Atomistic modelling of radiation damage in zircon

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ABSTRACT

We report the results of simulation of radiation damage in zircon structure using molecular dynamics technique. We detect, quantify and visualise the phases of damage production process, including ballistic and thermal spike phase. The simulation at higher temperature shows the substantial decrease of the damage throughout the damage production. We simulate the overlap of the displacement cascades and find that the damaged structure is less able to resist the damage, in that more damage is produced in the structure that is already damaged, and relaxation time increases. The calculated density of the damaged region shows the increase in its core. We relate this densification to the appearance of connected into chains SiO_n polyhedra, n=4,5,6, in the damaged structure. We find that the number of connected polyhedra increases with the increase of damage, consistent with recent NMR results. "Polymers" of connected SiO_n are found to be essentially stable on annealing during the timescales available in computer simulations. Their alignment may possess the "memory" of alignment of SiO_4 tetrahedra in crystalline zircon.

Keywords: zircon, radiation damage, molecular dynamics

1 Introduction

Zircon, $ZrSiO_4$, has been widely studied recently for its response to radiation damage. The interest is dictated by several important applications in which zircon is exposed to radiation, including using natural zircon in geochronology and as a host material to immobilize radioactive nuclear materials and waste. During an internal alpha-decay event the energetic recoil atom produces a displacement cascade of about 1000 atoms and the alpha particle produces several hundred isolated atomic displacements. At high radiation doses zircon becomes heavily damaged, or metamict, as judged from the diffraction experiments [1], [2].

Recent experimental work has concentrated on the nature of radiation damage in zircon on a macroscopic level [3]. To model the macroscopic effects of radiation damage, we proposed a general stress model of irradiated material discussed previously [4]. This model, applicable to any material under irradiation, allowed us to study the mechanism of macroscopic volume swelling, percolation of damaged and crystalline regions, and adequately reproduced scattering profiles observed experimentally [1]. In the recent years, atomistic simulations of radiation damage effects have been intensively employed, for they addressed the processes of radiation damage that happen over length and time scale that are small by the standard of experiment, i.e. nm and ps respectively. During that scale the so-called primary damage process takes place during which damage is produced in the structure. The first atomistic simulations of radiation damage in zircon have been made recently [5].

In this paper we present further detailed analysis of the radiation damage in zircon using the molecular dynamics simulation. We study the response of the structure of zircon to radiation impact at different ambient temperatures. The phases of damage production are observed and quantified, including the ballistic phase and thermal spike phase. It is demonstrated that the higher temperatures significantly reduce the number of atoms displaced by radiation damage event. We simulate the overlap of the displacement cascades by implanting several radiation events at adjacent sites of the simulation box and find that a damaged structure appears to be less resistant to further radiation damage, in that more damage is created by an event with the same energy and relaxation time increases. The damage production process is visualised in the form of mpeg animations, available at http://www.esc.cam.ac.uk/movies. We observe the structural changes beyond the creation of disorder, particularly the appearance of "polymers" of connected SiO_n polyhedra, n=4,5,6, that are vertex or edge linked. The number of polyhedra connected in "polymers" increases as more damage is introduced in the structure, consistent with recent NMR measurements [6]. We find that the density of the damaged region becomes close to that of the crystalline at the boundaries of the region. We discuss this point in the context of different factors that may contribute to significant macroscopic swelling of zircon under irradiation. Finally, the density in the core of the damaged region shows an increase over the density of region crystalline. We relate this densification to the appearance of connected chains of SiO_n

polyhedra.

2 Development and relaxation of damage in zircon structure

In modelling atomic interactions in zircon, we used potentials for Si and O atoms from the simulation of quartz, complemented with the the Zr–O potential from a simulation of ZrW_2O_8. The experimental values of unit cell parameters, bond lengths and bond angles were found to be in good agreement with the calculated optimised values (see [7] for comparison details as well as for the details of potential used). In addition to that, we calculated low-energy dispersion curves and compared them with recent neutron scattering experiments. The comparison gave a good agreement as well [8].

We used the DLPOLY molecular dynamics simulation package [9]. A structure containing 8640 atoms was equilibrated at 300 K and 600 K, and one atom (usually called the primary knock-on atom and chosen to be Zr in our case) was given a velocity corresponding to an implantation energy of about 1 keV. Computational limits prevented us from using higher values of energy. We employed different integration algorithms, including coupling the system to Nose-Hoover and Berensden thermostats. The choice of either algorithms proved to have little effect on the results. The periodic boundary conditions were applied. It should be noted that the energy damping at the boundaries is often employed to prevent the kinetic disturbances to reenter the simulation box. However, as was demonstrated in [10], the use of periodic boundaries is acceptable if the size of the simulation cell is large enough, which was the case in our simulations.

