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# Coherent Interfaces: Efficient Boundary Conditions in Solid State Reactivity. Study in $V_2O_5$–$AlNbO_4$, $V_2O_5$–$GaNbO_4$, and $V_2O_5$–$TiNb_2O_7$ Systems

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The thermodynamically unexpected reduction of $V_2O_5$ in the presence of the mixed oxides $AlNbO_4$, $GaNbO_4$, and $TiNb_2O_7$ under nitrogen at 630°C is reported and gives a supplementary example of the kind of interfacial reaction observed in the $V_2O_5$–$TiO_2$ system. It is shown that this phenomenon comes from the establishment of coherent interfaces between the cleavage planes of two crystals belonging to the same crystallo-chemical family. The reduction enables the system to diminish the elastic stress created by the slight interfacial misfit. A thermodynamic and kinetic explanation, based on structural factors, is given.

## Introduction

Structural microscopic study of transition metal oxides in solid state, especially of groups IVA, VA, and VIA, has led in the last two decades to the discovery of a great number of close, stoichiometrically related phases, such as vanadium oxides of general formula $V_{2n}O_{5n-2}$ (*1*) or $V_nO_{2n-1}$ (*2*), titanium oxides $Ti_nO_{2n-1}$ (*3*), or niobium oxides $Nb_{3n+1}O_{8n-2}$ (*4*) and mixed oxides (Ti, Nb), (W, Nb), (Ga, Nb) (*5–7*).

These different compositions are often observed in one crystal within microdomains of different structures, the nature and distribution of which are clearly dependent on sample history (*8–10*). Such observations have reemphasized the problem of nonstoichiometry with better experimental evidence (*11, 12*) and also led to a reconsideration of any question dealing with the reactivity of these crystals (*13, 14*). Indeed, whether these oxides are the scope of point or extended defects (the relative importance of the two types varying with the degree of evolution of the studied reaction), the reaction always is a function, first, of the faculty for chemical species to diffuse, and second of the facility of nucleation for a new phase within the mother matrix, which is a more macroscopic manner of considering the same phenomenon whenever the reaction is not entirely destructive, that is, provided the growth is sufficiently *coherent.*

The physical importance of this phenomenon was pointed out on other systems by Ubbelohde (*15*) and enabled him to explain qualitatively hysteresis and the singularities of some properties of crystals at second-order phase transitions. This was also similarly considered by Hyde and Bursill (*16*) in the study of the chemical reduction of such oxides under vacuum by electron microscopy since, consecutive to the appearance of a preliminary disorder, they observed the creation of microdomains and interfaces in the crystal making improper the use of thermodynamic laws of equilibrium. A

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more quantitative approach was given by Anderson (*17*) describing the progress of the reaction with composition and structure fluctuations. This allows nonequilibrium thermodynamics. Thus we are facing the competition of problems of long- and short-range order establishment, which is local and individual, and of problems of stability and growth of a new phase, of a cooperative but discontinuous type, for it generates numerous interphase boundaries in each grain.

Unfortunately for a better understanding of these phenomena, the nature of the relationship between two phases at the interface is not well known and studying it *in situ* proves to be difficult, given the number of unchecked boundaries. We shall therefore describe here a series of experimental facts artificially reducing to one the number of active interphases, from which we shall see how they determine at the same time the thermodynamic and kinetic properties of the new constituted system with respect to the properties of isolated phases.

Contrary to the above-mentioned authors who generally studied these phases by electron microscopy under vacuum, we try to observe directly the reactivity of many phases belonging to the same crystallochemical family.

## Choice of Initial Material

We have therefore chosen to work on the $V_2O_5$–$AlNbO_4$, $V_2O_5$–$GaNbO_4$, and $V_2O_5$–$TiNb_2O_7$ systems. Indeed, these four oxides belong to the same above-mentioned families (*18, 19, 5*) widely studied by Wadsley and co-workers from a structural point of view. Classified as block-structures, or $ReO_3$ type, all of them follow the same octahedral-based building pattern: columns, infinite along **b** direction, of vertices-sharing octahedra are joined by edge-sharing, thus creating tetrahedral sites that may or may not be occupied (Fig. 1).

