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SYMMETRY IN DIET PHASE TRANSITIONS

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Analysis of the route of the phase transitions in transition metal oxides driven by DIET of oxygen from the surfaces observed by high resolution electron microscopy indicates that there is a symmetry selection rule. The phase transitions are to a structure with a higher point group symmetry where the new phase with a lower oxygen content is either one with a supergroup symmetry with respect to the original phase, or is an amorphous intermediary. The final phase has the highest symmetry and is also a metallic conductor. If a possible lower oxygen content phase does not have the correct supergroup symmetry, it is not formed. It is also found that the point group is conserved during the phase transition if the oxide belongs to the highest groups O_h or D_{6h}. This symmetry selection rule can therefore be used to predict the route of the phase transition. The symmetry rule operates when the phase transition is diffusional.

1. Introduction

For many years there has been substantial interest in desorption induced by electronic transitions or DIET, particularly from transition metal oxides, see e.g. refs. [1,2]. Almost independent of whether the radiation driving the desorption is electrons, ions or photons, the general model is that oxygen ions or neutrals, and in some cases metal ions or neutrals leave the surface. The prevailing mechanism is believed to be an electronic excitation which becomes coupled to atomic motion imparting 10 to 20 eV of kinetic energy to an atom which is sufficient to eject it from the near surface region. Clearly, if oxygen is being lost from a transition metal oxide at some stage, the initial phase has to become unstable and there must be a phase transition to a lower oxide. Understanding the character of this phase transition is therefore crucial to understanding material behavior in an ionizing radiation field, for instance structural and optical materials in the space environment or during electron beam writing processing.

Knowledge of the secondary phases so produced is not readily available in conventional surface science experiments. Even if one starts with a single crystal, the secondary phases will nucleate at many different sites and the end product will be polycrystalline and therefore cannot be readily characterized

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by techniques such as LEED. In the last few years high resolution electron microscopy has been applied to study the structural transitions during DIET, and can readily resolve the phase transition routes, see e.g. refs. [3,4]. In this paper we collate the results from a number of different transition metal oxides, showing that there is a simple symmetry selection rule which can be used to predict the phase transition route. In all cases, the secondary phases belong to a higher symmetry point group which is a supergroup of the original phase, or the phase transition goes via an amorphous intermediary. Lower oxygen phases which are not supergroups are not produced. The stable end product which is resistant to further damage has the highest symmetry.

The structure of this paper is as follows. In the next section, we briefly review the symmetry criteria during phase transitions which have been established over the years. We then summarize data on lower oxygen phases produced during electron stimulated desorption experiments in an electron microscope; details of the latter can be found elsewhere and are referenced in the text.

2. Symmetry relationships during phase transitions

There is an extensive body of work on phase transitions, primarily in metal systems and the theoretical symmetry considerations have been discussed by many authors, see e.g. refs. [5,6]. As discussed by Tendeloo and Amelincks [5], phase transition from the high temperature phase to the low temperature structure results in a group–subgroup relation of G_1 and G_2, where G_1 and G_2 represent the space groups of the high and low temperature phases respectively. A classic example is the ordering transformation in Cu_3Au where the space group changes from Fm3m to its subgroup Pm3m; the atoms occupy the positions of an fcc structure randomly at high temperature and order at low temperatures [7]. Another typical example is $BaTiO_3$ where the low temperature rhombohedral structure is derived from the high temperature perovskite through a small displacement of the titanium atoms [8]. These are called "displacive transformations" and the character of the transformation is through rearrangement and displacement of atoms, but the atomic site space does not change during transition (i.e. the number of total atom sites is constant and the change in dimensions is negligible). In this work we turn to an another type of phase transformation driven by DIET, "diffusional transformations" because the mechanism in this case involves diffusion of atoms from A to the A/B interface and growth of the new B phase. Examples of this type of phase transition are in TiO_2 [4,9], MoO_3 [10], WO_3 [3,11,12], V_2O_5 [13,14], Ta_2O_5 [15] and NiO [4,16,17]. In a diffusional phase transformation, the atom site space changes due to mass loss. The data indicates that the secondary phases have higher symmetry, similar to what one would expect at high temperatures even though the temperature of the irradiated specimen is much lower than the melting point. Displacive phase transformations are generally thought to occur via soft phonons, and move through the solid at close to the speed of sound which is, as a rule, far faster than the speed of a diffusional phase transition.

