

## LETTER TO THE EDITOR

## Large swelling and percolation in irradiated zircon

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### Abstract

We study the effect of large swelling in irradiated zircon. We perform molecular dynamics simulation of the overlap of two radiation events and find that the damage produced in the second event scatters away from the densified boundary of the damaged region implanted previously. This serves as the microscopic mechanism of the increase of volume occupied by the damage. The additive nature of this effect results in large swelling observed experimentally. We translate the damage accumulation into the percolation problem, and show that volume swelling is a percolation phenomenon, with the swelling curve increasing rapidly at the percolation threshold.

Zircon,  $\text{ZrSiO}_4$ , has been proposed as a host material to encapsulate highly radioactive nuclear waste, since in Nature it contains radioactive ions over geological times [1]. In these applications zircon is exposed to  $\alpha$ -decay irradiation and experiences a large increase in volume, up to about 20% at high dose [2, 3]. The origin of this effect is unknown. Since in other materials swelling is often accompanied by the appearance of cracks in the structure, the large swelling in zircon is a concern for encapsulation application. Here we perform atomistic simulations of highly energetic recoils in zircon. We find that the overlap of two radiation events leads to the damage produced by the subsequent event scattering away from the densified boundary of the previous one. This serves as the driving force for the local increase of the volume occupied by the damage, causing large macroscopic swelling due to the additive nature of this effect. We translate the damage accumulation into the percolation problem and show that the volume swelling is a percolation phenomenon, setting in at the percolation threshold.

Atomistic simulations of radiation damage effects in solids have been employed to gain insights into the microscopic processes associated with the damage. In monatomic solids the damage production depends crucially on the crystal structure, but the density changes associated with the damage are relatively small [4]. In zircon, a complex silicate, surprisingly large volume swelling is observed experimentally [2, 3], but previous simulation studies of

low-energy radiation damage events have not revealed any precursor to swelling [5]. Recent simulation of recoils with energies typical of  $\alpha$ -decay has shown that the density distribution in the damaged region is very non-uniform, with a depleted core in the centre and a densified boundary [6]. This boundary was found to be highly polymerized with connected  $\text{SiO}_n$  polyhedra. The stability of this phase, seen experimentally [7], results in the stability of the non-uniform distribution of the density in the damaged region [6]. In this letter we use molecular dynamics (MD) simulation to investigate the effect of the high-density boundary on subsequent nearby  $\alpha$ -decay events, and use the insights obtained to develop a model of volume swelling.

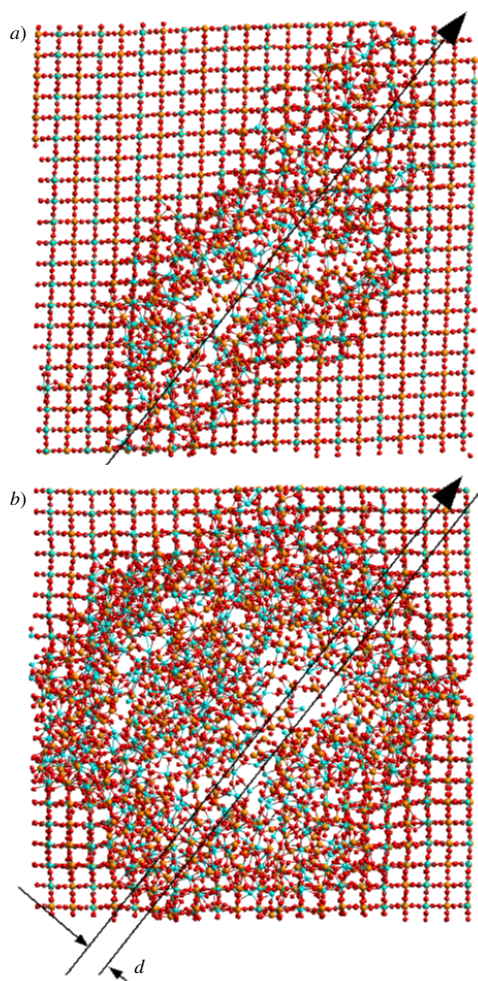
In an  $\alpha$ -decay event, the most damage inflicted on the zircon structure is produced by the heavy recoil atom that displaces several thousand other atoms [7]. In the MD simulation of radiation damage, one of the atoms is assigned a velocity that corresponds to a given implantation energy. Here we have simulated events of 30 and 70 keV, with the latter being the energy of the recoil ion in the  $\alpha$ -decay event. Atomic configurations were equilibrated at 300 K and one Zr atom was given a velocity corresponding to the desired energy. The MD program DL\_POLY was used in this study [8]. We worked with both constant-volume and constant-stress ensembles, finding the choice of the ensemble insignificant for the purpose of this study. The force field included pair and three-body potentials as used in our earlier study [6]. Configurations containing 81 000, 192 000 and 375 000 atoms were used, and a check of finite-size effects was made<sup>3</sup>. Time steps of 0.01–0.05 and 1 fs were used to simulate cascade development and relaxation phases respectively. In the MD simulation, the damaged structures were evolved for 20 ps at 300 K.

