Accomplishments

What were the major goals and objectives of the project?

The major goals of this project, as originally proposed, were: It is the fundamental premise of this project to study excited electrons and their influence on ion dynamics in out-of-equilibrium materials. By means of time-dependent first-principles simulations we explore to what extent excited-electron effects and their interplay with ion dynamics underlie the fundamental atomistic mechanism that dominate ion diffusion, especially during the early stages of flash sintering or defect clustering in materials under particle radiation conditions. This research goal was derived from exciting earlier preliminary data for proton-irradiated MgO, for which we found that interatomic forces act on the ions of the target material due to the presence of excited electrons, following proton irradiation. We showed that in a material with a defect present (oxygen vacancy, in this case), the electrons excited by the proton beam become localized in the vicinity of the defect. Based on experimental literature data, the excitation persists for long enough that the strong resulting force experienced by ions that immediately surround the defect causes their displacement with respect to equilibrium positions. For MgO we also found that as a result of the excitation, the diffusion barrier for oxygen diffusion was lowered, leading to increased diffusion of the oxygen atoms/vacancy defects.

From the overall goal of studying these effects, we derived the following tasks/objectives:

* Ehrenfest MD For Classical Heavy Projectiles: In our previous work, we explained the influence of channeling trajectories and of tightly bound core electrons on electronic stopping in both metallic and semiconducting targets. However, an important question remained: How does this mechanism affect a semiconductor under swift-heavy ion irradiation? Preliminary simulations hinted at a dependence of electronic stopping on the initial charge state of the projectile, something that we did not observe for light projectiles. Depending on whether or not the projectile atom is initially charged, the predicted electronic stopping differs by a factor of three. In the first task, we planned to investigate the origin of this behavior.

* Ehrenfest MD For Quantum-Mechanical Projectiles: The second task aims at systematically exploring the influence of the excitation mechanism: We showed that a hot-electron mediated ion diffusion mechanism can be triggered by proton irradiation in MgO and that diffusion of neutral oxygen vacancies is enhanced by orders of magnitude. We identified electronic excitations of the oxygen vacancy due to proton irradiation as the reason for this enhancement and we demonstrated that the excitation can be manipulated by controlling the kinetic energy of the proton beam. However, it is an open question, whether the diffusion enhancement is limited to a particular type of radiation or, instead, can also be triggered by electron irradiation. Other mechanisms are equally unexplored. To explore this, we intended to overcome approximating the projectile as a classical particle, using an approach described in the literature.

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14. ABSTRACT
This report summarizes the goals and results of the ONR YIP Award to Prof. Andre Schleife.

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* Nudged-elastic Band Model and Diffusion Calculations: Our preliminary data for MgO compared three different excited-electron configurations to ground-state DFT: (i) non-equilibrium occupation numbers right after the interaction of the projectile with the material, (ii) equilibrated occupation numbers for a given Fermi temperature, and (iii) charged defect, using constrained DFT. For proton-irradiated MgO we showed that the Ehrenfest occupation numbers lead to a large reduction of the diffusion barrier by almost 1 eV. In this task we aimed at analyzing this effect for different Navy-relevant target materials. We initially also aimed to use these results for site total energies and transition-state energies to compute diffusivities using the open-source ONSAGER code.

* Ceramics and Semiconductors Important to the Navy: In the final task we will use the computational framework developed in the previous tasks and tie all aspects together. This will allow us to investigate several materials of interest to the Navy, in order to both produce data that can guide experimentalists working with these materials and to produce knowledge on how much the above-mentioned effects depend on a specific material. These calculations will be mostly run by the graduate student, while the postdoc will be focusing on publishing the results obtained in this project. We envision that at this point we have established and tested a production-ready first-principles approach that is capable of predicting and quantifying the influence of excited electronic states on ion dynamics starting from very fine-grained electronic structure calculations and taking these results all the way to diffusivity data.

While the overall goal of studying excited electrons and their influence on ion dynamics is unchanged, we have adjusted the individual subgoals to better reflect insight gained along the way and will describe the results in the following.

What was accomplished towards achieving these goals?

