regions or incipient precipitates of Pu_3Ga are small, as we expect them to be, a strain field contrast should in principle be observable in transmission electron microscopy. However, the strain mismatch of a coherent, spherical ζ′-precipitate within the δ-phase is only about −1.7%, and the strain field contrast will be weak. In view of the fact that a non-uniform oxide film typically covers plutonium specimens, it is doubtful that such weak strain field contrasts can be seen, much less attributed unequivocally to incipient Pu_3Ga precipitates.

Acknowledgements

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Appendix. Lattice parameter change due to helium bubbles

Let us assume that an elastically isotropic material contains helium bubbles with an average radius of r and occupying a volume fraction of $S = 4\pi r^3 N/3$, where N is the number of bubbles per unit volume. Then, the average lattice strain (or relative lattice parameter change) in the material surrounding the bubbles is given by [20]

$$\frac{\Delta a}{a} = \left(\frac{1}{3K} + \frac{1}{4G}\right)\frac{p_{\mathrm{ex}}S}{1-S}. \tag{A.1}$$

Here, the excess pressure is defined as

$$p_{\mathrm{ex}} = p_{\mathrm{He}} - \frac{2\gamma}{r}, \tag{A.2}$$

where p_{He} is the helium pressure in the bubbles, and γ is the surface energy or surface stress. Although the surface tension for small bubbles can be of the same order of magnitude as the helium pressure, we shall omit this term, and thereby obtain an upper bound for the lattice parameter change.

The helium density in bubbles of aged plutonium is found to be on average 2.5 helium atoms per atomic volume of plutonium in the δ-phase [4]. From the helium equation of state [21] one computes then at ambient temperature a pressure of about 4 GPa in the bubbles. Using a bulk modulus of $K = 30$ GPa and a shear modulus of $G = 17$ GPa [22], one finds that

$$\frac{\Delta a}{a} < 0.1\frac{S}{1-S} \approx 0.04C_{\mathrm{He}}, \tag{A.3}$$

since $S = C_{\mathrm{He}}/2.5$, where the helium content is given in atomic fractions. After 10 years or a dose of 1 dpa, this fraction is about 400 appm, and hence, $\Delta a/a < 0.0016\%$.

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