A sequence of snaphots of the sample containing the displacement cascade at different times is shown in Figure 1, showing how damage develops in the structure. The energy of the primary knock-on atom is distributed, by multiple collisions, among surrounding atoms which leave their lattice sites. This results in the creation of a highly damaged core surrounded by relatively undistorted regions which move outwards, with the number of displaced atoms reaching its maximum at about 0.15 ps (Figure 1). A substantial fraction of displaced atoms return to their original position during a period of several ps. The atoms that are unable to occupy their original lattice sites form a displacement cascade, with a high degree of topological disorder in the core, which is stable during times of simulation of 100 ps. The animations showing the creation and development of displacement cascades at different temperatures can be downloaded from http://www.esc.cam.ac.uk/movies.

We consider an atom as being displaced if it leaves the sphere centered at its initial lattice position with the radius of half a nearest-neigbour distance. The number of displaced atoms, N_d, was averaged over seven different events simulated by giving the primary knock-on atom different velocity components. We plot N_d as a function of time in Figure 2 for Zr, Si, and O atoms simulated at 300 K and 600 K. One can observe N_d reaching its maximum value at about 0.15 ps, corresponding to the maximum in disorder in Figure 1. After this phase, known as the thermal spike, N_d becomes a constant value at about 0.5 ps and 1 ps for simulations at 300 K and 600 K, respectively.

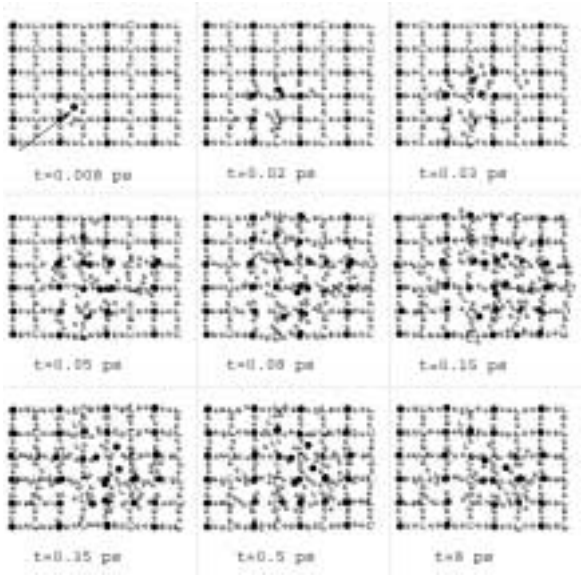

Figure 1: Snapshots of zircon structure showing the development of a displacement cascade in time (view at along [001]). The arrow shows the direction of velocity of the primary knock-on atom. Larger black and white balls represent Zr and Si atoms respectively, and smaller gray atoms represent O atoms.

Comparing Figures 2a and 2b shows that the temperature has a significant effect on N_d during both the thermal spike phase and longer times. The total number of displaced atoms is about 1.8 larger in the sample at 300 K than at 600 K. This effect is believed to be due to the increase in the lifetime of the thermal spike as the temperature increases, which allows more defect motion to take place before cooling and hence leads to more interstitial-vacancy recombination [10]. The increase in the lifetime of the thermal spike phase with temperature can be seen in Figure 2, consistent with the results of simulation of damage production in metals [10]. The interesting point from Figure 2 is that N_d is also lower at the higher temperature at the times corresponding to the maximum of N_d and the thermal spike. This is different from the results of simulation of radiation damage in metals [10], which showed that as the initial temperature increases, N_d decreases at the final stages of damage production, but increases during the thermal spike phase.

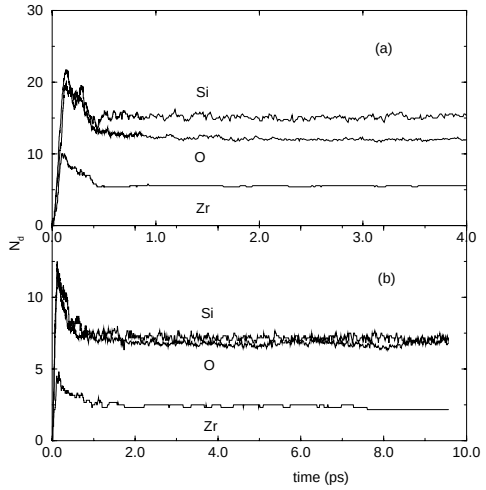

Figure 2: Number of displaced atoms as a function of time during the simulation at (a) 300 K and (b) 600 K. For comparison with other atoms, the number of displaced oxygen atoms was divided by 4.

