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REDETERMINATION OF THE CRYSTAL STRUCTURE OF α-$Bi_2O_3.3MoO_3$ BY NEUTRON DIFFRACTION AND THE CATALYTIC OXIDATION OF PROPENE

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ABSTRACT

The powder profile obtained by neutron diffraction was analysed by the Rietveld method. The catalytic oxidation of propene over α-$Bi_2O_3.3MoO_3$ is examined. The high activity is related to the fact that the principal cleavage plane contains together Bi and Mo ions. On the contrary γ-$Bi_2O_3.MoO_3$ is less active, probably because only small faces are active. The lone pairs disposition is not favorable to oxygen ionic conductivity ; this rather low conductivity may favour a rather high selectivity in acrolein.

Introduction

A precise location of O atoms in bismuth molybdates and other oxides is of major interest to catalytic research devoted to heterogeneous oxidation of alcenes. We have recently resolved the controversy about the structure of the γ- phase ($Bi_2O_3.MoO_3$) using neutron powder diffraction [THEOBALD, LAARIF & HEWAT, 1984], while the crystal structure of the α-phase, $Bi_2O_3,3MoO_3$ has been solved by VAN DEN ELZEN et al. (1973) by X-ray diffraction. In a recent paper TELLER, BRADZIL, GRASSELLI, THOMAS, CORLISS & HASTINGS [1984] suggested that neutron diffraction should also be used to determine the crystal structure of the α-phase in order to establish a reference for the $(Bi,Ce)_2(MoO_4)_3$ solid solution. The substitution of Ce, presumably for Bi and cation vacancy, was found by these authors to affect only the Mo(3) site, leaving

the coordinations of the remaining molybdenum and bismuth sites unchanged. It is a purpose of this paper to show that in the pure material, all three molybdenum sites are equivalent. The unexpected results for the Ce-doped material may then indeed be relevent to the catalytic activity of the material.

The second aim is to use well-established coordinates of the atoms, and especially of the oxygen atoms to locate lone pairs, relate these positions to ionic conductivity and catalytic properties.

A/ Neutron diffraction

1) Experimental

The sample of α-phase was prepared by the coprecipitation method. About 3 cm^3 was packed into a 15 mm diameter vanadium can. Data were collected at 300 K on the powder diffractometer D1A at the ILL Grenoble with a neutron wavelength of 1.909 Å from a vertically focusing germanium monochromator. The 2θ range 10 ° - 158 ° was scanned at steps of 0.05 °. The separate scans from ten counters were calibrated, then summed and the background measured using the POWDER program (HEWAT, 1979).

Structural refinements were made with a modified Rietveld program (HEWAT, 1973), each profile point being weighted according to the number of counters used to measure it (Fig. 1). Final nuclear R factor : 5.7.

2) Results

a = 7.7104(3) b = 11.5313(4) c = 11.9720(5) β = 115.276(3)
V = 962.52(5) $Å^3$.

Atomic coordinates are listed in table 1 and interatomic distances are listed in table 2 together with their mean values M(5), M(6) or M(8) for 5, 6 or 8 neighbours resp.

Coordinates found in that refinement are consistent with those of VAN DEN ELZEN & RIECK (1973). But in many instances they are different by more than two times the standard errors assigned to these quantities. The most striking feature is the pairing of Mo polyhedra that share a corner O(10) or an edge (O(8) and O(12)). In particular, the order of increasing bond lengths is almost the same in both calculations, despite the fact that differences are noted in these values.