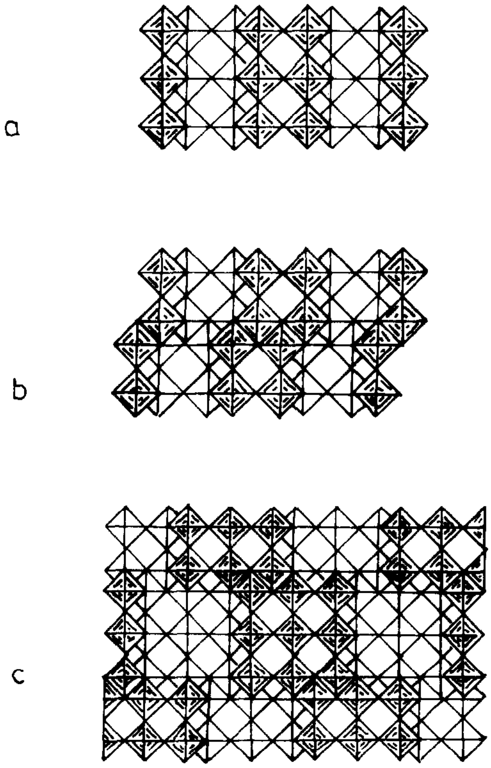

FIG. 1. Idealized $ReO_3$ block structure: (a) $V_2O_5$: dimension $2\times\infty$; (b) $AlNbO_4$ isostructural with $GaNbO_4$ and $VO_2$ (B): dimension: $(2\times2)_\infty$; (c) $TiNb_2O_7$: dimension $(3\times3)_\infty$;

Bonds in these structures are essentially of a covalent type (*20*). One could therefore suppose these matrices able to show privileged relationships when brought into contact.

On the other hand, we know, from the results obtained in our laboratory (*21a*) and by Van den Bussche and Jouy (*21b*) on the system $V_2O_5$–$TiO_2$ (anatase) that this one in the solid state reacts thermodynamically and kinetically quite differently than the two separate oxides, which has seemed a unique fact so far. The similarity of structure between anatase and block-structures caused us to believe that this result was a more general one, and we endeavoured to show this.

## Experimental

### 1. *Products and Samples*

$V_2O_5$ was supplied by Rhône Poulenc Industries.

$AlNbO_4$ and $GaNbO_4$ were obtained by solid state reaction from $\alpha$-$Al_2O_3$, $Ga_2O_3$, and $Nb_2O_5$ at 1150°C during 48 hr in air.

$TiNb_2O_7$ from $TiO_2$ and $Nb_2O_5$ at 1350°C during 24 hr in air.

$\alpha$-$Al_2O_3$, $Ga_2O_3$, and $Nb_2O_5$ (99.99% Alfa pure oxides).

Samples (a), (b), and (c) were ground in the following proportions: (a) (13%) $V_2O_5 + AlNbO_4$; (b) (13%) $V_2O_5 + GaNbO_4$; (c) (20%) $V_2O_5 + TiNb_2O_7$.

### 2. *Microgravimetric Analysis*

Thermal behavior under nitrogen ("Air Liquide," U-grade, $p_{O_2} = 10^{-5}$ atm) then under oxygen ("Air Liquide," N45 grade) of the so-called samples was studied with a SETARAM M.T.B. 10-8 microbalance, at isotherm 630°C, rate flow: 1 liter/hr (atmospheric temperature and pressure), sample mass nearly 150 mg. Precision of the balance in these conditions: $5.10^{-5}$ g. Among the four oxides used, $V_2O_5$ has the lowest melting point ($t_f = 690$°C). However, we experimentally checked that the solid state was preserved.

### 3. *X-Ray Diffraction*

Diffraction photographs of the products were obtained with a CGR 2080 generator on a Seeman-Bohlin chamber (radiation Cu$K\alpha 1$).

### 4. *Electron Microscopy*

Microscopic aspect of $AlNbO_4$, $GaNbO_4$, and $TiNb_2O_7$ crystals was examined with a JEOL 100 C electron microscope.

## Results

Plate 1 shows the morphology of the powders used in the case of $GaNbO_4$ and $V_2O_5$; they are constituted of single crystals of very low specific area (1–5 m2/g).

After a few hours at 300°C under nitrogen, it is assumed that samples have been sufficiently desorbing and the isotherm at 630°C is rapidly reached: we can then observe a loss of weight that should correspond, if interpreted as a loss of oxygen from $V_2O_5$, to a mean stoichiometry between $V_3O_7$ and $V_4O_9$ as far as are concerned samples (a) and (b), and exactly to $V_4O_9$ for $TiNb_2O_7$: this weight is quickly and almost entirely regained under oxygen.

