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Computational Materials Science Network
sponsored by the U.S. Department of Energy
Division of Basic Energy Sciences
*Coordinated and administered at the
Department of Physics
University of Washington, Seattle*



Appointment of the new Program Manager (TCMP)

Michael Lee has been named Program Manager for the Theoretical Condensed Matter Physics (TCMP) program in Basic Energy Sciences at DOE. He replaces Dale Koelling, who retired at the end of November 2007. For a short background description on the BES web site for the TCMP program, see

http://www.science.doe.gov/bes/dms/Research_Programs/tcmp.htm, and for a short bio of Michael Lee, visit http://www.science.doe.gov/bes/dms/Staff_Contacts/Lee.htm.

Two New CRTs: *Resonant Inelastic X-Ray Scattering and Predictive Modeling of the Growth and Properties of Energy-Relevant Thin Films and Nanostructures*

We are very pleased to announce the addition of two new CRTs to the CMSN community. One team, led by Arun Bansil (Northeastern University), Jim Freericks (Georgetown University), Bob Markiewicz (Northeastern University), and Michel van Veenendaal (Northern Illinois University and Argonne National Laboratory), is titled *Resonant Inelastic X-Ray Scattering*.

The scientific purpose of the team is summarized on the CMSN's website, and is excerpted here.

“Resonant elastic and inelastic x-ray scattering have the potential to become two of the most powerful experimental probes of strongly correlated electronic systems. These probes directly couple to the two-particle excitations of highly correlated materials and are unique in providing both energy and momentum resolution: resonant x-ray scattering can image exotic ordering such as orbital or magnetic ordering; and resonant inelastic x-ray scattering can directly image the charge excitation spectra for all momenta. Unfortunately, experimental progress has been limited due to the fact that these probes involve complicated many-body processes and, for example, the meaning of different spectral peaks and how they disperse are not well understood. Even less is known about how to correlate the experimental data with the underlying microscopic low-energy models of the strongly correlated electrons. Our cooperative research team (CRT) proposes to significantly enhance the understanding of resonant x-ray scattering techniques both inelastic and elastic to allow for a more rigorous interpretation and use of the experimental data.”

The Predictive Modeling team is lead by Kai-Ming Ho (Iowa State University and Ames Laboratory) and Zhenyu Zhang (University of Tennessee and Oak Ridge National Laboratory). Please visit the group's web site (<http://www.cmp.ameslab.gov/cmp/cmsn-energy/>) for more information. An overview of their work is excerpted here.

A team of leading researchers with highly complementary expertise and a proven record of collaboration has been assembled to address fundamentally important and computationally challenging issues in the broad areas of thin-film growth and nanostructure formation, with emphasis on novel materials for renewable energy applications. The research thrusts are divided into two areas. The first area studies key materials and related computational issues in solar energy conversion for photovoltaic (PV) applications and water splitting via photocatalysis. Materials issues include semiconductor thin films with controlled morphology, dopant distributions, and band gaps. Control of thin-film structure during growth is crucial to achieving high-performance materials in cost-effective PV and photocatalysis applications. In multijunction solar cells, the control of dislocations is the key to further enhancement of cell efficiency; in polycrystalline PV thin films, grain boundaries and point defects may limit the performance of the systems. Predictive calculations provide a valuable tool for understanding the properties of these defects. Development of predictive theoretical techniques for such complex systems under nonequilibrium growth conditions demands a highly synergetic team effort of members covering different materials issues and length and time scales.

