Damage of swift ions in crystalline calcium fluoride. Evolution of the ion explosion spike into a thermal spike

D.A. Young

Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW7 2BY, UK

Abstract

The molecular dynamics simulation of the damage caused in calcium fluoride by the passage of a swift ion energetic enough to create vacant K-states in the host during passage in the [1 1 1] direction shows that the ion explosion characterised by a collective inward motion of anions, with an outward motion of cations which initially develops in close-packed $\langle 1 1 0 \rangle$ directions, is overcome by a chaotic process initiated by similar ionic motions in $\langle 1 1 2 \rangle$ directions. This ion explosion spike degenerates in <65 fs into a thermal spike some 55 Å in diameter. Annealing is a lengthy process but by 20 ps it had become plain that the thermal spike cools to give a stable, glassy structure some 46 Å across based on disordered fluoride-sharing CaF_n clusters with a central filament composed of neutral fluorine molecules.
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1. Introduction

The bombardment of crystalline calcium fluoride by recoiling fission fragments, ionised high-energy clusters or swift ions generates solid state nuclear tracks which can be etched [1], observed by electron microscopy [2] and examined *inter alia* by Rutherford back scattering and atomic force microscopy [3–6]. Colour centres form. However as with other simple binary compounds such as lithium fluoride it appears not to have been possible to examine track cross-sections by high resolution electron microscopy, whereby the track diameter could have been determined with certainty. It was this latter failing which led the author to attempt to simulate a swift ion-induced Coulomb explosion with the trajectory in the $\langle 1 0 0 \rangle$ direction of KCl and LiF using the method of molecular dynamics (MD) [7,8]. These attempts were not wholly

successful mainly because it was not possible to treat electrons as a distinct component, but they did give robust results with respect to at least the earliest and concluding stages of the ionic motions. Significantly it was shown that the overall maximum extent (diameter) of the radiation damage normal to the swift ion trajectory had fully developed after a few tens of femtoseconds, that the main response to the electrostatic field resulting from swift ion ionisation of the host was an inward collective motion of anions accompanied by an outward collective motion of cations, and that this could lead in specific crystal directions to a collision-free relative oscillation of the cation and anion sub-lattices whereby the potential energy of the system evolved with the effluxion of time as a damped oscillation. If the trajectory is along a $\langle 2 0 1 \rangle$ direction then, at least in lithium fluoride, the resulting track is very narrow, comprising a row of neutral fluorine atoms along the swift ion trajectory surrounded by an annulus of interstitial lithium ions some 5 Å distant. Since in this orientation there are no close-packed directions in planes

E-mail address: d.a.young@imperial.ac.uk

perpendicular to the trajectory, the initial potential energy of the spike decreases without oscillations to about 6% of its value over 35 fs or so, and the initial radiation damage does not reach out into the crystal. Calcium fluoride with its simple structure does not only produce more complicated results which required detailed evaluation, but the simulations are highly susceptible to the thermal instabilities which plague such ionic systems such that it became necessary to use very short time steps plus other stratagems which will be mentioned.

Since the most significant recent experimental work has involved the normal bombardment of single crystals of calcium fluoride cleaved on (1 1 1) [3,4,9], this geometry was adopted for the simulation.

2. The geometry of the system

It would not be necessary to use journal space to describe the detailed geometry of the system, a tablet with large (1 1 1) faces, were it not for the fact that the simulation revealed the details of curious, determinative phenomena along specific crystal directions which have to be considered before one can appreciate the duration and spatial extent of the Coulomb explosion spike. Since the GULP program [10] is simplest to handle in Cartesian coordinates, the conventional cubic unit cell of calcium fluoride is replaced by an orthorhombic unit cell, Fig. 1a, sketched in more detail in Fig. 1b. While these sketches are more than sufficient for crystallographers, the dynamic properties to be discussed demand a third representation,
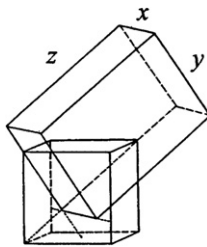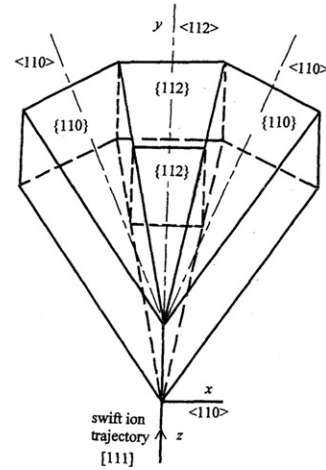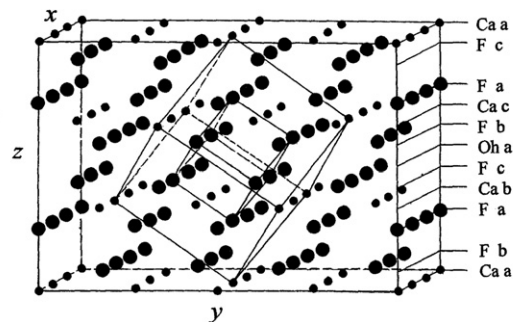

Fig. 1c. Prismatic flanking sectors 1 1 2 and 1 1 0 arranged around the swift ion trajectory [1 1 1] as axis. The upper and lower surfaces are (1 1 1) planes and the {1 1 2} plane within the 1 1 2 sector represents an intermediate location for **C**, the so-called Critical Coplanar Configuration.

Fig. 1c, where the top and bottom surfaces are (1 1 1) and the system is divided into flanking 1 1 2 and 1 1 0 sectors each 30° wide around the swift ion trajectory. The latter sector includes the close-packed directions. One should here think of calcium fluoride solely as a layer structure in which each layer contains but one species: calcium ion, fluoride ion or octahedral hole at the body centre of the conventional cubic unit cell.

The system examined in this paper comprises $22(x) \times 12(y) \times 3(z) = 792$ of these orthorhombic unit cells. It contains 4752 cations and 9504 anions. Only Miller indices valid for the conventional unit cell will be used, but the index relations are

$$(0\,0\,1)_{orthorhombic} = (1\,1\,1)_{cubic},$$
$$(0\,1\,0)_{orthorhombic} = (1\,1\,0)_{cubic},$$
$$(1\,0\,0)_{orthorhombic} = (1\,1\,2)_{cubic}.$$

The swift ion trajectory is along [1 1 1] so xy projections give the clearest indication of track dimensions normal to the trajectory. The lower surface of the tablet ($z = 0$) is composed of cations whereas the upper surface ($z = 28.324$ Å) contains only anions.

Fig. 1a. The relationship between the orthorhombic unit cell used in the computation with the conventional cubic cell. $x = 3.8544$ Å [1 1 0]$_{cubic}$, $y = 6.6759$ Å [1 1 2]$_{cubic}$, $z = 9.4414$ Å [1 1 1]$_{cubic}$.

Fig. 1b. The cubic unit cell inscribed within the orthorhombic structure displayed as a layer lattice and compared with the rhombohedral unit cell.