X-Ray analysis[1] performed on samples that had stayed 72 hr at 630°C reveals the following reactions:

$$V_2O_5 + GaNbO_4 \xrightarrow{\text{heat in } N_2} \text{unchanged } GaNbO_4 + \text{residual}$$
$$V_2O_5 + \text{partial reduction to } V_6O_{13} \quad (22)$$

$$V_2O_5 + AlNbO_4 \xrightarrow{\text{heat in } N_2} \text{unchanged } AlNbO_4 + \text{residual}$$
$$V_2O_5 + \text{partial reduction to } V_6O_{13} \quad (23) \text{ (Plate 2)}$$

$$V_2O_5 + TiNb_2O_7 \xrightarrow{\text{heat in } N_2} V_4O_9 + \text{unchanged } TiNb_2O_7$$
$$\Big\downarrow \text{heat in } O_2$$
$$V_2O_5 + TiNb_2O_7 \xrightarrow{\text{heat in } O_2} TiO_2(\text{rutile}) + VNb_9O_{25} \text{ (solid solution)} \quad (24)$$

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[1] Taking into account the weakness of the lines belonging to the Vanadium phase (because of the weak concentration of Vanadium in the samples) the main lines attributed to $V_6O_{13}$ may coincide with those of the compound $VNb_9O_{25}$. However nothing, in the case of the occurrence of such a classical solid state reaction, can justify the experimental evidence of the reduction. Hence we suppose in the discussion that $V_6O_{13}$ is actually formed. Moreover the proposed model can be applied to both cases.

