Understanding mechanical properties and diffusion mechanisms of $NiFe_2O_4$ spinel by using kinetic activation-relaxation technique

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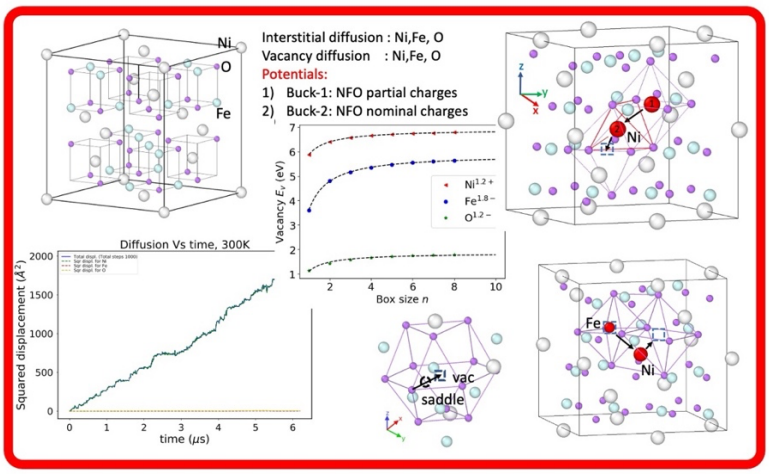

In recent years, spinel ferrites such as $NiFe_2O_4$ (NFO) have gained enormous interest due to their many applications such as steel making, corrosion problems, spintronic devices, lithium batteries, hydrogen production, etc. [1,2,3,4], but despite the progress in this field, their mechanical and diffusion properties at the atomic level still need to be better understood. For example, phenomena such as point defect diffusion play a relevant role in spinel formation, but point defect diffusion is a rare event that requires longer times than those allowed by techniques such as **molecular dynamics (MD**). In this seminar it is explained how the **kinetic activation-relaxation technique (k-ART)**, an off-lattice **kinetic Monte Carlo (KMC)** algorithm which allows longer time steps and direct calculation of diffusion barriers, this in contrast to Arrhenius graphics in MD, is used to obtain these rare events due to large transition barriers and their mechanisms are described in a proper way. It is explained how point defects are assumed to be responsible for ionic diffusion. Both cation and anion defects are studied. We first compare the mechanical properties and stability of NFO predicted using different empirical potentials, then we focus on vacancies and interstitials by comparing their properties and show that the energy landscape along different pathways is described in detail by k-ART. In this study, it is shown that ***diffusion of cation interstitials are, in part, responsible for the transition from normal to inverse spinel*** [1]. That is, the mechanisms by which a normal spinel is transformed to an inverse spinel via cation diffusion are predicted. Buckingham potentials are used to obtain how physical properties evolve in time for these kinds of spinel systems. Also, we find that interstitial Ni diffusion involves the movement of two Ni ions and that O interstitials trigger collective diffusion of O ions, while an O vacancy is diffused by an O ion moving to the centre of a cuboctahedron.

[1] Óscar A. Restrepo, Charlotte S. Becquart, Normand Mousseau, "*Unveiling the diffusion mechanisms for spinel ferrites NiFe2O4 by using kinetic activation-relaxation technique (k-ART)*", J. Chem. Phys. 161, 094307 (2024). https://doi.org/10.1063/5.0220397.

[2] Óscar A. Restrepo, Oscar Arnache, Normand Mousseau, "*An approach to understanding the formation mechanism of $NiFe_2O_4$ inverse spinel*", Materialia **33**, 102031 (2024). https://doi.org/10.1016/j.mtla.2024.102031.

[3] Óscar A. Restrepo, Óscar Arnache, J. Restrepo, Charlotte S. Becquart, Normand Mousseau, "*Comparison of different existing empirical potentials for Fe3O4 and NiFe2O4 spinel ferrites bulk basic properties*", Computational Materials Science 213 (2022) 111653. https://doi.org/10.1016/j.commatsci.2022.111653.

[4] Óscar A. Restrepo, Óscar Arnache, J. Restrepo, Charlotte S. Becquart, Normand Mousseau "*Structural modeling of ZnFe2O4 systems using Buckingham potentials with static molecular dynamics*", Solid State Communications 354 (2022) 114914. https://doi.org/10.1016/j.ssc.2022.114914.