Report on the manuscript entitled *Modeling of neutron radiation damage in ceramic construction materials for the Dual Fluid Reactor using heavy ions* by Ewelina Kucal, submitted in fulfilment of the requirements for the degree of Doctor of Physical Sciences at the *National Centre for Nuclear Research*

Madam Ewelina Kucal is submitting a manuscript entitled *Modeling of neutron radiation damage in ceramic construction materials for the Dual Fluid Reactor using heavy ions*. The manuscript comprises 88 pages, including references, it well organized, well written, and well documented. The research work is nowadays a hot topic with the renaissance of nuclear energy associated to the development of innovative nuclear reactors of the fourth generation. In this framework, research in advanced nuclear materials, capable to withstand radiation damage coupled with another thermodynamical parameter such as corrosion, is becoming a fascinating topic in fundamental physics and chemistry, and a topic of prime importance for technological applications. The work of Madam Ewelina Kucal is a significant step towards a better understanding of the radiation tolerance of silicon carbide upon ion bombardment – as structural material – in the medium energy range where atomic and electronic slowing-down processes contributes.

The first chapter of the thesis corresponds to an introduction to the PhD topic: it describes in a synthetic way motivation, main objectives, and the organisation of the manuscript.

The second chapter deals with the materials for nuclear energy applications and the challenges to be faced. A short description of the various types of nuclear reactors is provided, including the novel concepts referred to as Gen4 reactors, and the main materials considered. The specificity of the Dual Fluid Reactor (DFR) and of relevant materials is then described and finally the main structural properties of silicon carbide are mentioned. It enlightens the important issue of radiation and corrosion tolerance of solid submitted to both neutron bombardment, interactions with the liquid metal coolant (Pb or Pb-Bi) and the molten salt, that are well-known to be aggressive media, and high temperature, all parameters that might have a synergetic role. Although the Chapter provides main elements, more detail of the DFR itself and on the specific requirements on materials would have been a nice addition for a full information of the reader.

Chapter three discusses the very important topic of radiation damage. A short introduction to collision cascades, to the Kinchin and Pease model, to the difference between neutron an ion irradiation is given. A particular emphasis in put on the inelastic thermal spike model, generally used to describe the

electronic-induced effects generated by swift heavy ions into matter. Finally a short compilation of the state of the Art regarding irradiation effects in silicon carbide, focusing mostly on C and Si as projectiles, since they are creating the primary knock-on atoms, is discussed: beyond the numerous irradiation conditions that were already examined in silicon carbide, the PhD focuses judiciously on the intermediate ion beam regime corresponding to the mixing of both electronic and atomic contribution to the energy loss, relatively poorly explored up to now. Finally, the chapter finishes with the justification of using ions to simulate the radiation damage caused by neutrons. This last important section would be improved by adding more description and reference to the numerous works performed with the general idea to replace neutron irradiation, and by explaining why other sources of radiation (except neutron) are likely to play a minor role in the DFR concept. Moreover, comments on the primary recoil spectra expected to occur in SiC as structural for the DFR, in connection with the selected ion energies for the experimental measurements (see Chapter five) would be useful. Notwithstanding these limitations, the chapter is clear and contents the essentials.

The Chapter four aims to describe the main results of the PhD using computational methods and tools. The chapter starts with a description of the well-known SRIM simulation code, a Monte Carlo code based on the binary collision approximation to calculate trajectories of energetic impinging ions into amorphous targets. Both electronic as well as atomic stopping powers were calculated in silicon carbide in the relevant range of energies corresponding to experimental simulations performed in Chapter five. Similarly atomic displacements (dpa) were computed for the selected energies and projectiles (0.5 MeV C or Si, 1 MeV C, 5 MeV C or Si, 21 MeV Si). Although not a new approach, SRIM are clearly mandatory in the framework of this work. The second part of the Chapter is far more innovative. It deals with quantitative calculation of high temperature spikes (the so-called thermal spike) induced by electronic stopping of ions into matter. The solving of the coupled differential equations was performed using the Thermal Spike code developed at the CIMAP Caen. It was applied to silicon carbide submitted to C and Si irradiation in the same range of energy as mentioned before. One must note that the description of the underlying physical parameters is given with lot of details, a very nice feature. Physical units are missing in a few equations (4.7 and 4.8). The way the energy per atom is calculated is not described within the text. Nevertheless, results are interesting. Temperature in the inner part of the ion trajectory were calculated assuming target temperatures 300 and 1075 K, and at two different depths: at the surface, corresponding to the highest value of electronic stopping power, and at 400 nm below the surface, and for both C and Si projectiles. The maximum reached temperature (1827 K) is well below the melting temperature of silicon carbide. Moreover, except at very low irradiation energy (500 keV), temperature increase is almost the same at both depths, in agreement with the almost constant value of electronic stopping power. At first order, the target temperature leads to a shift the temperature raise, but $\Delta T = T_{irr} - T_{target}$, remains essentially constant. Radial distribution of energies across trajectories were also calculated. Although some calculations are