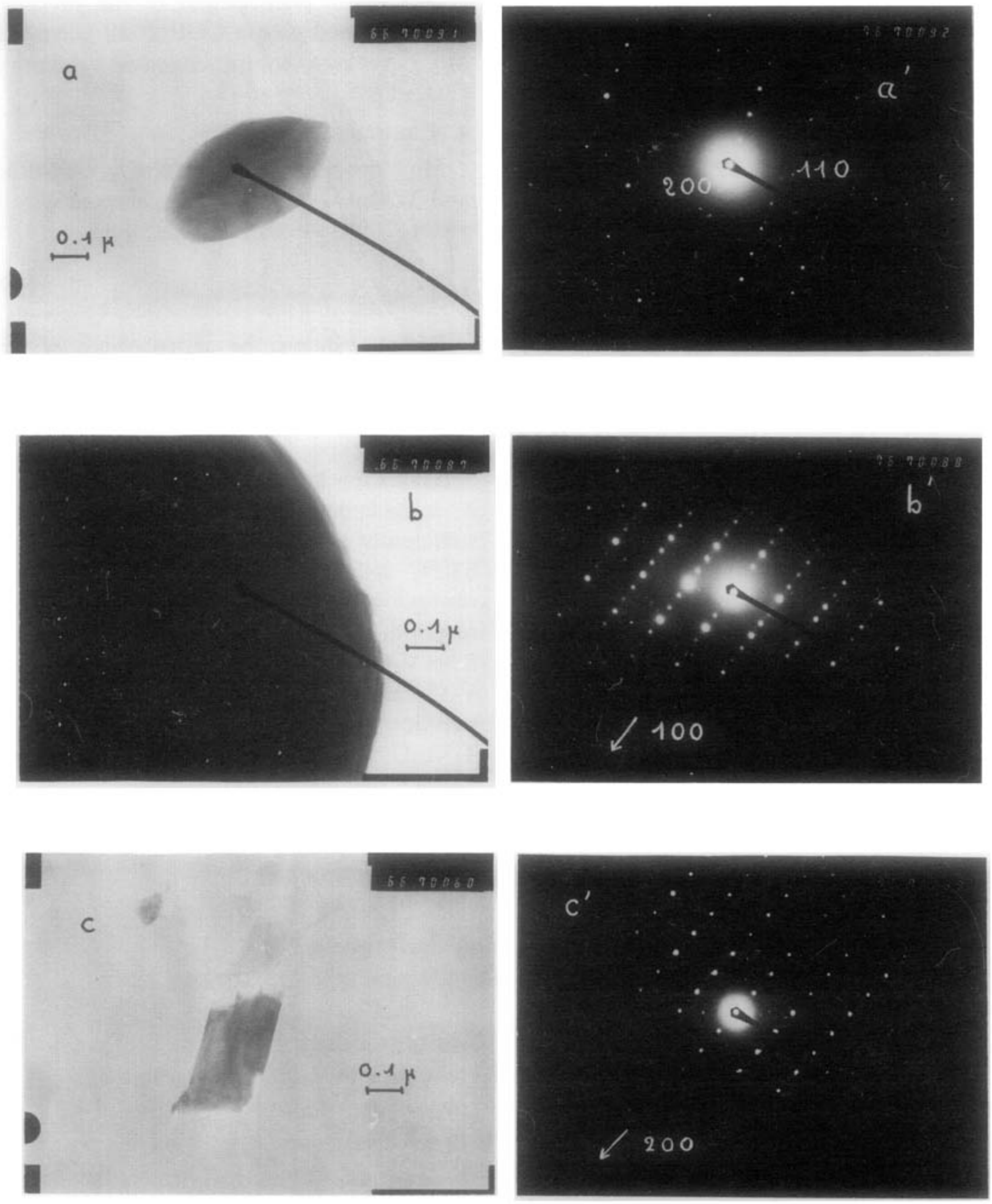

Plate 1. Two different textures (a, b) and diffraction pattern (a', b') performed on $GaNbO_4$ powder. These are single-crystals with (001) cleavage plane (as generally expected from $ReO_3$ structures) already reported by Wadsley (*19*). Texture (c) and diffraction pattern (c') performed on $V_2O_5$ showing the (010) cleavage plane.

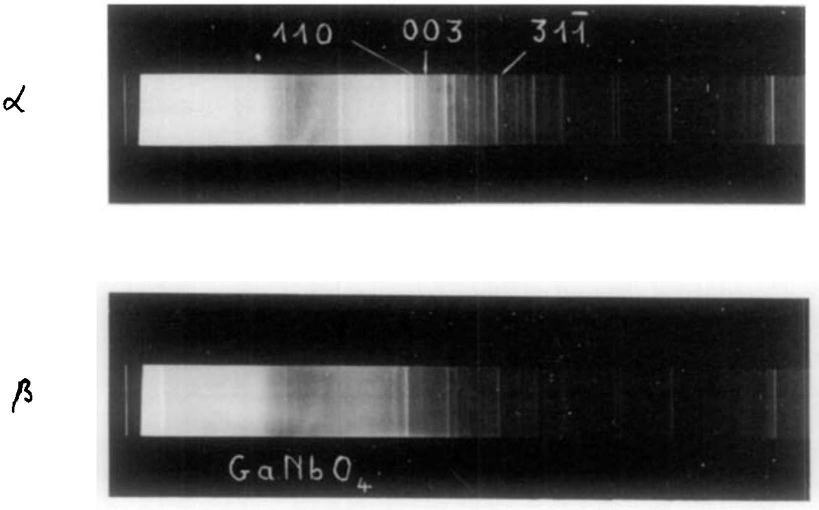

PLATE 2. X-Ray diffraction patterns performed on $GaNbO_4$ (β) and on (b) sample after the reduction (α). Three supplementary lines ($d = 3.52$ Å, 3.36 Å, 2.70 Å) correspond with the most intensive lines of $V_6O_{13}$; the same lines appear for the $AlNbO_4$-containing sample. Supplementary lines for $TiNb_2O_7$-containing sample ($d = 5.04$ Å, 3.41 Å, 3.35 Å) correspond to the most intensive lines of $V_4O_9$.

### Discussion

Analysis of the results under nitrogen shows without ambiguity that, in the bulk, the two original phases retain their individuality. Oxides $AlNbO_4$, $GaNbO_4$, and $TiNb_2O_7$ are stable when $V_2O_5$ is reduced, at least partially, into suboxides. We know, however, that the surface properties of $V_2O_5$ determine the reactivity of this oxide (*25*). Therefore we have checked that it was stable in these conditions, which are very different from those reported by Colpaert. We conclude then that the observed reaction is due to the presence of the other phase. One could object that this other phase contaminates the surface of $V_2O_5$. This contamination is allowed only if there is contact between them. And, since $AlNbO_4$, $GaNbO_4$, and $TiNb_2O_7$ have been prepared in air at high temperature, we suppose that their surface is clean and that *the observed reaction is only due to the creation of an interface between the two phases.* This can be considered as a contamination by the lattice of $AlNbO_4$, $GaNbO_4$, or $TiNb_2O_7$.

### Interpretation

(i) The exact atomic movement at the interface however escapes us, as generally does all surface phenomenon, by a lack of powerful and precise enough investigative means (not only the environment of each cation but also their charge and concentration gradient throughout the thickness of the interface is required; ESCA spectra and R.P.E. analysis certainly would be of interest but with caution not to alter such a metastable system). Since the employed powders happen to be small single crystals, we shall develop the following hypothesis: two crystals of each phase share their surface planes that are the cleavage planes of natural single crystals. This diminishes the total surface energy of the system and amounts to introducing a potential of attraction between different crystalline faces. As far as thermodynamics is considered, this involves the use of a superficial strain term, added to the ordinary value of the free energy of each crystal:

