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**LATTICE SHEAR DISTORTIONS IN FLUORITE STRUCTURE OXIDES**

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## LATTICE SHEAR DISTORTIONS IN FLUORITE STRUCTURE OXIDES\*

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### ABSTRACT

Crystallographic shear distortions have been observed in fluorite structure, single crystals of  $\text{UO}_2$  and  $\text{Zr}(\text{Ca})\text{O}_{2-x}$  by neutron-diffraction techniques. These distortions localize on the oxygen sublattice and do not require the presence of an external strain. The internal rearrangement mode in  $\text{UO}_2$  is a transverse, zone boundary  $\vec{q} = 2\pi/a (0.5, 0, 0)$  deformation with amplitude 0.014 Å. In  $\text{Zr}(\text{Ca})\text{O}_{2-x}$ , the mode is a longitudinal,  $\vec{q} = 2\pi/a (0, 0, 0.5)$  deformation with amplitude 0.23 Å. Cation-anion elastic interactions dominate in selecting the nature of the internal distortion.

### INTRODUCTION

We report the observation<sup>1</sup> of internal distortions in fluorite structure (Fm3m)  $\text{UO}_2$  and  $\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}$ . One unique feature of our observations is that both materials exhibit internal distortions which are not coupled to an external strain. Moreover, these shear distortions are internal rearrangements that basically involve cation-anion interactions.

Uranium dioxide,  $\text{UO}_2$ , exhibits a first-order, para to antiferromagnetic transition with the Néel temperature,  $T_N = 30.8$  K. The transition is characterized by a discontinuous jump in sublattice magnetization and a volume discontinuity  $\Delta V/V \sim 60$  ppm at  $T_N$ . For actinide magnetism, we anticipate a large spin-orbit and strong crystalline electric field effects. Moreover, the resultant spin-lattice interaction should reduce the symmetry of the lattice below  $T_N$  and thus produce an external strain. A number of x-ray experiments have failed to detect the presence of such a strain.

Calcia-stabilized zirconia,  $\text{Zr}(\text{Ca})\text{O}_{2-x}$  exhibits an order-disorder transition with  $T_c \sim 1275$  K. The transition is very sluggish from above, requiring several hundred hours just below  $T_c$  to produce the ordered state. The driving force for this transition is presumably related to the formation of microdomains of ordered structure with high Ca ion and oxygen vacancy concentrations. Again x-ray experiments have failed to detect the presence of an external strain.

### EXPERIMENT

The experiment for  $\text{UO}_2$ , is to cool a single crystal below  $T_N$  and measure the scattering that arises from the antiferromagnetic state.<sup>2</sup> Full three-dimensional neutron scattering Bragg intensities were obtained. For  $\text{Zr}(\text{Ca})\text{O}_{2-x}$ , the crystal was annealed at 1250 K for 400 hours to produce the ordered state.<sup>3</sup> The onset of ordering

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for both materials is apparent by a reduction in symmetry of the lattice. For the disordered state of an fcc crystal, only reflections with Miller indices  $h + k + l = 4n$ ,  $4n + 1$ , and  $4n + 2$ , where  $n$  is an integer are allowed. In the ordered state, "forbidden" reflections arise with  $h, k, l$  mixed odd and even.

## DISCUSSION

The problem then is to understand what mechanism gives rise to the "forbidden" reflections. The appearance of these reflections clearly show, however, that a superlattice representation is not required. A complete period of lattice modulation must occur over a unit cell dimension. In Fig. 1 we illustrate the internal rearrangement mode that occurs in  $UO_2$ . The shaded planes contain the ferromagnetic sheets which are stacked  $+ - + -$  yielding the type I antiferromagnetic structure. A modulated structure is defined by the arrows which show how the oxygen sublattice internal rearrangement mode arises from collective displacements of the oxygen ions from their ideal fluorite lattice sites. Oxygen (010) planes shear in alternate directions. From least-squares analysis,  $\Delta$ , the mode amplitude is 0.014 Å. In Fig. 2 we illustrate the internal rearrangement mode that occurs in nonmagnetic, but ordered  $Zr(Ca)O_{2-x}$ . The modulated structure is defined by the arrows which show (110) oxygen sublattice shear planes. The mode amplitude is 0.23 Å.