The second area is the first-principles-based design of novel nanomaterials for energy storage. We will focus on two systems in this area: quantum metallic alloy films for hydrogen storage and novel carbon-based nanomaterials for energy applications. In the first systems, we will capitalize on the recent advances in precise control of the growth morphology of metal films in the quantum regime and use the tunable electronic densities at the Fermi level to tailor chemical reactions on the surfaces of such quantum catalysts for efficient decomposition of molecular hydrogen and high-capacity hydrogen storage. The second class of model systems will concern predictive design of light-element-based nanomaterials, such as charged or metal-coated fullerenes and carbon nanotubes, metal-organic frameworks, as potential high-capacity hydrogen storage media. Here the challenge is to reliably describe the interaction energies of different natures, including weak/physical (van der Waals), chemical (Kubas), and/or electrostatic, between the molecular/atomic hydrogen and the nanoscale catalysts or storage materials; success in this area calls for team efforts of complementary expertise. The proposed research highly complements ongoing BES research programs and will be performed in close interaction with experimentalists for validation of conceptual advances, with the objective of advancing fundamental science in these areas.

Research Highlight

In this issue of the *CMSN Newsletter*, we feature a research highlight from the Multiscale Simulation of Thermo-mechanical Processes in Irradiated Fission-reactor Materials Cooperative Research Team (CRT): “Kinetically Driven Point-Defect Clustering in Irradiated MgO by Molecular-Dynamics simulation.”

Kinetically Driven Point-Defect Clustering in Irradiated MgO by Molecular-Dynamics Simulation

**Multiscale Simulation of Thermo-mechanical Processes in
Irradiated Fission-reactor Materials CRT**

Summary: An approach for performing molecular-dynamics simulations of radiation damage by inserting Frenkel pairs directly into the crystal is presented. By by-passing the ballistic phase of the radiation cascade of traditional radiation-damage molecular-dynamics simulation, this approach focuses entirely on defect evolution and not on defect creation. In addition to replicating the nature of interstitial clustering observed from the conventional collision-cascade radiation-damage simulations, the simulations reveal an intricate cluster-formation mechanism that involves not only the originally introduced Frenkel defects but also formation of new Frenkel pairs that stabilize a defect lattice.

Atomic-level simulation has long provided important insights into the fundamental processes associated with radiation damage. In particular, simulation has revealed that radiation damage usually involves two distinct phases. First, the “ballistic phase” involves the formation of the collision cascade arising from the high-energy “primary knock-on atom” (PKA). This phase is typically only a few picoseconds long, its net effect being the generation of Frenkel pairs (FPs) and small point-defect clusters.¹ Second, the “kinetic phase” captures the diffusion-controlled dynamical evolution of these vacancies and interstitials, their annihilation, and the formation of defect clusters. Thus it is this kinetic phase that determines the long-time, experimentally accessible behavior of the material: while the recombination events promote radiation tolerance, the cluster-formation process produces the irreversible damage that degrades materials performance and ultimately limits lifetime. Previous simulations of collision cascades followed by rather long temperature-accelerated dynamics (TAD) simulations^{2,3} have shown that the defect evolution during the kinetic phase is largely independent of the detailed nature of the initial damage created during the ballistic phase, suggesting that the role of the cascade simulation is mostly to introduce nonequilibrium point-defects into the system.

The standard PKA simulations introduce only a rather small number of point defects into the system. Thus a key question is whether they are able produce the wide range of defect environments that are present in experiment. Here we describe an approach that, by circumventing the ballistic-phase simulation entirely, allows a much wider range of different defect environments to be

explored. In this approach, the initial damage is introduced by randomly distributing a specific (variable, PKA-energy dependent) concentration of stable Frenkel pairs into the lattice and subsequently following their diffusion-controlled kinetic evolution at elevated temperature. When applied to MgO as a model material, this approach replicates the defect clusters seen in the full cascade simulation followed by the TAD simulation.^{2,3} More importantly, it also exposes an intricate cluster-formation mechanism that involves not only the original, radiation-induced Frenkel pairs but also formation of new “structural” FPs as a lattice response that stabilizes the larger clusters. The new approach also has the advantage of being a simpler, computationally less cumbersome and physically more transparent way of introducing the initial ‘collisional’ damage into the material.