$$G = G_0 + \sigma_{12} S, \qquad \sigma_{12} < 0$$

(where $G_0$ represents the free energy of the crystal only, $S$ is the contact surface, and $\sigma_{12}$ the difference of tension when face (1) of the crystal is brought from gas atmosphere to face (2) of the coupled crystal). Therefore, after the joining is made, the thermodynamic and kinetic properties of the initial phases are modified at the same time as the potential surface in their free-energy diagram. This can lead, according to the case, to a partial or complete reconstruction of the system. We saw, in the previous examples, that under nitrogen, $AlNbO_4$ and $TiNb_2O_7$ oxides are stable again; on the other hand, $V_2O_5$ is no longer so. Indeed, it seems to be contrary to the $V_2O_4$–$V_2O_5$ diagram (*26, 27*) and we have ascertained the spontaneous oxidation of $V_2O_4$ (rutile type) into $V_2O_5$ under experimental conditions: the contradiction is only apparent, as we try to explain, since the thermodynamic system is different.

(ii) Evolution toward a more stable configuration will, however, take place only if there is preservation of the interface during the reaction. This is made possible by the mechanism of reduction of $V_2O_5$, such as it was invoked by several authors (*25, 28, 29*): vanadium pentoxide occurs within slabs showing in surface the (010) plane (Bachmann notations: (*30*)) from which can nucleate the topotatic reduction by shear planes toward the inside of the crystal (Fig. 2a). Moreover, we notice that the reaction (apparently following single-order kinetics (Fig. 2b)) stops at a distance of the interface since $V_2O_5$ remains in part in reduced samples (a) and (b). When returned under oxygen ($P_{O_2} = 1$ atm) the reverse phenomenon happens: $V_2O_5$ reforms, which is quite coherent with a thermodynamic interpretation: in the third case however the instability of the $V_2O_5$–$TiNb_2O_7$ system with respect to $TiO_2$ (rutile)–$VNb_9O_{25}$ (solid solution) does not enable us to see the reversibility. On the other hand, the latter reaction is not described in the phase diagram $V_2O_5$–$Nb_2O_5$ (*24*) showing that only the mixture $V_2O_5$–$VNb_9O_{25}$ is stable at this temperature, but is nevertheless possible, given the great similarity of cations $Nb^V$ and $V^V$.

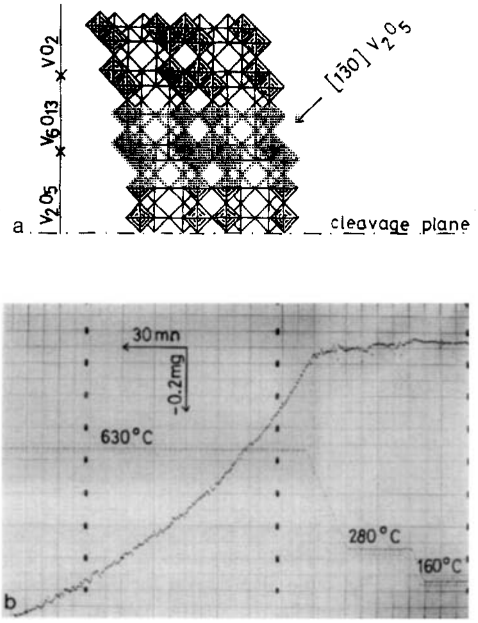

FIG. 2. (a) Idealized mechanism of reduction of $V_2O_5$ by $[1\bar{3}0]$ *CS* plane leading continuously from $V_2O_5$ to $VO_2$ (B). (b) Microgravimetric curve under nitrogen for $V_2O_5$–$TiNb_2O_7$ sample leading to $V_4O_9$ stoichiometry.

(iii) So far, we have, however, developed only the formal aspect of the phenomenon without studying the fundamental reason of its occurrence: it is indeed noticeable that, understood in this way, it is an exception in solid state chemistry. But the matrices $TiO_2$ (rutile) and $\alpha$-$Al_2O_3$ have caused no reduction of $V_2O_5$ under the above described conditions, and though the choice of an oxide is relatively critical, given the great reactivity of $V_2O_5$, it is likely other attempts should lead to the same conclusion. We think the term $\sigma_{12}$ that represents the interfacial stress *is null in the great majority of cases and becomes significant only when the interface is coherent.* This idea must be compared with studies relative to epitaxy, where the crystallographic fit between the two matrices plays an explanatory role, in spite of contestations

(*31*).[2] It seems logical that the quality of joining on which the $\sigma_{12}$ constraint factor partly depends, may be the better as the geometric patterns of the two lattices coupled fit better and on a greater scale. This implies a material continuity at the interface still preserving the discontinuity of phases, at least in the first step of the reaction, this being possible if one takes into account the covalent nature of bonds on the two sides of the interface. In fact we notice that such is the case for the studied matrices (Plates 3 and 4, and Tables I and II). Moreover, it is interesting to compare the crystallographic misfit before and after reduction: we come to the conclusion that the reduction decreases the lattice constraint at the interface (thermodynamic point of view:

$$\Delta G = \Delta G_0 + S\cdot\Delta\sigma_{12} < 0 \text{ with } \Delta G_0 > 0$$

so necessarily $\Delta\sigma_{12} < 0$).

