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A possible new mechanism for defect formation in irradiated UO_2

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ABSTRACT

A defect formation mechanism is proposed in order to explain recently observed Raman defect lines on He^{2+} irradiated UO_2. These defects are formed by electronic stopping of He^{2+} even though their dE/dx is less than the threshold for track formation. Referring to literature of self-trapped excitons, this mechanism is divided in three steps: creation of electronic defects by electron stopping, stabilization of self-trapped excitons on uranium sublattice and, after accumulation of self-trapped excitons, formation of structural defect on the oxygen sublattice. This proposed mechanism still needs to be validated by more experimental evidence of the Magneli type defect proposed to be the self-trapped excitons on uranium lattice.

1. Introduction

Irradiation effects in uranium dioxide have been studied for 50 years at least because this material is the main component of nuclear fuel. Usually these effects are considered to be created by either electronic or nuclear stopping of particles or ions in the irradiation field. Most of irradiation effects in UO_2 are interpreted considering point defects that are created by ballistic collision during nuclear stopping [1]. Consequently many efforts have been put on the description of point defects in UO_2, especially by first principle calculations [2], in order to derive thermodynamic models [3], in which irradiation effects could be included [4]. Electronic stopping in ceramics produce tracks above a threshold, that can be modeled [5]. In the case of UO_2, tracks were first observed by Wiss [6] and Sonoda proposed the threshold for track formation to be around 20 keV/nm [7]. Under fission conditions point defects would mainly form at the end of range of the fission fragments in the nuclear energy loss domain. Hence, little irradiation effects are expected in bulk UO_2 in the electronic stopping regime of fission fragments.

Recently, characterizations of UO_2 by Raman spectroscopy evidenced vibration modes that were created by irradiation and that were named defect modes [8]. Types of point defects were tentatively assigned to these defect modes. In this paper, we aim at identifying the formation mechanism of these defects. For that purpose we will first determine in which range of electronic and nuclear stopping these defects are created. Then a formation mechanism is proposed from available literature.

2. Formation conditions of defects detected by Raman spectroscopy

In [8], a UO_2 sample was irradiated with He^{2+} ions of 25 MeV produced by the CEMHTI cyclotron accelerator, in the DIAMANT device (alpha irradiation device for nuclear materials under temperature). Irradiation was performed with a flow of 200 nA for 2 h, which corresponds to a final fluence of 1.6×10^{16} He cm^{-2}. Post mortem micro-Raman line scan measurements were performed at room temperature on the cross-section of the irradiated sample parallel to the He^{2+} ionic beam direction.

Fig. 1 pictures the whole spectra of the Raman scan in an iso-intensity representation. The most prominent feature is the T_2g Raman-active mode appearing at 445 cm^{-1} characteristic of the fluorite structure of Uranium dioxide. A triplet of defect bands called U1, U2, and U3, also appear in the 500–700 cm^{-1} range that progressively grow up from the surface (0 μm) up to 130 μm. The defect bands are signatures of the structural modifications in UO_2. U2 was interpreted as due to the activation of the Raman-forbidden LO mode, U3 to an over-stoichiometric structural defect of cuboctahedral symmetry and U1 might be the signature of sub-stoichiometric structural defect.

SRIM [9] calculation of the depth of He implantation (black arrow) and theoretical distribution of energy deposit (dE/dx) by He^{2+} ions during irradiation (orange line) are presented on the same depth scale at the top of Fig. 1. Nuclear stopping is maximum at He implantation depth but represents only about 1% of the total deposited energy at this location. Therefore, at least for the first 100 μm of the implantation depth an electronic stopping has to be considered in order to interpret the apparition of the Raman defect modes. Moreover the calculated electronic power loss is less

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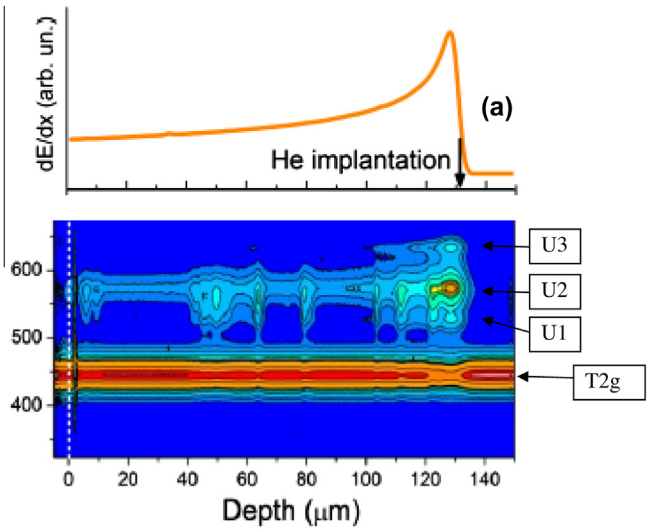

Fig. 1. Raman spectrum as a function of the implantation depth in He^{2+} irradiated UO_2.

than 1 keV/nm at maximum. So Raman defect modes would be formed at an electronic dE/dx that is less than the threshold for track formation.