missing (especially at 400 nm), energy profiles typically extend up to 10 nm. Finally, a very insightful investigation of the role of electron-phonon coupling on the sensitivity of results was performed: such a sensitivity analysis is essential since electron-phonon coupling is the sole free parameter of the simulation, and it can vary over a large range of experimental values differing by several orders of magnitude. Both temperature of electrons as well as temperature of atoms as function of time and for various values of electron-phonon mean free path were computed. Simulations confirm that the higher the electron-phonon coupling constant, the higher the energy transfer the lattice, leading a more pronounced temperature reached along the ion path. The next section of this Chapter discusses molecular dynamics simulations. A short introduction to the method is given, and energy potential used to model the SiC solid. More comment on the various parameters that are used on Formula (4.15) to (4.24) would have been a nice addition to help the reader. Simulations were performed using 5 keV Ar ions to damage the 3C polytype of silicon carbide in the atomic collision stopping regime at 300 and 600 K. The number of vacancies per ion correlates with the reconstruction of the solid and saturates at about 140 and 100 at 3 ps, demonstrating a clear effect of temperature on the damage recovery. Finally, the thermal spike parameters deduced from the simulation code previously described were used at input parameters for MD simulations. They show that the crucial role of electron-phonon coupling constant on the dynamics of defects formation: amorphization can be achieved regarding 21 MeV Si ion irradiation at 1 ps while g reaches 10^{14} W cm^{-3} K^{-1}. It would be nice to obtain the behaviour at larger times to check whether the amorphous structure can be annealed, and to which extend. A brief description of the McChasy simulation code, which calculates the trajectories of light probing ions in monocrystalline structures most useful for the analysis of channelling experiments, concludes the Chapter.

The Chapter five describes the experiments performed in the framework of this thesis. Cubic silicon carbide monocrystalline layers grown on Si were bombarded with C or Si ions at energies ranging from 0.5 to 21 MeV. Fluences were selected to achieve low doses from 0.01 to 0.1 dpa. There is no clear justification for such a deliberate choice, likely related to the will to simulate neutron-induced damage: such as choice has to be clearly emphasised. In this energy range, results from the literature supports the idea that atomic collisions are mostly responsible for the radiation damage and that electronic stopping might play a role in defect annealing. Ion channelling analysis was used to characterize the radiation damage and Monte Carlo simulations using the McChasy code to get a quantitative estimation. Collected spectra on virgin crystals were used to fix some experimental parameters, such as corrected stopping power and root-mean-square amplitude of thermal vibrations. An interesting comparison of radiation damage induced by 21 MeV Si ions bombardment at various incident angles was performed: it shows that Si implantation along the main crystallographic axis leads to a higher damage in comparison to implantations in random directions. Such a result is not straightforward and certainly deserves more experiments for a complete understanding. The next section discusses the

radiation damage created at the same nominal number of dpa 0.01 (0.05) at the 400 nm (500 nm, respectively), but using various energy for ion; the main idea is to track a possible effect of electronic stopping on damage generated by atomic collisions. For the most irradiated crystals (0.05 dpa), the comparison between 21 MeV and 5 MeV Si irradiation induced indicates a possible recovery of radiation-induced damage by electronic stopping (about 5 keV nm^{-1} and 1.9 keV nm^{-1} at the two energies, respectively). Such an effect would benefit from being demonstrated in a larger dpa range. The role of the temperature during irradiation was investigated by performing irradiation at room and at 1073 K. Irrespective of the bombarding ion, temperature decreases the defect concentration. More surprisingly, thermal annealing at 1073 K of pre-irradiated crystals, leads to a an almost full recovery of defects, a feature likely related to the rather low concentration of formed defects. In a last class of experiment, pre-damaged crystals bombarded with 500 keV Si ions in the atomic collision regime are subsequently irradiated with 21 MeV Si ions. Results show that the total damage in the zone where both defect profiles contribute is not the arithmetic sum of both contributions: electronic stopping of 21 MeV Si ions likely plays a role on the recovery of atomic displacements. However, the formation of defects induced by the sole 21 MeV ions in not a proof of evidence of the absence of recovery: indeed 21 MeV Si ions generates atomic collisions that can be partially recovered as well, but RBS/C yield provides information to the final state of matter only. In summary, despite a rather limited number of experiments, several irradiation conditions were explored, and main results constitutes a good basis for future works.

The Chapter six discusses the results. With respect to the limited size pf this part (3 pages), a suggestion to merge this Chapter with the two previous Chapter could be considered. In fact, it mostly summarizes the previous results and discussions and expresses in a clear way what were initially the objectives of the thesis: (i) to investigate the role of neutron irradiation on silicon carbide as structural material using ions; (ii) to explore medium energy ion irradiation, where both atomic and electronic processes are involved in the processes of ion-mater interactions.

The last Chapter concludes the manuscript.

In summary, this interesting PhD work investigate the radiation tolerance of cubic silicon carbide polytype upon ion irradiation in the range of energy (typically MeV) where both atomic and electronic processes are expected to play a significant role, and potentially generate dual effects, i.e., non-additive effects of pure atomic and electronic stoppings. Both computational works and experiments were performed to achieve a better understanding of the atomic-scale mechanisms, an effort that deserves a special emphasis. Despite some lacks, likely related to the types of performed experiments that requires beam-time access limited by calls and proposals, the manuscript provides a satisfactory

description of silicon carbide upon irradiation, and it opens many routes for future explorations. In particular, since neutrons are the main source of radiation damage in the Dual Fuel Reactor, an improved connection between ion and neutron irradiation representativeness will be most useful. On the basis of the above consideration, I do confirm that the reviewed doctoral dissertation by Master of Science in Engineering Ewelina Kucal entitled *Modeling of neutron radiation damage in ceramic construction materials for the Dual Fluid Reactor using heavy ions* meets the relevant regulations to fully fulfil of the requirements for the degree of Doctor in Physical Sciences in the Nuclear Centre for Nuclear Research.

Orsay, November 10, 2023

Frederico Garrido

Full Professor in Physics and Chemistry of Materials

Associate Scientific Director of the Pole Energy & Environment at IJCLab