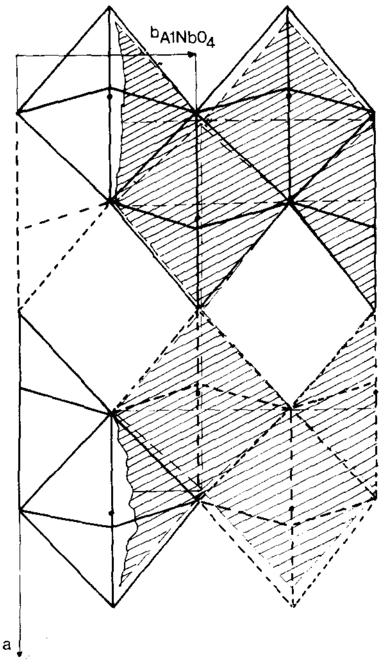

PLATE 3. Superposition with the actual relative magnitude of $(010)_{V_2O_5}$ (dashed) and $(001)_{AlNbO_4}$ from crystallographic data, showing an almost perfect adaptation of geometric patterns and symmetries before and after the reaction.

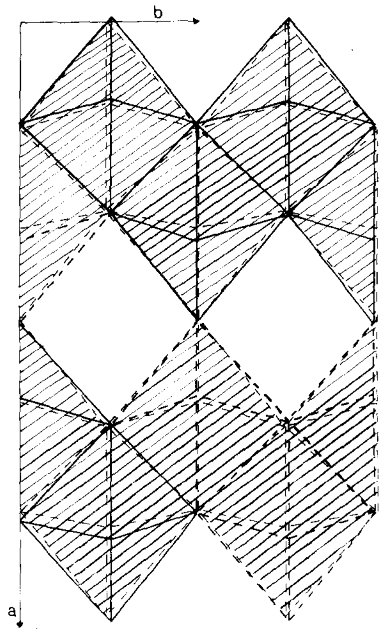

PLATE 4. Superposition with the actual relative magnitude of $(001)_{V_6O_{13}}$ (dashed) coming from $(010)_{V_2O_5}$ and $(001)_{AlNbO_4}$: a better adaptation than in the case of Plate 3 can be observed, which is assumed to be the cause of the observed reduction.

The evaluation of crystallographic misfits at room temperature before and after the reaction for the three samples is obtained as

TABLE I

CRYSTALLOGRAPHIC DATA[a]

| | *a* (Å) | *b* (Å) | *c* (Å) | $\pi$(Å$^2$) | Cleavage plane |
|---|---|---|---|---|---|
| $AlNbO_4$ | 12.13 | 3.73 | | 45.24 | (001) |
| $GaNbO_4$ | 12.66 | 3.79 | | 47.98 | (001) |
| $TiNb_2O_7$ | | 3.81 | 20.44 | 77.87 | (100) |
| $V_2O_5$ | 11.52 | | 3.56 | 41.01 | (010) |
| $V_6O_{13}$ | 11.92 | 3.68 | | 43.86 | (001) |
| $V_4O_9$ | 17.96 | 3.63 | | 65.19 | (001) |

[a] $\pi$ = unit cell surface along the cleavage plane.

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[2] Elsewhere (*36*) we give a theoretical justification based on quantum mechanics (which does not take into account the geometric pattern at the interface).

TABLE II

LATTICE MISFIT[a]

| $\rho$ | $V_2O_5$ | $V_4O_9$ | $V_6O_{13}$ |
|---|---|---|---|
| $AlNbO_4$ | 9.4 | | 3.1 |
| $GaNbO_4$ | 14.5 | | 8.6 |
| $TiNb_2O_7$ | 48.3 | 16.3 | |

[a] $\rho$ is definite with an example and gives the lattice misfit

$$\rho_{V_2O_5,\, AlNbO_4} = \frac{|\pi_{V_2O_5} - \pi_{AlNbO_4}|}{\pi_{AlNbO_4}} \times 100.$$

follows: the calculation is related to the cleavage planes, observed by electron microscopy for $AlNbO_4$, $GaNbO_4$, $TiNb_2O_7$, and $V_2O_5$; the cleavage plane of $V_6O_{13}$ is deduced from the $V_2O_5$ one (Fig. 1).