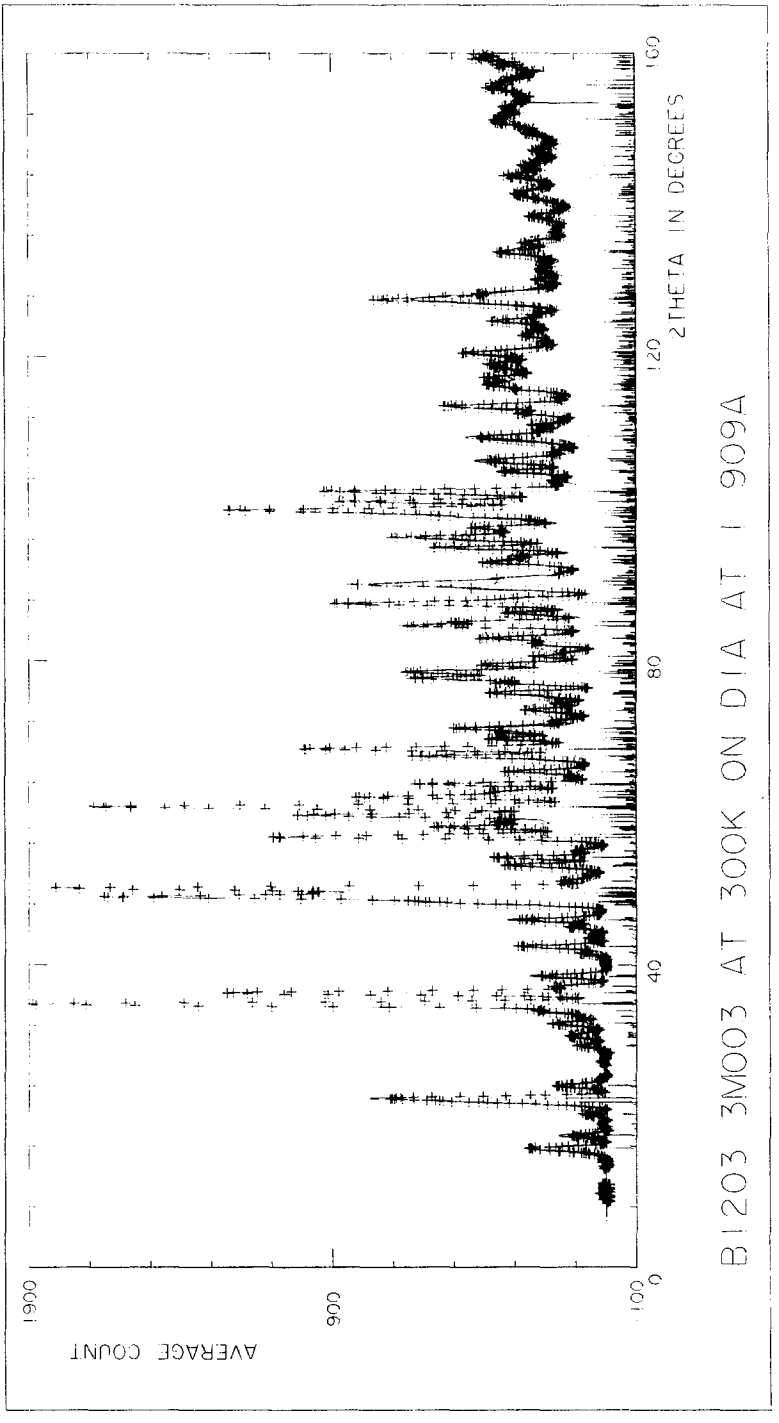

FIG. 1

Neutron diffraction profile recorded with λ = 1.909 Å

Table 1

Atomic coordinates

obtained from neutron powder diffraction

	x	y	z
Bi(1)	0.2552(7)	0.3612(4)	0.2607(4)
Bi(2)	0.9055(8)	0.1314(4)	0.0840(5)
Mo(1)	0.0254(9)	0.1122(5)	0.4150(5)
Mo(2)	0.4288(10)	0.1496(5)	0.1037(5)
Mo(3)	0.7325(9)	0.3685(6)	0.1943(5)
O(1)	0.5436(11)	0.0503(7)	0.2189(6)
O(2)	0.9362(12)	0.0527(8)	0.2556(7)
O(3)	0.2158(10)	0.1969(7)	0.1543(6)
O(4)	0.8525(13)	0.2074(6)	0.4126(8)
O(5)	0.2308(12)	0.2002(7)	0.4441(6)
O(6)	0.6068(12)	0.2003(8)	0.0588(7)
O(7)	0.9491(11)	0.2874(7)	0.1968(7)
O(8)	0.5052(10)	0.3166(7)	0.1974(7)
O(9)	0.2877(10)	0.4405(8)	0.4811(8)
O(10)	0.1294(13)	0.4492(6)	0.0783(8)
O(11)	0.8313(11)	0.4478(7)	0.3372(7)
O(12)	0.6827(11)	0.4690(7)	0.0873(8)