3. Phase transitions during DIET

In order to categorize the phase transitions, it is necessary to know the point group of both the initial and secondary phases as oxygen or metal is lost from the material. The basic approach for all the experimental data that we will include here is to examine clean surfaces at 300 kV in an electron microscope, using diffraction pattern data and high resolution imaging to identify the secondary phases. At 300 kV there is the possibility that oxygen can escape from the material via ballistic knock-on damage. We have therefore repeated all the experiments at 100 kV where ballistic damage will be very slow or nonexistent, but DIET processes should proceed at a slightly faster rate; ballistic processes show a threshold which is generally above 100 kV for oxygen and then will be much faster at 300 kV whereas the rate for DIET processes goes roughly as one over the electron energy if the energy is far larger than the threshold (which is in the range of 10 to 100 eV). We have only included data where this experimental procedure has demonstrated that DIET is the key process, for instance we have not included MoO_2 which damages at 300 kV but not at 100 kV [10]. In addition, we have also repeated the experiments for most of the systems in UHV at 1.5×10^{-10} Torr, and where appropriate we will briefly mention cases where the surface modifications are in fact a consequence of contamination, although this is not the major emphasis of this work.

Table 1 shows a collation of the phase transformation data showing both the initial phase, any transitional phases and the end product. The compounds listed as type 1 all show both intermediaries and end products which have higher symmetry. The symmetry relation is that the space groups of the derived structures are supergroups of the initial oxides. Therefore their point groups also have group–supergroup relationships. For instance, in the rutile form of TiO_2 the DIET process ends in γ-TiO which has Fm3m (O_h) symmetry, rather than the low symmetry α-TiO phase which has A2/m (C_{2h}) symmetry. Similarly, in V_2O_5 the end product is VO which has Fm3m (O_h) symmetry, and there is no further reduction to $VO_{0.532}$ which has the lower symmetry I4/mmm (D_4h). It appears that the DIET phase transition ends in the phase with the highest symmetry.

Table 2 shows results listed as type 2, where the initial phase belongs to one of the highest point groups. In NiO which has O_h symmetry the resulted

Table 1
Collation of materials showing the intermediaries and final phases observed by electron microscopy and the stoichiometry and point group symmetry

Initial phase	Intermediaries		Final phase	Ref.
CuO	Cu_4O_3;	Cu_2O	Cu	[18]
(C2/c, C_{2h})	($I4_1$/amd, D_{4h});	(Pn3m, O_h)	(Fm3m, O_h)	
MoO_3	Amorphous		Mo	[10]
(Pbnm, D_{2h})			(Im3m, O_h)	
L-Ta_2O_5	Amorphous		TaO_2	[15]
(C2mm, C_{2v})			($I4_1$/amd, D_{4h})	
L-Ta_2O_5	Amorphous		Ta	[15]
(C2mm, C_{2v})			($P4_2$/mnm, D_{4h})	
H-Ta_2O_5	TaO_2		Ta	[15]
(C2, C_2)	($I4_1$/amd, D_{4h})		(Im3m, O_h)	
TiO_2			TiO	[4,9]
($P4_2$/mnm, D_{4h})			(Fm3m, O_h)	
WO_3			W	[3,4,11,12]
($P2_1$/a, C_{2h})			(Im3m, O_h)	
V_2O_5	V_4O_9 a)	V_6O_{13} a)	VO	[13,14]
(Pmmn, D_{2h})			(Fm3m, O_h)	

a) The point and space groups of V_4O_9 and V_6O_{13} are not well established.

structure is a spinel Ni_3O_4 which has same point group but its space group is a supergroup of NiO, while the initial phase of ZnO of D_{6h}, which in the microscope can transform to ZnO_2 [19]. Whereas at first sight both of these systems appear to have a different symmetry selection rule, in fact the reason for this is that the phase transitions in both cases are not due to DIET. Careful study of NiO in UHV indicates that the spinel phase only occurs in contaminated specimens and does not occur in UHV [17]; the data indicates that nickel is lost from the surface possibly as the carbonyl $Ni(CO)_4$, although the exact form of the gaseous nickel species has not been determined. Similarly, the transformation from ZnO to ZnO_2 is found to only occur in the presence