3 Density of the damaged region

In order to study the structural changes in the damaged zircon, density variation and other features, a damaged region of an appropriate size defined by the locations of displaced atoms was required. This called for the need to simulate several consecutive radiation events implanted at the adjacent regions of the simulation box. Besides, it was appealing to study the effect of the overlap of displacement cascades. At this point it is worthwhile mentioning that the damaged structure was found to be less able to resist the damage, in that a consecutive radiation event that occurs in the structure that is already damaged, results in a larger number of displaced atoms. We also found (see [7], [8] for more detail) that the lifetime of the thermal spike phase is larger in the repeated event than in the single event, approximately by a factor of two. It means that the time of return to equilibrium positions by athermal relaxation reduces when the atoms are not located on the ideal lattice positions before the radiation event, having been displaced before. The value of the "return" potential is effectively reduced in the damaged structure and the response of the structure becomes more "loose" in that sense.

For the damaged region, we calculate the number of atoms n that are located within the sphere with the centre defined as the geometrical centre of mass of displaced atoms, together with n_0 for atoms located on undistorted lattice sites, and plot the relative difference $\Delta n/n_0 = (n - n_0)/n_0$ as a function of sphere radius in Figure 3.

A 10–15% increase in $\Delta n/n_0$ can be seen up to 6 Å in the radial direction, giving 12 Å as the characteristic size of the densified region. The densified region occupies a relatively small 6% portion of the total volume of damaged region. Later we will relate the densification in the core of the damaged region to the appearance of connected SiO_n polyhedra.

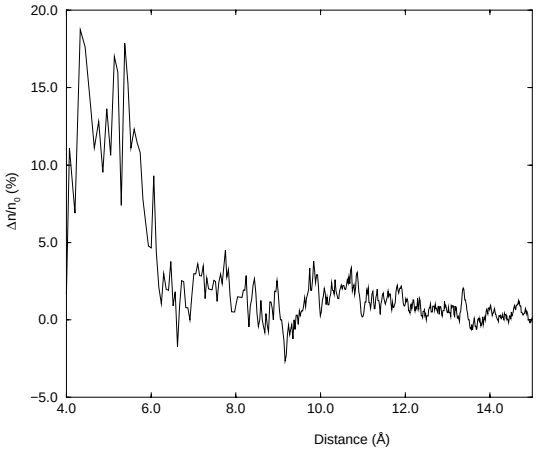

Figure 3: Change of relative number of atoms $\Delta n/n_0$ as a function of distance from the centre of damaged region.

As can be seen from Figure 3, the density of the damaged region becomes very close to that of the undistorted region after about 6 Å in the radial direction, up to the boundaries of the damaged region of 15 Å. This suggests that the change of local volume associated with mere transition from ordered to disordered state may not play an important role in the overall macroscopic swelling of zircon which reaches substantial swelling of 18 % at saturation [2]. In [11] it was suggested that other factors, including point defects and cracks may contribute to volume swelling. It remains to find out what is the major contributing factor to the observed swelling. For example, at high radiation dose heavy irradiating particles that become point defects in the structure can make a noticeable contribution volume swelling.

4 "Polymerization" in the damaged region

The structure of the damaged region reveals an interesting feature: "polymers" in the form of connected SiO_n (n=4, 5, 6) polyhedra have appeared. During multiple collision processes SiO_4 tetrahedra which are separated in ideal zircon, distort and move relative to each other, which enables them to share one or two common oxygen atoms, thus corresponding to vertex or edge-shared polyhedra. The radial distribution function calculated for displaced Si atoms showed a new maximum which is very close to the average Si–Si distance in silicates with linked SiO_4 tetrahedra, and corresponds to Si–Si neighbours in connected "polymers". (see [7], [8] for more details). An example of connected SiO_n poly-

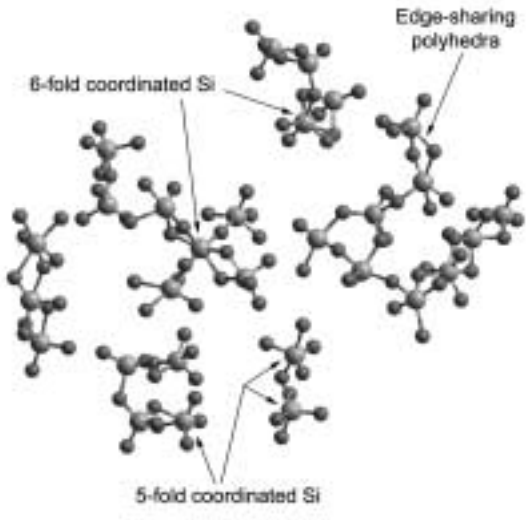

Figure 4: Connected polyhedra in the damaged region of zircon, showing 2,3,4,7 and 9 polyhedra sharing one or two common oxygen atoms. Larger light balls represent Si atoms and smaller dark balls represent O atoms.