In figure 1(a) we show the damage caused by one example  $\alpha$ -decay event. The depleted core region and the densified shell can be seen, and are described above and in [6]. In figure 1(b) we show an identical  $\alpha$ -decay event (i.e. the same recoil atom with the same velocity, here called event 2) but now in the vicinity of an earlier  $\alpha$ -decay event, which is the damaged region seen towards the upper-left portion of the diagram (here called event 1). The comparison of the damaged region shown in figure 1(a) with the damaged region due to event 2 shown in figure 1(b) clearly shows that the spread of the damage from event 2 is away from the damage due to event 1, i.e. towards the bottom-right corner of the diagram. The comparison suggests that the damage associated with event 2 is being scattered or deflected away from the damaged region associated with event 1. The arrow in figure 1(b) shows the initial trajectory of the recoil atom, and the line below this indicates the approximate central axis of the resultant damage. This point is even more graphically revealed in dynamic animations of this process, which can be obtained from <http://www.esc.cam.ac.uk/movies>. These clearly show the trajectory of the recoil atom being deflected away from the damage caused by event 1.

The origin of the scattering process causing the damage due to one event to be deflected from a pre-existing damaged region can be ascribed to the existence of the densified shell of the pre-existing damaged region. This shell has a higher number of scattering centres relative to the crystalline matrix. Moreover, because the shell contains polymerized  $\text{SiO}_n$  polyhedra, it is elastically harder than the crystalline matrix, which only contains isolated  $\text{SiO}_4$  tetrahedra. The trajectory of the recoil atom of event 2 in figure 1(b) sees a denser harder matrix on its left, and this leads to a small overall deflection of the damage towards the less-dense softer matrix on the right.

We have simulated a large number of pairs of events, with different directions of overlapping recoils and various degrees of overlap, and have found similar effects every time.

<sup>3</sup> The number of atoms in the damaged region is about 4000, consistent with the direct count of displaced atoms using NMR [7], and with the size of the damaged regions deduced by x-ray diffraction experiments [3]. The number of displaced atoms is significantly smaller than the total number of atoms in the simulation box.



**Figure 1.** (a) An  $xy$ -projection of the portion of the structure damaged by 30 keV event. Large grey balls represent Zr and Si atoms, and small dark balls represent O atoms. The depleted region in the centre and the polymerized phase in the densified boundary are seen. The arrow shows the initial direction of the recoil. This direction is the axis of symmetry of the isolated damaged region. (b) The location and impetus of the event that produces the lower region (event 2) are exactly the same as in (a), but this event is simulated *in the presence* of event 1 above it. The arrow shows the initial direction of the recoil in event 2 (the same as in (a)). This direction is no longer the axis of symmetry of the damaged region produced by event 2. Consequently, the centres of the damaged regions move away from each other. The damage produced by event 2 moves to the right and bottom parts of the figure, due to the overlap. The animation of this event is available in the electronic version of this journal and can be downloaded from <http://www.esc.cam.ac.uk/movies>. (This figure is in colour only in the electronic version)

As would be expected with our proposed mechanism for scattering outlined in the previous paragraph, the extent of the deflection (indicated by the parameter  $d$  in figure 1(b)) depends on the extent of the overlap.

As more radiation events take place, there will be a greater likelihood of the overlap of damaged regions, and hence there will be a greater spread of damage due to the scattering

processes. In this letter, we pursue the idea that when the damaged regions are connected to the surface, the scattering processes will lead to an overall increase in volume. The existence of the scattering processes is the critical insight from the simulations, which we will now develop into a testable theory.