We choose MgO as the model material in which to demonstrate this approach, as the point-defect evolution due to the collision-cascade PKA simulation has already been reported by Uberuaga *et al.*^{2,3} Their work showed that in relatively low PKA-energy (0.4-5.0 keV) cascade simulations, most of the FPs formed in the ballistic phase recombine during the kinetic phase; those that do not recombine kinetically evolve to form charged, highly stable clusters containing a maximum of seven ions. Particularly noteworthy is the fact that these clusters are not formed during the ballistic phase but as a consequence of interstitial diffusion during the kinetic phase during which the defects diffused long distances and were not confined to the spatial region affected by the initial ballistic cascade.

We have performed MD simulations in a single crystal consisting of 20x20x20 cubic rocksalt crystal structure unit cells containing 64,000 ions. A classical Lewis and Catlow⁴ Buckingham-type potential is chosen to describe interionic short-range interactions. The long-range Columbic interactions are calculated by using Wolf’s 1/r-summation method⁵ with a spherical truncation at the cut-of radius of 8.139 Å. The time step of 0.5 fs ensures good energy conservation in the tests in the NPE ensemble. All the simulations are performed at 1000K. The FPs are created randomly and every vacancy and interstitial is initially separated by at least 5 lattice parameters to minimize the uninteresting rapid recombinations. However, no constraint is put on interstitial-interstitial or vacancy-vacancy distance.

To elucidate the defect evolution and clustering mechanisms, we have performed two different types of simulations, differentiated by the FP defects present on the either or both sublattices. The first type involves FPs on the Mg and O sublattices separately; in the second type, FPs are created simultaneously on both sublattices.

Fig. 1 shows the time evolution of a system into which initially 100 FPs were inserted into only the Mg sublattice at T = 1000 K. At t = 0 ps and t = 2450 ps, the number of Mg FPs are 100 and 18 respectively. As we can see in Fig. 1b, no clustering of the defects takes place. Similarly, all the FPs when created only on the O sublattice recombine without forming clusters. In a collision-cascade simulation it is, of course, not possible to selectively create defects on only one of the sublattices; this demonstrates a unique aspect of our approach in understanding the defect evolution. These simulations provide a baseline against which to compare the results of simulations of FPs on both sublattices.

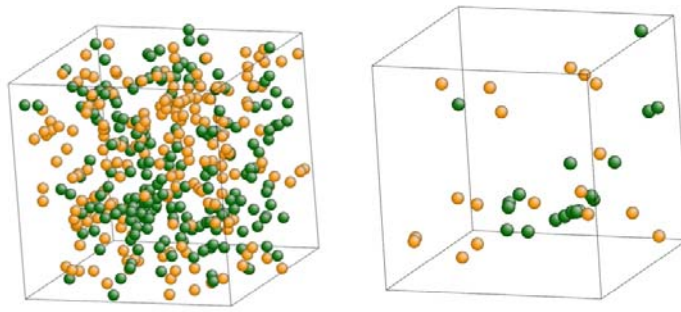


Fig. 1. Evolution of the 100 initially-introduced Frenkel pairs in only the Mg sublattice at $T = 1000$ K. Color scheme used in all figures - dark green spheres represent Mg interstitials and orange spheres represent Mg vacancies. Shown are two snapshots at (a) $t = 0$ ps (containing 100 FPs), and (b) $t = 2450$ ps (18 FPs). Due to the absence of O point defects (see also Fig. 2) no Mg interstitial clustering occurs during the annihilation by interstitial-vacancy recombination on the Mg sublattice. (*Lattice atoms are not shown.*)

Next, we create FPs on both sublattices simultaneously. Figure 2 shows snapshots taken at (a) $t = 0$ ps and (b) $t = 2450$ ps for a system containing initially 100 FPs on each of the two sublattices. Compared to the case of Mg or O FPs only, this annealing simulation reveals much less interstitial-vacancy recombination but, instead, significant interstitial aggregation into clusters. This aggregation starts quickly by the formation of highly mobile di- and tri-interstitials. Identical di- and tri-interstitial clusters were observed in the lower-temperature, combined collision-cascade and TAD simulations by Uberuaga *et. al.*^{2,3}