The situation is more complicated for $V_4O_9$ and the study is still in progress. Two crystallographic forms have been reported for this oxide (*23, 32*) Moreover, it has been reported that the actual formula of the first one (*23*), which we have observed, is not $V_4O_9$ but $V_4O_8(OH)$(*33*) taking into account the hydrothermal conditions used for its preparation. Our results do not seem to be consistent with this conclusion, since water is absent from the atmospheric conditions used in our experiments and leading to this oxide. But no further attempt has been made in this direction. We only calculated the misfit in the $(001)_{V_4O_9}$ plane, assuming the latter to come from $(010)_{V_2O_5}$ because (i) of a good adaptation with $(100)_{TiNb_2O_7}$, (ii) of the conservation of $b$ axis ($d = 3.63$ Å) equal for $V_4O_9$ and $V_2O_5$. But so far we have found no rigorous adaptation of patterns contrary to the case of $AlNbO_4$. Indeed, the $V_2O_5$ lattice parameters do not depend on temperature along the cleavage plane (*34*). We assume this is a general fact in Wadsley matrices, but with no demonstration.

(iv) Last, we must note the very close symmetry group of the oxides used:

$C2/m$ for $AlNbO_4$ and $GaNbO_4$

$A2/m$ for $TiNb_2O_7$

The importance of symmetry groups in chemical reactivity (*35*) leads us to think they play an essential role as an imperative condition in sight of the joining of crystalline faces.

## Conclusion

(a) We are now able to propose a mechanism describing the whole phenomenon observed and completing by experimental evidence the model proposed in the case of $V_2O_5$–$TiO_2$ (anatase) (*21*). When temperature is increased, though it is not operated under vacuum, but in a controlled atmosphere, the great mobility of adsorbed molecules and the insaturation of surface atoms lead different crystals to share their surface planes, even if only van der Waals bonds are broken, as far as $V_2O_5$ is concerned; this is possible first because of common symmetry elements and second because of the crystallographic fit between the two cleavage planes: this first step, very analogous to sintering, is allowed by the fact that the reaction takes place 60°C below the melting point of $V_2O_5$, therefore well above the Tammann temperature: 200°C.[3] This step is also to be compared with all growth phenomena, and ends at the creation of a *coherent* interface. (So many particular conditions explain that this situation is not commonly observed in solid state chemistry.) Then the slight crystallographic misfit generates lattice strains on the two crystals; the nature of these strengths is different from those which have formed the interface, since, in this case, atomic coordinence of interfacial atoms is satisfied. According to Ubbelohde's theory, atoms on both sides occur in a relatively excited state on long time life *which can lead to chain reactions*: the system will

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[3] The existence of the reaction $V_2O_5 + TiNb_2O_7 \rightarrow TiO_2 + VNb_9O_{25}$ is further evidence for the great mobility of the atoms in these conditions.

relax by nucleating the shear planes of $V_2O_5$ until the suboxide is formed, for which the residual strains equilibrate the free energy difference with respect to the isolated phase. This means that the reaction propagates from the interface through the $V_2O_5$ crystal, the coherence strain being transferred from one sheet of atoms to the next one.

(b) Thus, the second step of the reaction seems to belong to cooperative type reactions described by Anderson by means of fluctuations to explain the structural chemistry of these oxides; it is now possible to distinguish three cases when two crystals of different composition or structure are brought together in favorable kinetic conditions:

(1) One of them reacts: it is the case in the example we studied here: the second crystal acts as an external boundary condition.

(2) The two react separately: see, for example, the system $V_2O_5$–$TiO_2$ (*21*).

(*3*) A new compound is formed from the two primaries.

In the first two cases, although the approach consisting in a description of the reaction by a topotactic mechanism from local constraints is enough, clearly, fluctuations and resulting fluctuations waves provide a more universal language for chemical reactivity. Moreover the study of interphase boundaries, that may be coherent, semicoherent, or incoherent, and arising at the beginning or as an intermediate step of the reaction by the way of discontinuity of the fluctuation, certainly will clarify the structural mechanism of the chemical reactivity of solids which could well occur by the same path as the above described reduction: that is, the role of electronic as well as structural factors along the interface would be emphasized to answer the following questions: How is a reaction *possible*? Why and how *will it take place* when two solid phases are put together?