We note that the volume swelling is not an elastic effect. Instead it is simply due to the additional atoms in the matrix that get displaced, as damage scatters away from the boundary of previously implanted damaged region. That swelling in irradiated zircon is not an elastic effect is proved experimentally, in that the macroscopic swelling considerably exceeds unit-cell swelling [2].

We now develop a model of swelling based on the insights from the simulations above. We start by considering the completely damaged structure filled with overlapping damaged regions. We introduce  $d$  as the increase in spatial separation between two damaged regions due to the overlap (see figure 1(b)) and  $L$  as the characteristic size of the damaged region, both parameters averaged over events with different orientations and overlap degree. On average, the centres of the damaged regions, separated originally by distance  $(L - d)$ , increase their separation to  $L$  due to the overlap. For the purpose of calculating volume increase, the completely damaged structure can be defined as the assembly of touching damaged regions which increase their size by some value  $d$ . The associated relative volume increase  $f_0$  is

$$f_0 = \frac{1}{(1 - \frac{d}{L})^3} - 1. \quad (1)$$

$f_0$  depends on one parameter,  $\chi_0 = \frac{d}{L}$ , which quantifies swelling on the microscopic level. Experimentally,  $f_0 \approx 0.19$ , and hence  $\chi_0 = 0.06$ . Assuming that  $L$  is on the scale of the size of the individual damaged region found experimentally of 50 Å [2],  $d$  is estimated to be about 3 Å. This is in reasonable agreement with 4 Å found in the simulation of the overlap event (see figure 1(b)). Since  $d \ll L$ ,  $f_0 \approx 3\chi_0$ .

In order to calculate volume swelling at any given fraction of damaged material  $p$ , we invoke the concepts of percolation theory [9, 10], since the connectivity of damaged regions is related to local volume swelling. We associate a damaged region with a random point on the lattice in the percolation problem. Each two points in contact correspond to the damaged regions that become separated due to the overlap by distance  $d$ . The cluster of connected points corresponds to the damage increasing its volume in multiple-overlap events. Note that in the picture of local swelling originating from the separation between the damaged regions due to the overlap, the increase of volume in the bulk does not contribute to measurable volume swelling. However, when the damage is not surrounded by the matrix, i.e. when it comes to the sample's surface, the volume increase becomes measurable, similar to what is observed in the surface-irradiation experiments [11]. Formation of the percolating cluster marks the point at which the correlation between the damaged regions extends on a macroscopic level.

In the percolation problem, we define a cluster as a surface cluster if it has at least one point at the surface. From the picture of volume increase due to the overlap, the volume increase of the cluster is proportional to its 'mass'  $n^{\text{surf}}$ , defined as the number of points in that cluster. The overall increase in volume can be written as

$$f \propto \frac{\sum_i n_i^{\text{surf}}}{N} \quad (2)$$

where  $N$  is the total number of points in the lattice, and  $n^{\text{surf}}$  varies with  $p$ . We write  $\rho(p) = \sum_i n_i^{\text{surf}} / N$  as the fraction of points that belong to surface clusters for a given value of  $p$ . We note that when  $p = 1$ ,  $\rho = 1$ . At this point,  $f = f_0$  from equation (1), and we recall that  $f_0 = 3\chi_0$ . Therefore by analogy we write  $f \propto \rho$  as

$$f(p) = 3\chi(p)\rho(p) \quad (3)$$

noting that  $\chi \rightarrow \chi_0$  as  $p \rightarrow 1$ . In fact  $3\chi(p)$  gives a measure of local swelling analogous to  $3\chi_0$  introduced earlier, but now averaged over all damaged regions in surface clusters. The fact that local swelling is more significant in a more damaged structure is indicated by the dependence on  $p$ . In this sense we note that the effective displacement  $d$  defined in figure 2 will tend to zero for two damaged regions that are widely separated, that is in the limit  $p \rightarrow 0$ . For a given  $p$ , the averaged local swelling increases proportionally with the average number of damaged regions present in the vicinity of a radiation decay event, which is given by the factor  $p$ . Thus we can write<sup>4</sup>  $\chi(p) = p\chi_0$ , so