Table 2

Interatomic distances

		X-ray (Van den Elzen)	Neutron
Bi(1) -	O(10)	2.12	2.223(9)
	O(3)	2.22	2.232(9)
	O(7)	2.32	2.312(10)
	O(8)	2.34	2.411(11)
	O(1)	2.61	2.629(10)
	O(2)	2.64	2.619(11)
	O(9)	2.75	2.705(11)
	O(5)	2.94	2.946(10)
Mean	M(8)	2.49	2.509
Bi(2) -	O(2)	2.16	2.166(11)
	O(7)	2.24	2.190(10
	O(3)	2.32	2.301(10)
	O(6)	2.33	2.333(12)
	O(9)	2.61	2.587(10)
	O(4)	2.68	2.670(10)
	O(11)	2.78	2.805(10)
	O(11)	2.84	2.905(10)
Mean	M(8)	2.50	2.494
Mo(1) -	O(4)	1.69	1.720(12)
	O(5)	1.72	1.787(11)
	O(2)	1.85	1.863(10)
	O(10)	1.91	1.903(10)
	O(10)	2.25	2.248(10)
	O(12)	2.69	2.803(11)
Mean	M(6)	2.02	2.054
Mean	M(5)	1.884	1.904
Mo(2) -	O(1)	1.72	1.720(9)
	O(9)	1.74	1.748(10)
	O(6)	1.86	1.775(13)
	O(3)	1.89	2.054(12)
	O(8)	2.13	2.182(10)
	O(12)	2.62	2.550(9)
Mean	M(6)	1.993	2.005
Mean	M(5)	1.868	1.896
Mo(3) -	O(12)	1.69	1.648(11)
	O(11)	1.78	1.799(10)
	O(8)	1.85	1.869(12)
	O(7)	1.87	1.905(12)
	O(6)	2.30	2.450(11)
Mean	M(5)	1.90	1.934

3) Mo coordination

A convenient and concise way of comparing coordination around atoms is to calculate the so-called "bond strengths" s and their sum, the valence charge S. The calculations may be performed by different methods, according to BROWN & WU (1976) or ZACHARIASEN & PENNEMAN (1980). Results are very similar : differences found in the present example are smaller than errors, which are considerable (about .1). Nevertheless the BROWN & WU formulation offers more possibilities since a more complete list of constants is available.

S values are given in table 3 and compared with those of the Ce-doped compound studied by TELLER et al.

The first point to note is that for our neutron work, the valence charges S for the three different Mo atoms are more nearly equal than for the X-ray work, all lying within the small interval 5.58 ± 0.15 electrons. This confirms the tentative conclusion of TELLER et al. that for the pure material, the different Mo co-ordinations are all equivalent.

Secondly, our work emphasis the low value found for Mo(3) by TELLER et al. for the Ce-doped material. Apparently, only the Mo(3) site is affected by Ce substitution, with the Bi sites and the Mo(1) and Mo(2) sites unchanged.

Since catalytical properties change from α to the Ce-doped material, these changes are not due to changes in Bi-coordination but to changes in Mo-coordination. This agrees with GRASSELI's and BURRINGTON's (1981) interpretation that Mo coordination is responsible for the selectivity of the compound.