## Acknowledgments

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## References

*1.* S. ANDERSSON, *Bull. Soc. Chim. Fr.* **4**, 1088 (1965).

*2.* G. ANDERSSON, *Acta. Chem. Scand.* **8**, 1599 (1954).

*3.* S. ANDERSSON AND L. JAHNBERG, *Ark. Kemi.* **21**, 413 (1963).

*4.* R. S. ROTH AND A. D. WADSLEY, *Acta. Crystallogr.* **18**, 724 (1965).

*5.* A. D. WADSLEY, *Acta. Crystallogr.* **14**, 660 (1961); **14**, 664 (1961).

*6.* R. S. ROTH AND A. D. WADSLEY, *Acta. Crystallogr.* **19**, 26 (1965).

*7.* P. L. GAI AND J. S. ANDERSON, *Acta. Crystallogr. A* **32**, 157 (1976).

*8.* J. S. ANDERSON, *Chem. Soc. Dalton*, 1107 (1973).

*9.* R. GRUEHN, Proc. 5th Mater. Res. Symp. (1972). Nat. Bur. Res. Stand. Special Publication 364, Solid State Chem.

*10.* J. G. ALLPRESS, *J. Solid State Chem.* **1**, 66 (1969).

*11.* S. IIJIMA, *Acta. Crystallogr. A* **31**, 784 (1975).

*12.* J. S. ANDERSON, "Problems of Nonstoichiometry." North-Holland, Amsterdam (1970).

*13.* K. M. NIMMO AND J. S. ANDERSSON, *J. Chem. Soc. Dalton*, 2328 (1972).

*14.* A. D. WADSLEY AND S. ANDERSON, "Perspectives in Structural Chemistry," Vol. III, Wiley, New York (1970).

*15.* A. R. UBBELOHDE, *J. Chim. Phys.* **62**, 33 (1966).

*16.* B. G. HYDE AND L. A. BURSILL, "The Chemistry of Extended Defects in Non-metallic Solids," North-Holland, Amsterdam (1970).

*17.* J. S. ANDERSON, *Proc. Int. Symp. 7th* **79**, 150 (1972).

*18.* B. F. PEDERSEN, *Acta. Chem. Scand.* **16** 421 (1962).

*19.* B. MOROSIN AND A. ROSENZWEIG, *Acta. Crystollogr.* **18**, 874 (1965).

*20.* P. PASCAL, Nouveau Traité de chimie minérale," Vol. XIII, p. 356, Masson (1956).

*21a.* A. VEJUX AND P. COURTINE, *J. Solid State Chem.* **23**, 93 (1978).

*21b.* F. VAN DEN BUSSCHE AND M. JOUY, private communication (1970).

*22.* K. A. WILHELMI, K. WALTERSSON, AND L. KIHLBORG, *Acta. Chem. Scand.* **25**, 2675 (1971).

*23.* K. A. WILHELMI AND K. WALTERSSON, *Acta. Chem. Scand.* **24**, 3409 (1970).

*24.* J. L. Waring and R. S. Roth, *J. Res. Nat. Bur. Stand. A* **69**, 119 (1965).

*25.* M. N. Colpaert, P. Claws, L. Fiermans, and J. Vennik; *Surface Sci.* **36**, 513 (1973).

*26.* K. Kosuge, *J. Phys. Chem. Solids* **28**, 1613 (1967).

*27.* J. B. MacChesney and M. J. Guggenheim, *J. Phys. Chem. Solids* **30**, 225 (1969).

*28.* R. J. D. Tilley and B. G. Hyde, *J. Phys. Chem. Solids* **31**, 1613 (1970).

*29.* S. Horiuchi, M. Saeki, Y. Matsui, and F. Nagata, *Acta. Crystallogr. A* **31**, 660 (1975).

*30.* H. G. Bachmann, F. R. Ahmed, and W. H. Barnes, *Z. Kristallogr.* **115**, 110 (1961).

*31.* D. W. Pashley, *Advan. Phys.* **14**, 361 (1965).

*32.* G. Grymonprez, L. Fiermans, and J. Vennik, *Acta. Crystollogr. A* **33**, 834 (1977).

*33.* A. Casalot, *Mater. Res. Bull.* **7**, 903 (1972).

*34.* T. Beguemsi, P. Garnier, and D. Weigel, *J. Solid State Chem.* **25**, 315 (1978).

*35.* R. G. Pearson, "Symmetry Rules for Chemical Reactions." Wiley-Interscience, New York (1969).

*36.* J. G. Eon and P. Courtine, *C. R. Acad. Sci. Paris* **288**, 17 (1979).