Table 2
Collation of type 2 materials showing the intermediary and final phases and the point group symmetry (note that in these materials only electron beam induced reactions occur, not DIET)

Initial phase	Final phase	Ref.
CoO	Co_3O_4	[17]
(Fm3m, O_h)	(Fd3m, O_h)	
NiO	Ni_3O_4	[4,16,17]
(Fm3m, O_h)	(Fd3m, O_h)	
	Ni	
	(Fm3m, O_h)	
ZnO	ZnO_2	[19]
($P6_3$/mmc, D_{6h})	(Pa3, T_h)	

Table 3
Oxides [a] with different oxygen contents which could or could not be produced showing their point group symmetries

Initial phase	Secondary phases		
	Possible	Impossible	
CoO	Co_3O_4		
(Fm3m, O_h)	(Fd3m, O_h)		
CuO	Cu_2O		
($C2/c$, C_{2h})	(Pn3m, O_h)		
NiO	Ni_3O_4 [b]	$Ni_{15}O_{16}$	($I4_1/amd$, D_{4h})
(Fm3m, O_h)	(Fd3m, O_h)		
MoO_3		MoO_2	($P2_1/c$, C_{2h})
(Pbnm, D_{2h})		$MoO_{2.8}$	($P2_12_12$, D_2)
		Mo_4O_{11}	($P2_1/a$, C_{2h})
		Mo_9O_{26}	(P1, C_i)
		Mo_8O_{23}	($P2/a$, C_{2h})
TiO_2	TiO	Ti_2O_3	($R\bar{3}c$, D_{3d})
(P_{42}/mnm, D_{4h})	(Fm3m, O_h)	Ti_3O_5	($C2/m$, C_{2h})
		Ti_5O_9	(P1, C_1)
		Ti_2O	($P\bar{3}m1$, D_{3d})
		Ti_3O	($P\bar{3}1c$, D_{3d})
		Ti_6O	(P31c, C_{3v})
V_2O_5	VO	VO_2	($P2_1/a$, C_{2h})
(Pmmn, D_{2h})	(Fm3m, O_h)	V_2O_3	($R\bar{3}c$, D_{3d})
	$V_2O_{0.532}$	$V_{12}O_{26}$	($C2/m$, C_{2h})
	($I4/mmm$, D_{4h})		
WO_3		WO_2	($P2_1/c$, C_{2h})
($P2_1/a$, C_{2h})		$W_{18}O_{49}$	($P2/m$, C_{2h})
		$W_{20}O_{58}$	($P2/m$, C_{2h})
		$WO_{2.96}$	($P2/c$, C_{2h})
		$WO_{2.98}$	($P2_1/c$, C_{2h})
ZnO		ZnO_2	(Pa3, T_h) [c]
($P6_3/mmc$, D_{6h})			

[a] The oxides listed here have been reported unambiguously by X-ray or neutron diffraction.

[b] The spinel structure reported earlier in γ-$Ni_{28}O_{32}$ by electron diffraction has been identified as Ni_3O_4 by HREM [4].

[c] The ZnO–ZnO_2 transition is associated with carbon [19].

of carbon [19]. To summarize, type 2 compounds show transformations driven by radiation induced reactions, but no DIET consistent with the type 1 results.

For reference, table 3 shows the possible oxides which appear in the phase diagram for the different oxides which could be produced by thermal reduction. Two points are important about the results. First, in most of the systems many more oxides appear in the phase diagrams than are found experimentally. Second, all the intermediary and final phases have a specific symmetry with respect to the initial phase, or are amorphous. In particular, they are supergroups of the original material for the type 1 oxides. As an example, for MoO_3 which has D_{2h} ($\neq O_h$ and D_{6h}) symmetry, thermal reduction would lead to coherent shear plane phases such as Mo_4O_{11}, or MoO_2. The point group symmetry of the shear phases is C_{2h} that of MoO_2 is C_{2h}. None of these are supergroups of MoO_3 and therefore do not occur. What does occur is amorphous Mo_2O_3 and then metallic Mo. The same rule can be applied to all the other systems.

