# **First Principles Calculation of Raman Spectra of Anion defects in Fluorite Systems**

# INTRODUCTION

Materials with fluorite structures are important materials in both technical applications and science studies. The cation sublattice is very stable and the long-range order is maintained while doped with large numbers of impurities. Ceria is of interest as a solid fuel cell electrolyte and catalyst applications. Uranium and Thoria are nuclear fuels.

# BACKGROUND

## Fluorite Systems

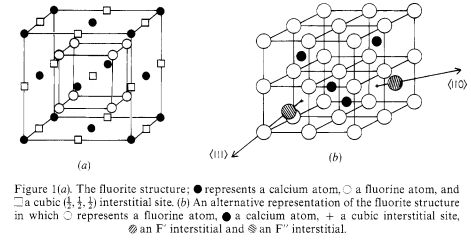
The fluorite structure belongs to the space group, , the Raman tensor transforms as the irreducible representation

[Interstitial] <http://journals.aps.org/prb/pdf/10.1103/PhysRevB.20.3481>

## Anion Interstitial

Compounds with the fluorite structure are known to be capable of accommodating a large excess of anions (ions with net negative charge).[1]

<http://journals.aps.org/prb/pdf/10.1103/PhysRevB.20.3462>



[16] M. A. H. Nerenberg, T. M. Haridasan, J. Govindarajan, and P. W. M. Jacobs, J. Phys. Chem. Solids 41, 1217

(1980).

[17] T. M. Haridasan, J. Govindarajan, M. A. Nerenberg, and P. W. M. Jacobs, Phys. Rev. B 20, 3462, 3474 (1979).

## Anion Vacancies

Yttria doped CaF2.[2]

Sodium doped CaF2.

**Raman Spectra**

**Frankel Defect**

In the case of a Frenkel defect, we shall assume that the vacancy and interstitial are far apart such that their interaction is not important. This assumption is made to make the calculations tractable, so that we can take the case of an isolated interstitial and then an isolated vacancy separately.

[**http://journals.aps.org/prb/pdf/10.1103/PhysRevB.20.3481**](http://journals.aps.org/prb/pdf/10.1103/PhysRevB.20.3481)

**Defect Structures**

Defects to the anion sublattice

# Computational Methods

Umari and Pasquarello describe a technique where both IR and Raman spectra are calculated from first principals for an amorphous silicate system[3] which uses results from the modern theory of polarization to treat finite electric fields.[4] This method gives derivatives with respect to the electrical field equivalent to perturbational methods[4, 5] but only requires the addition of a term to the ground energy functional[3]:

is the energy functional in the absence of an electric field, is the electronic polarization and is the ionic polarization.

This approach is attractive for several reasons. First, by defining the polarizability tensor as derivatives of atomic forces with respect to finite electric fields approximations for the Raman spectra can be calculated using density functional theory (DFT) software such as VASP.

With this approach, dielectric susceptibilities, can be calculated by taking finite differences of the polarization of the system subject to an electric field[3].

Born effective charge tensors are defined as induced polarization along the direction by a unitary displacement of the Ith atom in the direction [6]:

Using finite electric field DFT calculations, we can calculate the Born effective charge tensors by taking finite difference of atomic forces with respect to the electric field.

For a Raman scattering process, an incoming photon of frequency and polarization is scattered to an outgoing photon of frequency and polarization . This either creates on annihilates a phonon of frequency by Stokes or anti-Stokes processes, respectively. We consider the nonresonant Raman scattering process[3, 7, 8].

Calculation of Raman tensors alpha[3, 8] is defined the formula:

Third rank tensors which are derivatives of the dielectric susceptibility tensor with respect to ionic displacements can be alternatively calculated by second derivatives of the atomic forces with respect to changes in the finite electric field.

Lattice dynamics provides an analytical solution of the equations of motion resulting in a vibrational system where atoms are displaced from their equilibrium positions. A rigorous development of the theory of lattice dynamics is described in the seminal book on the subject by Born and Huang[9]. For the proposed work, relevant key results are distilled from the mathematical machinery.

An atomic system can be represented by the atomic masses of the systems combined with an interatomic potential that describes the forces between the atoms are captured in a dynamical matrix.

To calculate the dynamical matrix, either by numerical derivatives using finite displacements of individual atoms. The eigenvalues,, and eigenvectors, , of this matrix represent the frequencies and vibrational modes associated with the material. Since these modes are linearly independent and form an orthonormal basis set, the state of any vibrational system can be represented by a linear combination of its modes.

All discussions of DFT will assume the use of code VASP[10, 11]. In the proposed work, the projected augmented plane wave (PAW)[12, 13] to describe the interactions between the core and valence electrons. The exchange-correlation functional is treated with the LDA functional. The present study employs the VASP code with a cutoff for the plane wave basis set tabulated below, the LDA exchange-correlation functional and a 2x2x2 supercell containing 96 lattice sites and a 1x1x1 k-point grid.

Calcium Floride computational details.

Thoria computational details

Uranium Oxide computational details

Ceria computational details

DFT often fails to describe systems with localized d and f-elections due to approximations to the exchange-correlation energy (e.g. LDA and GGA) having the consequence of an erroneous electron self-interaction; this causes repulsion which favors electron delocalization. To correctly characterize the localization of the U f-electrons, the DFT+U approach of Dudarev[14], will be used for all calculations, with all +U parameters originating from previous studies which have used this method. The Hubbard DFT+U method is applied to the f-electrons of the U species in UO2 (U = 4.50 eV and J= 0.51 eV), with occupancy control to ensure that lowest energy configuration is identified [Dorado,Amandon,Freyss-2009].

Thoria Notes

Murphy does point defects in ThO2[15].

The DFT calculations described here were performed using the frozen-core all-electron projector-augmented-wave PAW method[12, 16], as implemented in the *ab-initio* total energy code VASP (Vienna *ab-initio* simulation program).

UO2

Defects in UO2

Dorado +U corrections for UO2[17]

**Calcium Fluoride**

CaF2

CaF2 + vacancy

CaF2 + vacancy +

CaF2 + interstitial

Mp-602 -> Moly Telluride

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