The following description is grouped according to the above-mentioned four main tasks:

* Ehrenfest MD For Classical Heavy Projectiles: To answer the important question of how heavy projectiles affect a semiconductor under swift-heavy ion irradiation we specifically aimed to study silicon target material under silicon irradiation, since this process is a knock-on effect. This task is now completed. We thoroughly addressed the multi-scale nature of electron-ion dynamics in heavy-ion irradiated silicon by combining real-time time-dependent density functional theory and molecular dynamics based on a two-temperature model. Our first-principles simulations revealed the detailed charge state dynamics of projectile ions and we explained the consequences on electronic stopping. We explored channeling and off-channeling projectiles and accounted for the contributions of core electrons. This data was compared to experimental results and the SRIM/TRIM database whenever data is available. We showed that electronic stopping of highly ionized Si projectiles on channeling trajectories is higher than for off-channeling ones across a wide kinetic energy range. While this finding is opposite to what is expected for weakly ionized Si projectiles, we explain it by invoking the charge state of the projectile and find consistency with some of the previous experiments. Furthermore, integration with full-cascade molecular dynamics simulations demonstrates the importance of

understanding the detailed electron-ion dynamics during the impact. We showed that different electronic stopping gives rise to qualitatively different cascade structures, which is critical for cascade simulations, e.g. for understanding ion-beam techniques and radiation damage. This work is published in Phys. Rev. B.

* Ehrenfest MD For Quantum-Mechanical Projectiles: The postdoc hired on this project, Tatiane Santos, has worked with the group of Prof. Yosuke Kanai, University of North Carolina at Chapel Hill, and incorporated their implementation of a Gaussian wave packet into our code. Simulations were run that represented the incoming projectile as a finite-sized wave packet within time-dependent Kohn-Sham equations. Unfortunately, COVID slowed these activities, but she accomplished the implementation in the meantime and was able to test it. We now have a working implementation of a quantum-mechanical electron, represented as a Gaussian wave packet, and have preliminary simulations for this wave packet in vacuum and inside of a material. She also tested the numerical convergence parameters of this implementation and these tests are part of a recent publication in MRS Communications. In addition, Tatiane has explored early results towards a new method to extract electronic stopping. This need arises due to the following: For ion projectiles we measured electronic stopping via energy transfer from the ionic to the electronic system. However, since the quantum mechanical wave packet is part of the electronic system, this is not possible anymore and Tatiane started exploring whether electronic stopping in this case can be derived from the change of Kohn-Sham occupation numbers. This work will need to be completed in the future and is an important open question in the community. In addition, Tatiane performed simulations using a classical electron as a projectile and compared this to proton projectiles. This work is still in the process of being finalized as a manuscript. Lastly, we also compared ion beam excitation of electronic defect states to laser excitations instead. These results were accomplished by working with Xavier Andrade, LLNL, to implement a laser field into the Qb@ll code and Yifan Yao, graduate student in my group applied this code to MgO, in order to explore whether diffusion is similarly enhanced as we reported for proton-irradiated MgO before. Yifan showed that laser excitation can achieve the same effect and this can render this process much more relevant for Flash sintering, due to the easier availability of lasers in laboratory settings. The implementation of the time-dependent electric field is part of our MRS Communications publication and the application to MgO remains to be published. In this context it is also worthwhile mentioning that we worked together with Carsten Ullrich on an improved description of exciton by means of the exchange-correlation functional used in real-time propagation. This work, based on a vector potential, is published in Physical Review Letters.

* Nudged-elastic Band Model and Diffusion Calculations: Prior to this reporting period, we have obtained thorough expertise in using a combination of nudged-elastic band calculations and constrained DFT to compute diffusion barriers under occupation-number constraints for proton-irradiated MgO. We paused this task initially to focus on the quantum-mechanical wave packet implementation. In addition, the comparison of proton and laser irradiated MgO convincingly shows that both excitation mechanisms can produce similar occupation numbers and should, thus, behave similarly in nudged-elastic band simulations. More recently, Yifan

started nudged-elastic band simulations for divacancies in diamond to study the splitting of this defect in the excited state (see motivation for this system in the next section).

* Ceramics and Semiconductors Important to the Navy: In order to expand our materials space, we started to work on materials that are relevant to the Navy, which, for the purpose of this project, includes SiC, as well as diamond as an important material for Qbits. The work on diamond started with Tatiane working with an undergrad student, Tomoko Sakurayama, on defect simulations. She has explored stopping of light (proton and helium) projectiles, and classical electron projectiles, in diamond with and without various defects and is currently working on publication of this work. Furthermore, this work now has progressed under Yifan, towards studying the excited-state dissociation of divacancies in diamond. These defects occur as detrimental side product when creating NV centers by means of ion-beam irradiation. Dissociating them is typically achieved by means of annealing, and our work is exploring whether this can be accomplished at lower temperatures when simultaneously illuminating with appropriately chosen laser frequencies. This work is currently in progress and highly promising, including experimental collaborators at Sandia National Lab. In addition, a graduate student in my group, Cheng-Wei Lee, had started working with an undergraduate student, Mustafa Tobah, to studied defects under proton irradiation in SiC. This work was presented at the MRS Spring meeting and we are currently working on a manuscript. Graduate student Gillian Nolan performed a thorough literature review to identify materials in the interest space of the Navy, that are particular promising to show the predicted behavior. This includes materials with defect states that are occupied in their electronic ground state and small diffusion barriers of these defects in the material. In addition, the electronic defect excitation occurs at lower energies than the excitation of electrons across the bulk band gap of the material. Currently, we believe that GaN or Ga_2O_3 could be promising moving forward, in addition to the materials that we are currently studying.