B/ Some structural features of interest to catalysis

1) Catalytic properties

The α-phase is a well-known catalyst for heterogeneous oxidation and the propene oxidation has been chosen as a test reaction. From the literature it appears that the α-phase is more active and more selective for acrolein formation than the γ-koechlinite phase. In our experiments typical conditions were : T = 660 K ; O_2 : C_3H_6 : N_2 = 200 : 100 : 460 torrs ; gas flow 1 cm^3 s^{-1}. Average activities of the α and γ phases were resp. 37 × 10^{-8} and 8 × 10^{-8} mol s^{-1} m^{-2}. Selectivities in acrolein were resp. 88 % and 66 % [CARSON, COUDURIER, FORISSIER, VEDRINE, LAARIF & THEOBALD, 1983].

Table 3

Sums of bond orders (valence charges) S for α-$Bi_2Mo_3O_{12}$ and Ce-doped α-phase

The first line gives the Zachariasen et al (1980) value, and the second line the Brown and Wu result.

	α - phase		Ce-doped α-phase	
	Van den Elzen X-rays	This paper neutron	Our calculations using Teller's data	Teller's calculations
Mo(1) 5 neighbours	**5.99** 6.00	**5.43** 5.48	**5.66** 5.68	5.6
Mo(2) 5 neighbours	**5.84** 6.08	**5.70** 5.72	**6.39** 6.30	6.1
Mo(3) 5 neighbours	**5.63** 5.66	**5.70** 5.70	**5.07** 5.11	4.9
Bi(1) 8 neighbours	**3.22**	**3.00**	**3.09**	
Bi(2) 8 neighbours	**3.13**	**3.20**	**3.12**	

2) Cleavage plane in α-$Bi_2(MoO_4)_3$

Crystals have a platelet shape. From X-ray diffraction on single crystals the preferred cleavage plane was found to be (010) ($\beta \neq 90^{\circ}$).

An examination of the cell content at different levels along y shows that whatever the level of the cleavage plane, the composition is the same, i.e. there are 3Mo, 2Bi and 1 vacancy with regard to the fluorite structure for example.

Many authors agree that both Bi and Mo sites are necessary to the selective oxidation mechanism [GRASSELLI, R.K. & BURRINGTON, J.D. (1981). GRZYBOWSKA, B., HABER, J. & JANAS, J. (1977)]. So the orientation of the cleavage plane in the α-phase is favourable to the catalytic process.

3) Comparison with another catalyst : role of the cleavage plane in koechlinite

Koechlinite, the γ-phase, is a convenient reference material for catalytic properties, since its structure is easy to understand. In a precedent paper [THEOBALD, LAARIF, FORISSIER], we have shown that most probably the catalytic process appears on the small lateral faces of the crystal (faces perpendicular to (010) (b = 15.5 Å). These lateral faces contain simultaneously Bi and Mo ions since they intersect Bi_2O_2 layers and MoO_4 layers. X-ray photoelectron spectroscopy experiments (XPS) performed on the γ-phase show that the Bi : Mo ratio obtained by this analytical method is enhanced compared to the bulk composition [CARSON et al., 1983]. Since the cleavage plane is parallel to (010) we assume that the top layer in γ crystals is a Bi_2O_2 layer. The orientation of the cleavage plane is not favourable to the catalytic process, since it is the smallest part of the outer area which is active.

So a simple comparison of the structure of the surface of the two compounds explains the fact that the activity of α is at least 4 times higher than that of γ (same specific areas).

4) Lone pairs disposition and ionic conductivity

In a recent paper we have shown that the disposition of the $6s^2$ lone pair in Bi^{3+} compounds could be related to the oxygen ionic conductivity. For example, among four Bi_2O_3 oxides the variety which offers the largest gaps in the structure around E pairs and the shortest E-E distances is the best O conductor [LAARIF, A. & THEOBALD, F., 1985]. Symmetry has an influence and a bi-dimensional net of short E-E distances like in γ-koechlinite gives a higher conductivity than a 1-dimensional arrangement like in Sb_2MoO_6 [THEOBALD, LAARIF & FORISSIER, 1985].