$$f(p) = 3p\chi_0\rho(p). \quad (5)$$

Macroscopic volume swelling, written in the form (4), is the product of two terms, one of which is defined by the microscopic driving force for local swelling  $3p\chi_0$ , and the other depends on the fraction of points that belong to surface clusters  $\rho$ . Generally,  $\rho$  should be calculated on the topologically disordered random-close-packed (rcp) lattice, but we note that the behaviour of this quantity is universal for different lattice types (including the rcp lattice), differing in the location of the percolation threshold  $p_c$  only<sup>5</sup>. Since the values of  $p_c$  for rcp and simple cubic (sc) lattices are close (0.27 and 0.31, respectively [9]), we simulate a simpler case of percolation on the ordered sc lattice. The dependence of  $\rho$  on  $p$ , calculated from the simulation of the percolation problem on the sc lattice, is plotted in figure 2(a). Critical behaviour of  $\rho$  near  $p_c$  is seen, and originates from the fact that after the percolation threshold the newly introduced point has a higher probability of belonging to the surface cluster.

In figure 2(b) we plot relative volume swelling measured in [2] as a function<sup>6</sup> of  $p$ , together with  $f$  calculated according to (4). The overall agreement between calculated and experimental data is very good, given the scatter in the experimental data<sup>7,8</sup>. Note that we have used only one parameter, specifically the experimental value of swelling  $f_0$  at  $p = 1$ , and hence the location of  $p_c$  is not fitted in either calculated or experimental data. The value of  $f_0$  in turn gives a value for  $d/L$  from equation (1). As noted below equation (1), the values of  $d$  and  $L$  implied from experiment are consistent with the values suggested by the simulations (e.g. figure 1). There is thus an important consistency check in our work: simulation has provided the insight that has driven the development of the theory; the theory has used a single parameter obtained from experiment in order to give the good agreement between equation (4)

<sup>4</sup> That  $\chi(p) = p\chi_0$  is supported by the subsequent analysis in this letter, and can also be proved analytically. Detailed proof will be presented elsewhere. Here we note that volume swelling  $f(p)$  can be written as

$$f(p) = \alpha \int_0^p p \, d\rho \quad (4)$$

where  $\alpha$  is the proportionality coefficient. It can be shown rigorously that  $f(p) = f_0 p \rho$ , where  $f_0 = f(p = 1)$ .

<sup>5</sup> Firstly, for values of  $p$  greater than  $p_c$ ,  $\rho = p$ , reflecting the general trend that after the percolation threshold is reached, predominantly all newly introduced points belong to the surface clusters (see figure 2(a)). Secondly, in the critical regime near  $p_c$ , where  $\rho$  sharply increases its slope, the critical exponent that controls the near-threshold scaling behaviour of  $\rho$  is independent on the lattice type, like other quantities in percolation [9]. Finally, for values of  $p$  below  $p_c$ ,  $\rho$  decays rapidly independently of the lattice type.

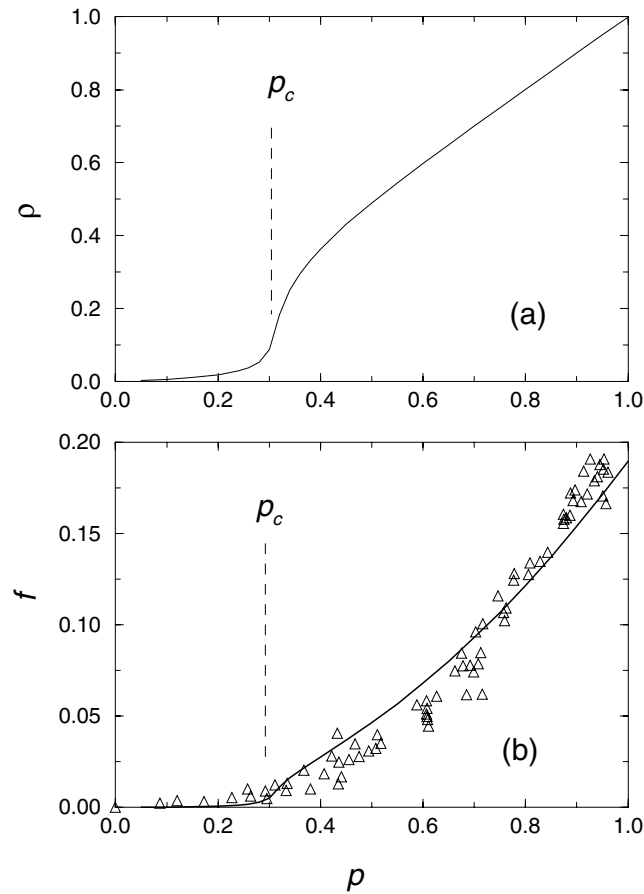
<sup>6</sup> Volume swelling is measured as a function of radiation dose  $D$ . Recently, it was shown that