hedra is plotted in Figure 4. As can be seen from Figure 4, the majority of connected polyhedra are four and five-fold coordinated, with some six coordinated polyhedra appeared. An oxygen atom which was forced away during multiple collisions forms a bond with another Si atom, and thus contributes to the observed increased coordination. It should be noted that the possibility for Si atoms to connect with each other by sharing O atoms was pointed out in one of [5]. The animation showing how polyhedra connect into chains can be downloaded from http://www.esc.cam.ac.uk/movies.

It is interesting that the structure damaged by one radiation event contains mainly chains consisting of two or three connected polyhedra while in some more heavily damaged structures up to 15 polyhedra connected in one chain are observed, vertex or edge-shared. This is consistent with the recent NMR studies of the structure of damaged zircon [6] which pointed to the presence of connected SiO_4 tetrahedra. The average number of tetrahedra connected into chains was observed to increase in heavily damaged samples relative to slightly damaged ones [6].

A detailed study of the structure of disordered regions reveals that the alignment of the chains of connected SiO_n polyhedra is not completely random, as it might appear from Figure 4. It appears that x and y are more preferable directions for alignment of SiO_n chains than z direction (see [7], [8] for more detail). Once connected, polyhedra move and rotate according to local stresses in the damaged structure, but their alignment often has some "memory" of the structure of the undamaged crystal.

We relate the connection of SiO_n polyhedra into chains to the observed densification in the cores of damaged regions. Indeed, connecting the units that have been separated in the undisorted structure into chains leads to the local contraction of the volume and it is likely that the maximum of contraction will be in the area with high population of SiO_n chains. We found that the size and location of the region that contains SiO_n chains was approximately the same as the size and location of the densified core of the damaged region. This suggests that "polymerization" is related to the microscopic mechanism behind the increase in density in the core of the damaged regions.

REFERENCES

[1] Chakoumakos B C, Murakami T, Lumpkin G R and Ewing R C 1987 *Science* **236** 1493; Murakami T, Chakoumakos B C, Ewing R C, Lumpkin G R and Weber W J 1991 *Am. Min.* **76** 1510

[2] Weber W J, Ewing R C and Wang L M 1994 *J. Mater. Res.* **9** 688

[3] Meldrum A, Boatner L A and Ewing R C 1997 *Phys. Rev. B* **56** 13805; Meldrum A, Zinkle S J, Boatner L A and Ewing R C 1999 *Phys. Rev. B* **59** 3981; Zhang M, Salje E K H, Capitani G C, Leroux H, Clark A M, Schluter J and Ewing R C 2000 *J. Phys.: Cond. Matter* **12** 3131; Rios S, Salje E K H, Zhang M and Ewing R C 2000 *J. Phys.: Cond. Matter* **12** 2401; Rios S and Salje E K H 1999 *J. Phys.: Cond. Matter* **11** 8947

[4] Trachenko K, Dove M T and Salje E K H 2000 *J. Appl. Phys.* **87** 7702

[5] Crocombette J P and Ghaleb D 1998 *Mat. Res. Soc. Symp. Proc.* **506** 101; Crocombette J P and Ghaleb D 1999 *Mat. Res. Soc. Symp. Proc.* **540** 343; Park B, Corales L R and Weber W J 1999 *Mat. Res. Soc. Symp. Proc.*

[6] Farnan I 1999, *Phase Trans., 69* 47; Farnan I and Salje E K H 2000, *J. Appl. Phys.*, submitted

[7] K Trachenko, M T Dove and E K H Salje 2000 *J. Phys: Cond. Matter*, submitted

[8] K Trachenko 2000, PhD Thesis, University of Cambridge

[9] Smith W and Forester T 1996 *J. Mol. Graph.* **14** 136

[10] Bacon D J, Calder A F and Gao F 1997 *J. Nucl. Mat.* **251** 1; Bacon D J, Gao F and Osetsky Y N 1999 *Nucl. Instr. and Meth. in Phys. Res. B* **153** 87; Bacon D J, Gao F and Osetsky Y N 2000 *J. Nucl. Mat.* **276** 1

[11] Weber W J et al 1998 *J. Mat. Res.* **13** 1434