Following the same theoretical method we tried to investigate the O ionic conductivity in the α-phase. E pairs have been located around Bi atoms approximately in positions symmetrical to the centers of gravity of the four closest O neighbours. Coordinated obtained in that way are E(1) : 0.311, 0.410, 0.365 ; E(2) : 0.884, 0.078, 0.002. Shortest E-E distances are listed in table 4 and represented in figure 2. From this figure it appears that lone pairs are almost parallel to the cleavage plane and that the sequence of shortest lone pairs follows an average direction parallel to [100] : it is parallel to the cleavage plane ; the longest distance in that sequence is rather high : about 3.97 Å compared to Sb_2MoO_6 for example. Furthermore this arrangement is one-dimensional. For these two reasons and according to our previous observations on Bi_2O_3, Pb oxides, koechlinite, Sb_2MoO_6, etc, O ionic conductivity should be smaller in the α-phase than in the γ-phase.

Measurements of conductivities for Bi-molybdates have been published recently by BOON & METSELAAR (1984). Up to 770 K conductivity $\sigma(\alpha)$ is lower than $\sigma(\gamma)$ by two orders of magnitude, which agrees with our "geometrical" theory.

Table 4

Shortest lone pairs distances in the α-phase

$E(2) - E(2^{i})$	2.56 Å
$E(1) - E(2^{ii})$	3.26 Å
$E(1) - E(1^{i})$	3.91 Å
$E(1) - E(2^{iii})$	4.01 Å