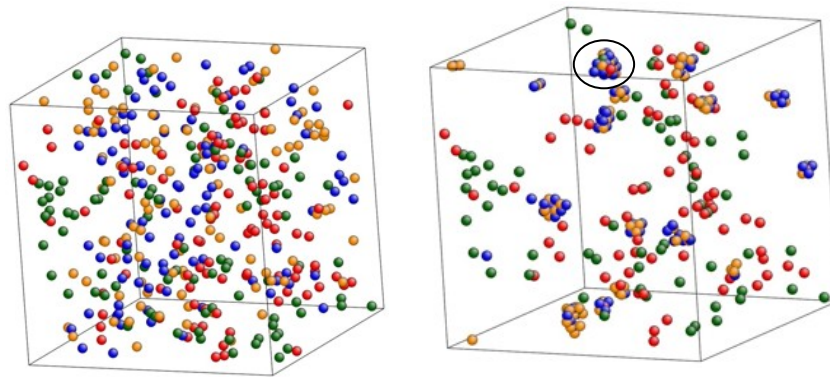


Fig. 2. Snapshots taken at (a) $t=0$ and (b) $t=2450$ ps showing the evolution at $T = 1000$ K of 100 FPs initially introduced into each of the two sublattices. Of the initially 100 Mg and 100 O FPs in (a), 72 Mg and 76 O FPs are still present in (b). Dark green and orange spheres represent Mg interstitials and vacancies; red and blue spheres represent O interstitials and vacancies. The circled cluster in (b) is

The comparison between the two simulations (Figs. 1 and 2) demonstrates that, when the FPs are present on only one sublattice, all the vacancies and interstitials eventually recombine due to the absence of clustering; hence, after 2450 ps only ~20% of the initial FPs remain (see Fig. 1). By contrast, in the system containing FPs on both sublattices, about 80% of the FPs become immobilized by precipitation into highly stable vacancy-interstitial clusters (see Fig. 2).

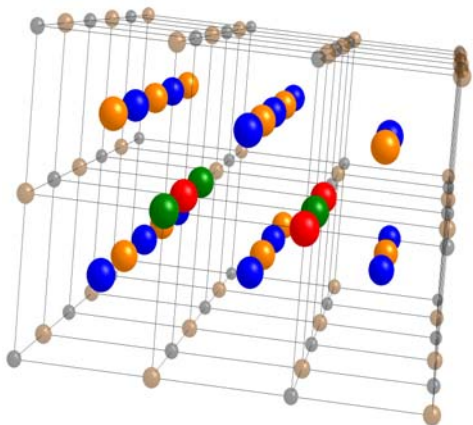


Fig. 3. Closeup of the all-interstitial cluster circled in Fig. 2(b). The cluster forms an interstitial rocksalt lattice that is displaced with respect to the parent lattice (not shown).

A closeup snapshot of one of the larger interstitial clusters, circled in Fig. 2(b), is displayed in Fig. 3. Investigation of the dynamic growth mechanism of this representative cluster reveals *two* distinct, coordinated mechanisms that control its formation and growth.

