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ELASTIC NEUTRON DIFFUSE SCATTERING IN  $Zr(Ca,Y)O_{2-x}$

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**RÉSUMÉ**

La diffusion diffuse élastique de neutrons a été mesurée dans  $Zr(Ca,Y)O_{2-x}$  à température ordinaire. La très forte intensité principalement par des déplacements d'oxygène le long de directions  $\langle 100 \rangle$  et de calcium suivant les directions  $\langle 111 \rangle$ . La faible contribution d'ordre à courte distance suggère fortement que les lacunes d'oxygène tendent à se placer en position de second plutôt que de premiers voisins autour des ions calcium.



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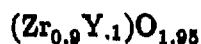
**ABSTRACT**

Elastic neutron diffuse scattering has been measured in cubic  $Zr(Ca,Y)O_{2-x}$  at room temperature. The very high diffuse scattering (up to 70 Laue) is explained mostly by the oxygen displacements along  $\langle 100 \rangle$  directions, and by Ca displacements along  $\langle 111 \rangle$ . The weak short-range order contribution strongly suggests that oxygen vacancies tend to place as second rather than at first neighbours of a Ca stabilizing ion.

## Elastic neutron diffuse scattering in $Zr(Ca, Y)O_{2-x}$

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Zirconia ( $ZrO_2$ ) can be stabilized in the fluorite structure by substituting about 10 % Ca or Y to Zr. Oxygen vacancies are needed to maintain charge neutrality, which explains the high ionic conductivity of these compounds. The fluorite structure with a disordered distribution of stabilizing cations and of vacancies is stable down to  $\simeq 1300$  K. The ordered structures (below  $\simeq 1300$  K) are not well known because of the low atomic mobilities. We have measured at room temperature the elastic diffuse scattering of neutrons in two "quenched" single crystals of yttria- and calcia-stabilized zirconia with the following chemical formulae :



The neutron experiments were performed on the two-axis G 4-4 spectrometer of Laboratoire Léon Brillouin (\*) with incident wavelength  $\lambda = 2.6$  Å, and time-of-flight analysis. The elastic diffuse scattering was measured in the {001} and {1 $\bar{1}$ 0} reciprocal planes for :

$$0.2 \text{ \AA}^{-1} \leq |q| = 4\pi \sin \theta / \lambda \leq 4 \text{ \AA}^{-1}$$

We observe a very high diffuse scattering (up to 70 Laue). Some of the peaks of the  $CaHf_4O_9$  superstructure (but not all of them) are present. The diffuse intensity, not periodic in the reciprocal space, is clearly dominated by the atomic displacements with a shortening of the  $\langle 200 \rangle$  oxygen-vacancy pairs of about 0.2 Å and of the zirconium-oxygen pairs.

The data were analysed by least-squares fit including second order atomic displacements.

Because chemical disorder affects the two sublattices (metal and metalloid), the formalism is somewhat more complex than in binary compounds. As shown by Morinaga et al. (1), three types of interatomic vectors can be defined (in units of  $a/4$  where  $a$  is the f.c.c. lattice parameter) :

type 1 :  $\ell+m+n = 4p$  (metal-metal and oxygen-oxygen)

type 2 :  $\ell+m+n = 4p + 2$  (oxygen-oxygen)

type 3 :  $\ell, m, n$  all odd (metal-oxygen).

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(\*) Laboratoire commun CEA-CNRS

The corresponding mean short-range order parameters are :

$$\bar{\alpha}_1 = 1/L \times (x_{Zr}x_{Ca}(b_{Zr} - b_{Ca})^2 \alpha^{ZrCa} + 2 x_O x_{\square} b_O^2 \alpha^{O\square})$$

$$\bar{\alpha}_2 = 1/L \times 2 x_O x_{\square} b_O^2 \alpha^{O\square}$$

$$\bar{\alpha}_3 = 1/L \times 4x_{Zr}x_O b_O(b_{Zr} - b_{Ca}) \alpha^{Zr\square}$$

$$(L = x_{Zr}x_{Ca} (b_{Zr} - b_{Ca})^2 + 2x_O x_{\square} b_O^2 = \text{Laue scattering})$$

where the  $b_i$  are the scattering lengths and  $x_i$  is the fraction of the component  $i$  on its sublattice.

The short-range order contribution is weak, but strongly suggests (in the case of calcium-stabilized zirconia) that the oxygen vacancies tend to place as second (at  $(1/4 \ 1/4 \ 3/4)$  a) rather than as first neighbours positions (at  $(1/4 \ 1/4 \ 1/4)$  a) around a stabilizing ion, as in the long range ordered structure  $\text{CaHf}_4\text{O}_9$ , but contrary to the results of previous X-ray diffuse scattering measurements (1).

On the other hand, an EXAFS study of yttria-stabilized zirconia (2) has shown that the mean first neighbours zirconium-oxygen distance was shorter than the mean yttrium-oxygen distance by about 0.17 Å. Although the displacements cannot be directly compared to ours, this is consistent with our result of oxygen vacancies being near the zirconium ions and the nearest oxygen atoms relaxing toward the vacancy.

(1) M. MORINAGA & J.B. COHEN *Acta Cryst.* (1980) A36, 520-530

(2) C.R.A. CATLOW, A.V. CHADWICK, G.N. GREAVES & L.M. MORONEY *J. Amer. Ceram. Soc.* (1986), 69 [3], 272-277