We can summarize the above results in terms of a selection rule for the DIET phase transformation. If G and P represent the space group and point group respectively, with the initial phase A and an end product B, then during DIET:

(1) $P_b \supset P_A$ and also $G_B \supset G_A$, if $P_A \neq O_h$ and D_{6h},

(2) $P_b = P_A$ and possibly $G_B \subset G_A$, if $P_A = O_h$ or D_{6h},

where the symbols $\supset$ and $\subset$ are standard set notation indicating a supergroup–group (or group–subgroup) relationship. In addition to these two rules, a third rule comes in to play when amorphous intermediaries occur. In this case:

(3) If there exists no intermediary phase with a lower oxygen content which has the correct supergroup–group relationship, then an amorphous intermediary may be produced.

We interpret the third rule in the following way. During oxygen loss from the material, point defects are produced, particularly oxygen vacancies. Diffusion of these vacancies or other point defects can nucleate a secondary phase only if it has the appropriate symmetry. If there is no available secondary phase, at some stage the energy locked into the point defects will become sufficiently large that it becomes favorable for the structure to collapse to amorphous. It should be noted that this argument is intrinsically the same as the arguments used to explain radiation induced amorphization in many intermetallics, see e.g. ref. [20].

4. Discussion

We have shown here that a relatively simple symmetry selection rule can be applied to DIET driven phase transitions. In many respects, the data is analogous to inverse oxidation of metals; oxidation of metals is via diffusional phase transformations from a higher to a lower symmetry structure and if you invert the process the DIET route can be rationalized. Another way of looking at the process is that when A transforms to B the structure would like to change as little as possible. For instance, for MoO_3 to go to MoO_2 would require extensive rearrangements of both the metal and oxygen atoms and this is impossible at least at room temperature. (It is well established that in the electron microscope the specimens are within 20 to 100 K of the ambient temperature.) The material cannot readjust the atom positions, so at some stage collapses to amorphous Mo_2O_3, similar to ballistic knock-on-induced amorphization in some metals [20].

In all of the systems, the end product is a metallic conductor, and one can argue that in a metallic conductor excitations are delocalised so no DIET occur. These metallic conductors are either simple metals, or oxides with the highest symmetry. It is of interest that instead of invoking metallic behavior as quenching DIET, there is a second possible interpretation. If we describe an oxide structure as an interpenetrating lattice of metal and oxygen atoms, the oxygen lattice tends to have a higher symmetry frame. The forces favoring equal bond lengths and rearrangement of octahedra in order to retain full metal atom coordination will play an important role when the oxygen content changes; it is well established that most oxides can be represented by packing metal–oxygen octahedra, and lower oxides by different octahedral packings with some edge or face sharing. When the rocksalt structure is formed, e.g. in TiO_2 and V_2O_5, both cation and anion form interpenetrating fcc arrays and each is situated at the center of the octahedral holes of the other array, and all the bonds are equal. If the cations do not form an fcc array, i.e. there is no stable MO (M: metal) compound in that system, DIET goes to the pure metal as in MO_3 and WO_3. When the material starts with the highest symmetry, for instance ZnO and NiO there is no DIET. One could interpret all this data as indicating that DIET stops at the structure with the highest symmetry, not with a metallic end product. This is a hypothesis which needs to be tested further.

One question of some relevance is the diffusional process occurring; at room temperature in almost all of these oxides the thermal diffusion rate is negligibly small. It should be noted that the same processes that occur at the surface and lead to DIET also occur in the bulk and are called radiolysis or ionization damage [21]. Indeed one can consider use of the more general term “Displacement Induced by Electronic Transitions” although, unfortunately, this might lead to confusion. In the bulk each event will displace an atom by perhaps 1 nm, for a perfect stoichiometric oxide producing defects but in an already defective oxide it may simply displace pre-existing defects. Each event can therefore be considered as a defect random walk, and summed over a large number of events this is equivalent to considering a diffusion component with a diffusion constant proportional to the incident beam flux, i.e. electron beam induced diffusion. Since as mentioned above thermal diffusion is negligible, we are fairly certain that this is the key diffusion acting in experiments performed at room temperature; experimental evidence supporting this conclusion will be presented elsewhere [11,13]. The phase transition routes at higher or very low temperatures may well be different – this is an area for future research.

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