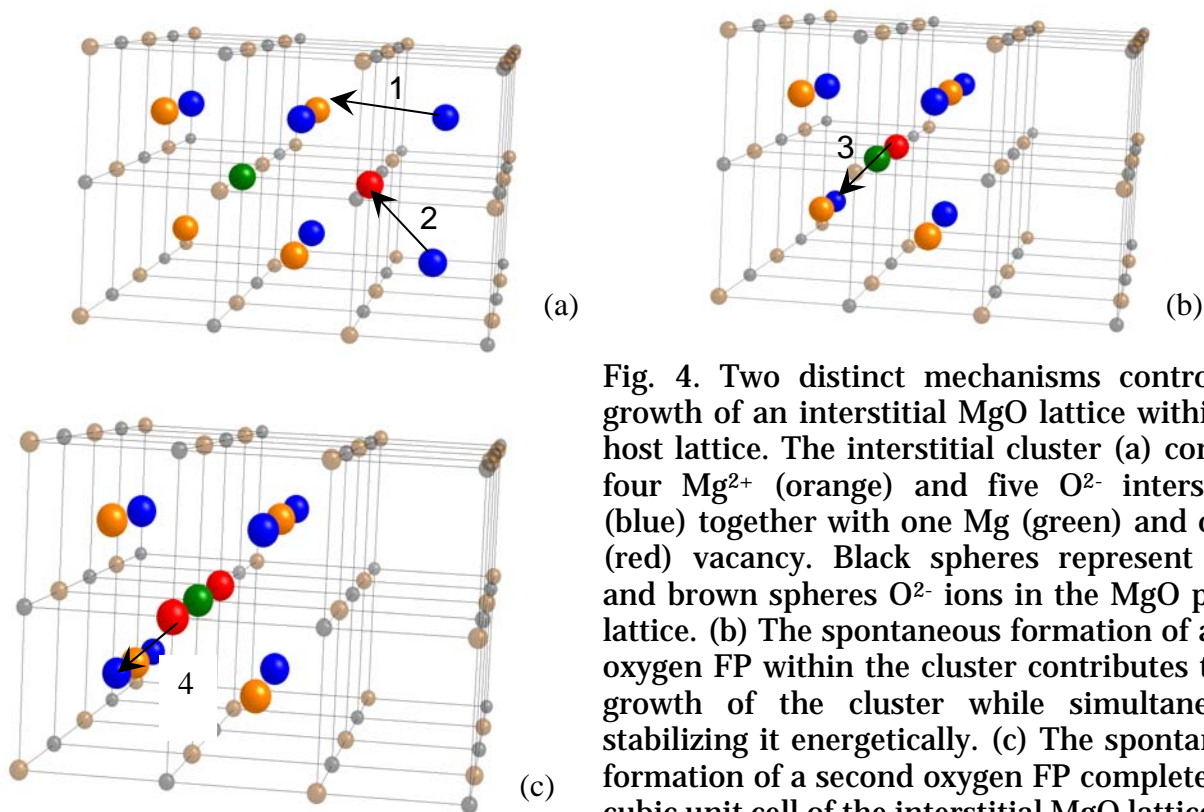


Fig. 4. Two distinct mechanisms control the growth of an interstitial MgO lattice within the host lattice. The interstitial cluster (a) contains four Mg^{2+} (orange) and five O^{2-} interstitials (blue) together with one Mg (green) and one O (red) vacancy. Black spheres represent Mg^{2+} and brown spheres O^{2-} ions in the MgO parent lattice. (b) The spontaneous formation of a *new* oxygen FP within the cluster contributes to the growth of the cluster while simultaneously stabilizing it energetically. (c) The spontaneous formation of a second oxygen FP completes one cubic unit cell of the interstitial MgO lattice.

These are: (i) the conventional mechanism involving diffusion-controlled aggregation and annihilation of the originally introduced interstitials, and (ii) the spontaneous formation of *new*, “structural” FPs by the coordinated displacements of lattice atoms within the cluster core.

The coordinated operation of the two mechanisms is illustrated in Fig. 4 which captures four sequential hopping events (see arrows) during the growth and stabilization of a cluster containing initially four Mg²⁺ and five O²⁻ interstitials together with one Mg and one O vacancy (see Fig. 4(a)). Arrow 1 indicates oxygen diffusion to a neighboring interstitial site while arrow 2 captures the annihilation of an oxygen FP by interstitial-vacancy recombination. Both are conventional diffusion events of interstitials already present at the beginning of the kinetic phase. By contrast, Fig. 4(b) reveals a novel mechanism involving the spontaneous creation of a new (not initially present) FP as a regular-lattice O ion hops to an interstitial site (arrow 3), leaving behind a new vacancy within the cluster core; this event is then repeated (Fig. 4(c), arrow 4). Two additional ions already present at the back of the interstitial cube in this figure act as nucleation sites for the completion of the next, adjacent cube. The net outcome of these events is a complete cube of an interstitial MgO crystal that has been formed and that continues to grow, on the displaced, interstitial lattice.