In fact in this range of electronic stopping power, self-trapped excitons are, from literature point of view, the only type of defect that can be formed in ceramics [10].

3. Self-trapped excitons in UO_2

Self-trapped excitons can be formed when a transient electronic defect is stabilized by atomic displacements in the crystalline lattice of the irradiated solid. In UO_2 a defect of this type, named polaron, has already been reported but the actual meaning of this term has to be better defined in order to precisely describe irradiation effects in UO_2. The existence of polarons was claimed in order to explain electrical conductivity enhancement at high temperature [11,12], heat capacity increase at high temperature [13,14], shortening of electronic gap as a function of temperature measured in UV absorption experiment [15], transient laser experiment [16]. In all these experiments, the interpretations using polaron consider only one aspect of this quasi-particle which can lead to confusing description. For example, in the interpretation of electrical conductivity measurements, a polaron is considered as a charge carrier while in heat capacity interpretation it is considered as an energy carrier which may be confusing because the mass of charge carriers is generally negligible compared to the atom one and as consequence they should have no influence on heat capacity. We shall here focus on the life time of polarons which is a key point for the understanding of irradiation effects.

Electronic stopping of a particle in matter is a very fast mechanism with fs characteristic time. Raman spectra of irradiated sample were performed several weeks after irradiation: the defects they evidenced must have a long life time. Therefore in order to have a comprehensive description of UO_2 irradiation, we need to consider defect life time in the irradiation process.

Electronic stopping in matter consist in the energy transfer from the incident particle to electrons that become hot electrons. Then these hot electrons release the energy they received by electronic collision and transition, eventually by direct energy transfer to phonons which results in an increase of temperature in the wake of the incident particle. These processes can be modeled in a simplified description of a two temperature system [17]. In the case of UO_2, polarons were proposed to store part of the electron energy, thus reducing the heating along the track core and releasing this energy at a later time when the polarons undergo their relaxation process [18]. The energy release from polaron relaxation (1 μs) would occur long after the end of the atomic displacements (typically less than 100 ns) produced by the electron–phonon relaxation [19]. Even though these polarons have a long life time compared to electronic desexcitation processes, they have still very short life time compared to defects detected by Raman spectroscopy at room temperature. So, two different types of defects have to be considered to describe electronic stopping power in UO_2. The first one will be called polaron and have a life time of the order of 1 μs, the second one will be called a self-trapped exciton and have an infinite life time compared to polaron.

A polaron is by definition a charge carrier coupled to phonons, i.e., deformation of the crystalline lattice. In the case of UO_2, it is associated to the dismutation reaction $2\ U^{4+} <> U^{5+} + U^{3+}$ which can also be viewed as the transfer of an electron from one regular uranium atom to an adjacent one. The polaron radius was determined equal to 2.3 Å by the interpretation of UV absorption data [xv]. This small radius implies that the transferred electron likely moved from one atomic shell to another. The electronic transfer induces only a small distortion of the crystalline lattice and should not induce the apparition of a Raman defect mode because the lattice symmetry is not changed. Moreover this electronic configuration is not the stable one that can be calculated by first principle methods. So it will rapidly recombine because of perturbations generated by phonons. However some displacements of uranium and oxygen atoms might also be produced. In some cases this would lead to the formation of self-trapped excitons.

Self-trapped excitons are analysed using Raman data considering that they are associated to the Raman defect modes described previously. They imply atomic displacements because new vibration modes of the crystalline lattice are formed after irradiation. They also should imply oxidation state of atoms different from the UO_2 regular one because are created by charge trapping. In UO_2, the lowest excited electronic state correspond U^{3+} and U^{5+} oxidation state, O^- or O^{2-} being much more unlikely defects. The proposed interpretation of Raman lines considers that U1 and U3 modes are related to oxygen sublattice. U_3 peak at about 635 cm^{-1} was assigned to a structural defect of cuboctahedral symmetry as present in the crystalline structure of unirradiated U_4O_9 [20]. The cuboctahedron in U_4O_9 is a cluster of five oxygen interstitial atoms. Its formation is consequently a process that implies many atomic displacements and therefore cannot be considered as a primary defect. These considerations led us to assume a three step process for defect formation under electronic stopping:

- Polaron formation by direct electronic excitation.
- Formation of self-trapped defect on U sublattice (STD-U) associated to U2 Raman mode.
- Accumulation of STD-U leading to oxygen displacements that eventually induce the formation of defects on the oxygen sublattice that correspond to U1 and U3.

This description relies on the existence of hypothetic STD-U defect that is still not reported in literature but that should correspond to the observed U2 Raman mode. In the following a tentative description of STD-U is proposed.

4. STD-U defect in UO_2

U2 peak at about 575 cm^{-1} can be assigned to LO mode. This LO mode is Raman-forbidden in the unirradiated UO_2 (perfect fluorite structure) and becomes Raman active due to a breakdown in the selection rules caused by the lattice damage. In fact only the