What opportunities for training and professional development did the project provide?

Graduate students on this project were trained in cutting-edge first-principles simulation techniques on various materials and using various high-performance computing resources. Training also included first-principles techniques for simulating electron-electron and electron-phonon scattering and, to predict lifetimes of excited electronic states at defects, solving the Boltzmann transport equation. While this goes beyond what we initially proposed, this project is an excellent opportunity to explore this technique and to use it to supplement our real-time time-dependent DFT simulations. Graduate students, in particular Yifan Yao, helped this project by implementing absorbing boundary conditions into the Qb@ll code and were trained in the necessary coding skills. This will be useful for simulations near surfaces or for low-dimensional materials. Graduate students have become very familiar with first-principles simulations based on real-time time-dependent density functional theory and the Qb@ll code. Yifan is now capable of routinely setting up and running their simulations and to develop analysis strategies, e.g. based on occupation-number analysis. Yifan has worked on the source code directly and compiled the code. Yifan is broadening his expertise at a summer program at Lawrence Livermore National Lab.

The postdoc, Tatiane Santos, has gained significant experience running real-time time-dependent density functional theory simulations using the Qb@ll code. She is also routinely setting up simulations. Within this project, she was trained in writing computer-time proposals and the corresponding reports. All students and the postdoc presented their results at the virtual APS March Meeting this year.

The PI meets each grad student and the postdoc for 30-45 minutes per week one-on-one where we discuss scientific progress as well as mentoring questions. In addition, our entire group meets weekly, where students and postdoc present once per semester on their work. All group members are writing reports and publications using the collaborative LaTeX online tool Overleaf and regularly prepare presentations and slides for our group meeting and weekly individual meetings. Tatiane is also trained to mentor an undergraduate student and to directly work with them on part of this project. She is responsible for pushing the research project with their undergraduate student independently, and the PI meets the team (graduate+undergraduate) by request to discuss progress and future directions as well as mentoring questions.

How were the results disseminated to communities of interest?

We published five papers in peer-reviewed journals, including Nano Letters, Physical Review Letters, and Phys. Rev. B. One of these is the "The 2021 Ultrafast Spectroscopic Probes of Condensed Matter Roadmap", which is published in J. Phys. Cond. Mat. Another collaborative project that emerged from this work on "Real-time exciton dynamics with time-dependent density-functional theory" is published in Phys. Rev. Lett. In addition, results from this project were disseminated in invited and contributed talks by the graduate student, the Postdoc, and the PI, at scientific conferences and department colloquia.
Finally, this work has led to establishing a new research direction in my group on using excited electronic states to modify defect properties in materials, that we plan to explore in much more detail in the future. It has led to foundational insight, both involving laser- and particle radiation induced defect modification. We are expanding towards collaborations with experimentalists to prove the existence of these sub-gap excitation effects and to develop practical strategies to exploit these for manipulating materials. To this end we successfully applied for a CINT rapid access proposal at Sandia National Laboratories and are pursuing this work currently.

What honors or awards were received under this project in this reporting period?

Nothing to report.

Technology Transfer

Nothing to report currently.

Participants

07/2021-06/30/2022:
Schleife, Andre (0.8 person months)
Tatiane Pereira dos Santos (1.72 person months)
Gillian Nolan (5.04 person months)
Yifan Yao (1.4 person months)

07/2020-06/30/2021:
Schleife, Andre (1.07 person months)
Tatiane Pereira Dos Santos (9.81 person months)
Cheng Wei Lee (4.44 person months)
Yao Yifan (4.88 person months)

07/01/2019-06/30/2020:
Schleife, Andre (0.4999 person months)
Cheng-Wei Lee (2.4404 person months)
Tatiane Pereira dos Santos (2.0028 person months)

07/01/2018-06/30/2019:
Schleife, Andre (0.50 person months)
Cheng-Wei Lee (2.44 person months)
Tatiane Pereira dos Santos (2.00 person months)

Products

Alina Kononov, Cheng-Wei Lee, Tatiane Pereira dos Santos, Brian Robinson, Yifan Yao, Yi Yao, Xavier Andrade, Andrew David Baczewski, Emil Constantinescu, Alfredo A. Correa, Yosuke Kanai, Normand Modine, and Andre Schleife, "Electron dynamics in extended systems within real-time time-dependent density functional theory", MRS Communications (2022). https://doi.org/10.1557/s43579-022-00273-7

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