From the viewpoint of simulation methodology, temperature-accelerated dynamics (TAD) simulations^{2,3} have largely overcome the issue of MD simulations only reaching out to nanosecond time scales. However, their application to single cascades and hence low defect concentrations limits the complexity of the defect structures that can thus be observed. By injecting a very high density of defects, the method proposed here allows large clusters to develop. Moreover, this high density essentially allows nanosecond simulations to produce defect structures only previously seen in much longer simulations. The initial defect concentrations introduced in this approach are extremely high. It might thus be argued that the dynamically generated complex defect structures seen here may in reality be rather uncommon. However, given that single defects and small clusters are annihilated as the system evolves, it is these large, structurally complex clusters that will survive and constitute the long-term radiation damage in the system.

To conclude, this robust and straightforward approach enables elucidation of the kinetics of radiation-damage development unencumbered by the initial damage due to one specific cascade. By following only the kinetic evolution at elevated temperature, it enables observation of defect aggregation up to significant cluster sizes, and with mechanistic detail not previously possible. In addition, the ability to selectively create defects on only one of the sublattices provides an additional perspective on the nature of radiation-damage development. Since it does not require particularly large system sizes, the approach thus provides a relatively simple and direct route for elucidating the competing roles of point-defect annihilation and aggregation in the development of radiation damage, including host-lattice responses in the process.

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Conferences and Workshops

Four CMSN CRTs have held or will be holding workshops. These include the following:

- *Predictive Capability for Strongly Correlated Systems* Annual Fall Coordination Meeting, University of Tennessee/Oak Ridge National Laboratory, November 13-16, 2008
<http://physics.ucdavis.edu/~savrasov/CMSN2008/>
- *Predictive Modeling of the Growth and Properties of Energy-Relevant Thin Films and Nanostructures* First Coordination Meeting, Gatlinburg, TN, October 31-November 1, 2008
<http://www.cmp.ameslab.gov/cmp/cmsn-energy/CMSN08-program.pdf>
- *Resonant Inelastic X-ray Scattering* First Planning Meeting, Argonne National Laboratory, October 26-27, 2008
- *2008 Advanced Light Source Users' Meeting: Theory Institute for Photon Sciences*, Berkeley Laboratory, October 14-15, 2008
<http://sbg.als.lbl.gov/tips08/index.html>
- *Multiscale Simulation of Thermo-mechanical Processes in Irradiated Fission-reactor Materials* Annual Fall Coordination Meeting, September 4-5, 2008, Santa Fe, NM
http://www.phys.washington.edu/~cmsn/conferences/past_mtgs.html

Please consult the CMSN website for updated information on conferences and workshops, at <http://www.phys.washington.edu/~cmsn/>.

CMSN Information

CMSN's teams, oversight, and administration are listed below. Further information can be found at <http://www.phys.washington.edu/~cmsn>.

Cooperative Research Teams

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Dynamics and Cohesion of Materials
Interfaces and Confined Phases Under
Stress

Mark Asta (University of California at
Davis), Alain Karma (Northeastern),
and Anthony Rollett (Carnegie-
Mellon)

Predictive Capability for Strongly
Correlated Systems

Richard Scalettar and Warren Pickett
(UC-Davis)

Multiscale Simulation of Thermo-
mechanical Processes in Irradiated
Fission-reactor Materials

Dieter Wolf (INL) and Simon Phillpot
(University of Florida)

Resonant Inelastic X-ray Scattering

Arun Bansil (Northeastern
University), Jim Freericks
(Georgetown University), Bob
Markiewicz (Northeastern
University), Michel van Veenendaal
(Northern Illinois University and
Argonne National Laboratory)

Predictive Modeling of the Growth and
Properties of Energy-Relevant Thin
Films and Nanostructures

Kai-Ming Ho (University of Iowa and
Ames Laboratory) and Zhenyu Zhang
(University of Tennessee and Oak
Ridge National Laboratory)

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