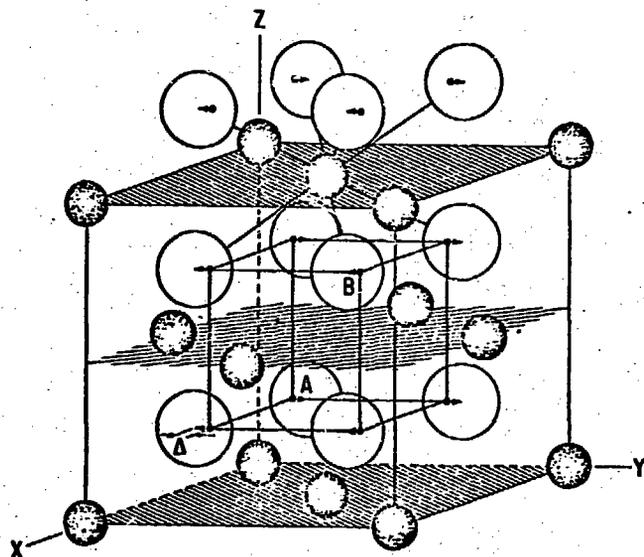


Fig. 1. The  $UO_2$  fluorite unit cell. The closed circles are the cations that form an fcc lattice. The open circles define the anions on sublattices A and B with fractional coordinates  $1/4, 1/4, 1/4$  and  $3/4, 3/4, 3/4$ .

A search criterion for the occurrence of internal rearrangements has been developed.<sup>4</sup> Let us assume that the mode that occurs is least unfavorable with respect to an increase in elastic energy. An internal distortion localized on the anion sublattice satisfies this constraint, and is observed experimentally. Moreover, let us assume that only short-range nearest-neighbor radial elastic forces need be considered. Elastic force equations can then be written and need only involve a nine-atom assembly of one anion and eight

cations. The constraint is that the net forces summed at the cation site should vanish, as they do in the undistorted crystal. If the anions displacements are

$$\vec{u}^{A,B} = \vec{u}^{A,B} \exp[i(\vec{q} \cdot \vec{r} + \delta)], \quad (1)$$

then for  $\vec{q}$  along a cube direction, only three possible solutions exist. The allowed solution for  $UO_2$  is a transverse,  $\vec{q} = (2\pi/a, 0, 0)$ , zone boundary internal rearrangement mode. The second allowed solution for  $Zr(Ca)O_{2-x}$  is a longitudinal,  $\vec{q} = (0, 0, 2\pi/a)$  zone boundary internal rearrangement (the phase of the mode is  $\pi$  between anion sublattices). These results suggest the dominance of (100) displacements in the disordered state of  $Zr(Ca)O_{2-x}$  and indeed this is the case.<sup>5</sup> This model clearly shows that successful predictions require a consideration of only cation-anion interactions. Although the underlying driving forces for these internal distortions is quite different for  $UO_2$  or  $Zr(Ca)O_{2-x}$ , in each case, the internal rearrangement mode that occurs is dominated by a minimal cost in elastic energy.

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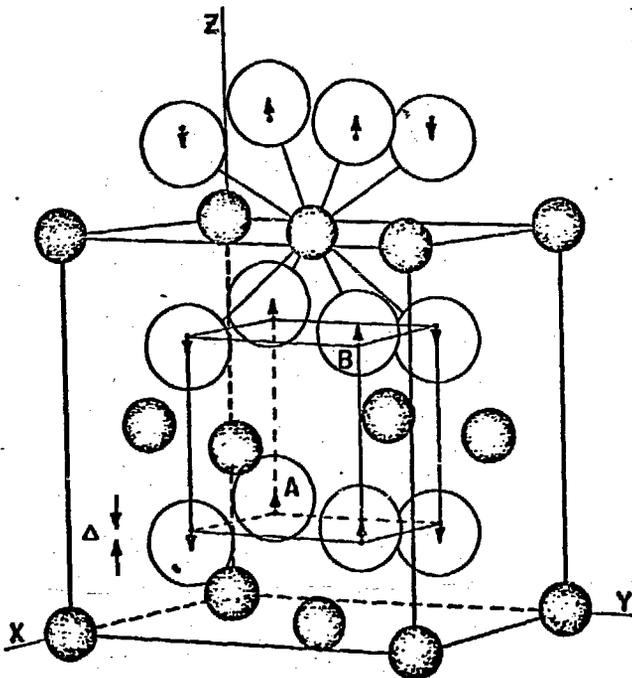


Fig. 2. The  $Zr(Ca)O_{2-x}$  fluorite unit cell.