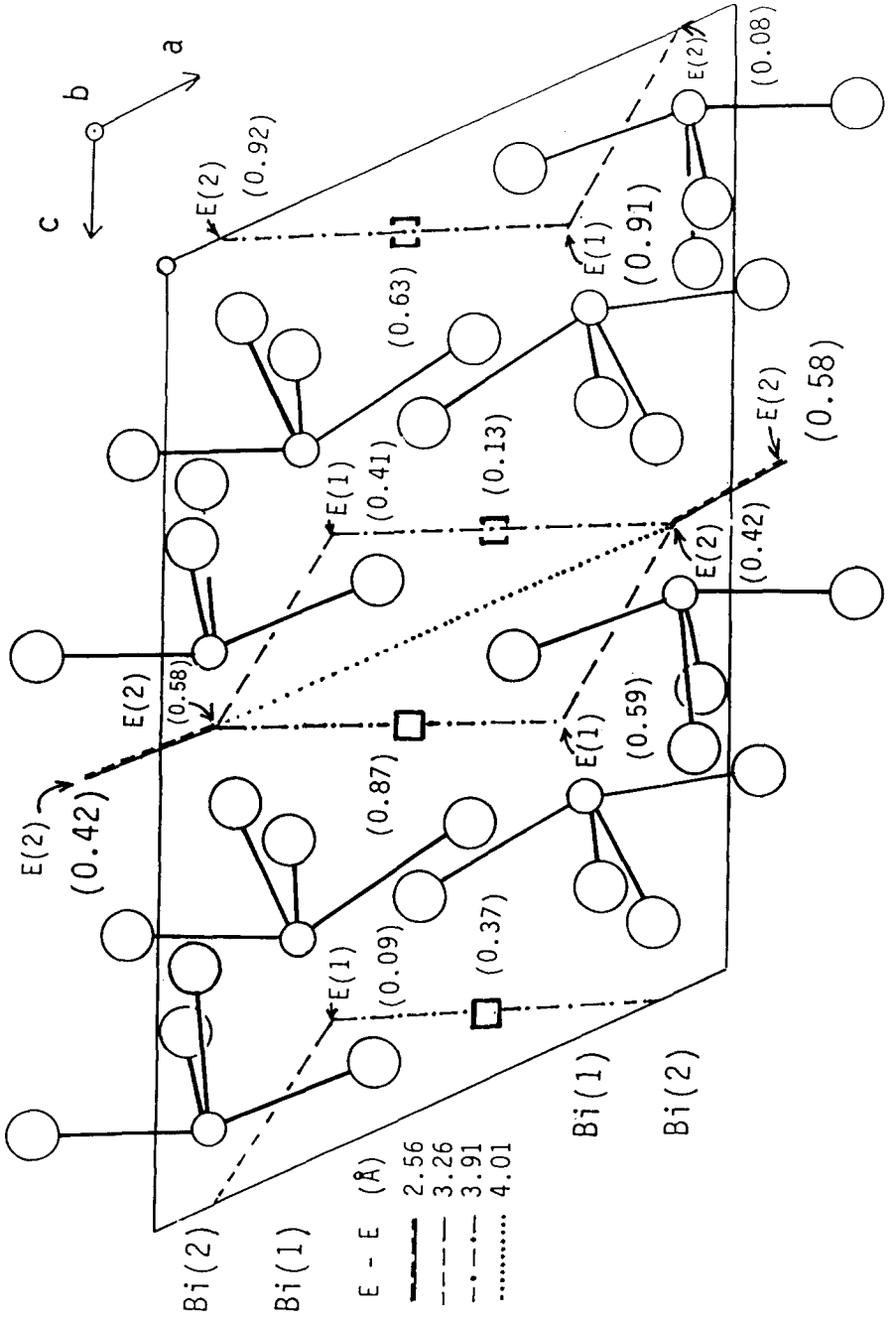

FIG. 2

Disposition of lone-pairs

C/ Discussion and assumptions on the relationship between bulk and surface structures and the calalytic properties of the α-bismuth molybdate

1) Importance of cleavage planes and the faces

In paragraph B2 and B3 we have shown that the orientation of the natural cleavage plane in an oxide containing Bi^{3+} might be sufficient to explain the difference of activity of several oxides towards the oxidation or propene in acrolein. Considering that Bi and Mo sites are necessary for that process it is obvious from a structural point of view that this condition can be offered only by small faces in the γ-koechlinite, whereas it is offered by the main face in α-bismuth molybdate. Here the case is favourable to our comparison since both compounds have the proper coordination for a high selectivity in acrolein according to BURRINGTON & GRASSELLI (1981) as demonstrated by neutron diffraction and bond orders calculations.

The importance of relative areas of faces of crystals in a powdered catalyst has been demonstrated in other cases like the propene oxidation over MoO_3 [VOLTA, FORISSIER, THEOBALD & TO PHONG PHAM, 1981]. Therefore it is wished that crystallographers always record Miller indices for major faces in crystals whenever possible, for the sake of surface structure examination.

2) Influence of ionic conductivity

In paragraph B4 it has been shown that the lone pairs disposition could explain why O-ionic conduction is smaller in α than in the γ-phase. Now we would like to suggest a relation between O-ionic conductivity and the selectivity in acrolein.

In a recent paper we compared the catalytic properties of Sb_2MoO_6 and Bi_2MoO_6 [THEOBALD, LAARIF & FORISSIER, 1985]. The main results are the following : Sb_2MoO_6 is 2 times less active for the formation of acrolein and 20 times less active for the CO_2 formation. As a consequence the selectivity in acrolein is higher despite the fact that the activity is much smaller.

In the α-phase the conductivity is smaller and the selectivity is higher. In bismuth oxides opposite properties are observed : they are good conductors and have a very low selectivity in acrolein. It seems as if conductivity was not necessarily a profitable property of an oxidation catalyst despite it is certainly useful for total oxidation.

3) Molybdenum coordinance and luminescence spectra

In a recent paper BLASSE and BOON (1985) recorded the luminescence spectra of the α-phase which is more complicated than the other bismuth molybdates. They proposed that non-stoichiometry or impurities (for example adjunctions of koechlinite) could explain these observations. But in our experiment no trace of koechlinite was noticed in α. The present neutron diffraction study may provide a simpler explanation : simply that the coordination of Mo(3) is different from the two others and responsible for the additional lines.

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