$$p = 1 - \exp(-\alpha D) \quad (6)$$

where  $\alpha$  is the mass of the damaged region produced by one radiation event [3]. We use the value that corresponds to the size of a damaged region—about 50 Å in diameter, as is found in the TEM [2] and x-ray experiments [3].

<sup>7</sup> Macroscopic swelling (measured by density changes) includes unit-cell swelling (measured by the position of Bragg peaks), believed to be caused by point defects caused by alpha-particles [2]. The unit-cell contribution essentially anneals out in natural samples.

<sup>8</sup> Another potential contribution to swelling, caused by alpha-particles, is the formation of helium bubbles. Seen in other irradiated materials, these defects were not reported in the detailed electron microscopy studies of irradiated zircon [2].



**Figure 2.** (a) The ratio of the number of points in the surface clusters to the total number of points,  $\rho$ , as a function of the concentration  $p$ . The percolation threshold  $p_c \approx 0.3$  is shown. (b) Triangles show the experimental data for volume swelling from [2], plotted as a function of the damaged part  $p$ . The solid curve is the volume swelling calculated according to (4). The experimental value of  $f_0$  [2] is used.

and the experimental volume swelling seen in figure 2(b); and the value of this experimental parameter is consistent with the simulation results.

The important feature from figure 2(b), not recognized previously, is the kicking in of swelling at  $p$  close to  $p_c$ . The kink in the swelling rate is better defined in the calculated than in the experimental data, due to scatter in the latter, but what is clear is that significant swelling in the experimental data sets in at  $p_c$  only. This is different from the elastic swelling picture, and enables us to suggest that swelling in irradiated zircon is a percolation phenomenon: the critical behaviour of the volume swelling is due to the fact that after  $p_c$  the newly introduced damaged region has a larger probability of belonging to a surface cluster (and hence contributing to the measurable volume swelling) than before  $p_c$ . This results in a considerably higher rate of volume swelling in figure 2(b), signalling the onset of large non-elastic swelling due to damage percolating in the structure. In addition to critical behaviour at  $p_c$ , our model predicts  $f \approx 0$  for  $p < p_c$  (since for  $p < p_c$ , the relative fraction of points in surface clusters is small) and  $f \propto p^2$  for  $p > p_c$  (since for  $p > p_c$ ,  $\rho \propto p$ ; see figure 2(a)). This behaviour can be seen in figure 2(b), given the scatter in the experimental data.

It should be noted that the critical behaviour of swelling is also present in the experimental data on Pu-doped zircon [2]. In these data, macroscopic swelling (measured by density changes) is matched by the unit-cell swelling (measured by the position of Bragg peaks) up to about  $p_c$ , and significantly exceeds it for  $p > p_c$ . This signals the setting in of large non-elastic effects, which in our model is attributed to the damage percolating in the structure.

In summary, we have proposed an explanation for the large macroscopic swelling observed in irradiated zircon. At the microscopic level it originates when newly introduced damage overlaps with previously created damaged region and is scattered away. The macroscopic volume swelling in zircon has been shown to belong to the class of percolation phenomena [9], with the change of slope of the swelling curve occurring at the percolation threshold  $p_c$ . As far as using zircon as the immobilization host for disposal of nuclear waste and weapon plutonium is concerned, the results of this work suggest that large macroscopic swelling in a homogeneously irradiated zircon can be explained without invoking the presence of cracks in its structure. However, if zircon is a constituent phase in the composite of various ceramics, large swelling, kicking in at  $p_c$ , can cause enhanced cracking due to large differential swelling in the grain boundaries.

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