

## Structure and Antiferromagnetism of Nickel Oxide-Copper Oxide and Nickel Oxide-Zinc Oxide Solid Solutions. Influence on Reactivity

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The antiferromagnetism of NiO-ZnO solid solutions is not always correlated to a rhombohedral distortion of the cubic cell. This confirms the previous results on the NiO-CuO system. An anomaly in the reducibility by hydrogen is found in a narrow range of temperature near the Néel point of these solids, even though the disappearance of the antiferromagnetism does not result in any detectable structural transformation.

### I. Introduction

It is known that nickel oxide is an antiferromagnetic solid with a rhombohedral structure below 520°K. At this temperature it becomes paramagnetic with a cubic symmetry (1). As noted by J. R. Singer, "it is believed that the lattice distortion is intimately related to the spin ordering and direction in antiferromagnetic materials" (2). This point has been matter of discussion: M. W. Vernon and M. C. Lovell, from conductivity measurements on single crystals, found that nickel oxide was cubic above 390°K (3). More recently C. J. Toussaint (4) found the crystallographic transformation at 483°K. Nevertheless, M. W. Vernon, after his study on the topography of antiferromagnetic domains (5), and from a similar study A. J. Sprinthorpe (6) concluded that the rhombohedral distortion is really related to the antiferromagnetic form. L. C. Bartel and B. Morosin (7), in a recent study of this question, have proposed a quantitative theoretical interpretation which proves the solidity of the first Singer point of view (2).

It is, however, still possible to try to distinguish between cause and effect. The works of Y. Shimomura *et al.* on the NiO-CuO solid solutions give a very valuable indication (8). They have shown that even if the rhombohedral distortion originates from the antiferromagnetic exchange interaction, this is not always sufficient to result in a deformation of the lattice. For example, a solid solution containing 24% copper is cubic at room temperature, but antiferromagnetic up to 455°K.

A similar effect was suspected by Rooksby (9) for NiO-FeO. He found that a sample of a 5% iron NiO-FeO solid solution was cubic at room temperature, whereas its Néel temperature, although not measured, was estimated to be 500°K. This leads us to ask two questions.

(1) Is it possible to find other antiferromagnetic solid solutions with no lattice distortion in spite of the exchange interaction?

(2) The older work of G. Nury and H. Forestier (10) and the more recent of A. Roman and B. Delmon (11), have shown that nickel oxide exhibits a transient enhanced reactivity at the Néel temperature. This is a sort of Hedvall effect (12). However, it is important to know whether the increase of reactivity is

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related to structural transformation, or to the disappearance of antiferromagnetism. Since the NiO-CuO solid solutions are reducible by hydrogen between 420 and 470°K, an interesting question is to see whether the Shimomura 24% solid solution shows an enhancement of reactivity at 455°K and whether this phenomenon can be found in other mixed oxides.

## II. Experiments

### 1. Preparation of Samples

Two series of solids were prepared corresponding to nickel oxide in solid solution either with cupric oxide or with zinc oxide.

NiO-CuO solid solutions containing up to 32% CuO were obtained by impregnation of a nickel oxide ( $S = 1.1 \text{ m}^2 \cdot \text{g}^{-1}$ ) with a cupric nitrate solution and calcination in air at 1100°C, according to a previously described technique (13, 14).

The NiO-ZnO solid solutions were prepared starting from nickel and zinc oxides obtained by thermal decomposition in air at 500°C of hexahydrated nickel nitrate, and zinc oxalate, respectively. The oxides were mixed in the correct proportions, and then ground during 5 hr in a rotating agate mortar. The resulting powders were compressed under  $1.7 \text{ ton/cm}^{-2}$  into pellets which were sintered in air at 1200°C for 24 hr.

Because these samples were found to be too sintered to be reduced easily, more reactive solids were prepared starting from Ni(OH)<sub>2</sub>-Zn(OH)<sub>2</sub> double hydroxides containing 83.5% nickel (15). The hydroxide solid solution was dehydrated at 225°C under vacuum for 20 hr to form a mixed oxide. Afterwards the resulting solid was heated at 650°C for 24 hr under 100 Torr oxygen pressure. Under these conditions traces of free zinc oxide contained in the hydroxide dissolve into the solid solution.

### 2. Analytical Procedures

#### (a) Radiocrystallographic analysis

The radiocrystallographic analysis were performed by the Debye-Scherrer method using CuK $\alpha$  radiation. A good line separation was ensured by using a 152.8 mm diam camera with a collimator defining a small

angle opening. The systematic errors in measuring Bragg angles (eccentricity and sample absorption, camera diameter) were reduced to a minimum. The Cohen least squares method was used to determine the cubic cell parameters. The 1200°C heated NiO-ZnO solid solutions gave very narrow lines and allowed an evaluation of the unit cells to within 0.0005 Å. However, for NiO-CuO solid solutions, line broadening did not allow such precise determinations. The parameters were only measured to within 0.001 Å.

#### (b) Thermomagnetic Analysis

The apparatus used was a self-balanced quartz spring, adapted for magnetic susceptibility measurements by the Faraday method (16). A nonmagnetic microoven permitted work up to 700°C. The temperature was controlled by a proportional controller with platinum resistor. The temperature was measured by means of a Chromel-Alumel thermocouple.

#### (c) Kinetics

The NiO-CuO solid solutions reductions were studied in a self-registering McBain balance. Apparatus and operating conditions have been previously described (17). The sample mass was 100 mg, and the desorption was carried out at 200°C during 15 hr under a residual pressure of  $3.10 \cdot 10^{-6}$  Torr. The hydrogen pressure was 500 Torr. The water vapour issued from the reduction was condensed in liquid nitrogen traps.

The reductions of NiO-ZnO solid solutions were carried out under 150 Torr hydrogen pressure. The weight was recorded by the self balanced quartz spring within  $\pm 0.02$  mg (16). In this case the sample mass was about 20 mg.

### 3. Control of the Samples

The NiO-CuO solid solutions were dissolved slowly in 15% HCl. The percentage of copper was determined by atomic absorption or for high concentrations electrolytically, and the percentage of nickel by EDTA complexometry. It was possible to show the homogeneity of the solids by progressive dissolution (13, 14).

The molar concentrations of the NiO-ZnO solid solutions prepared at 1200°C were

TABLE I  
UNIT CELL PARAMETERS AND NÉEL TEMPERATURE  
OF NiO-ZnO SOLID SOLUTIONS PREPARED AT  
1200°C

ZnO mole %	$a(\text{Å})$ ( $\pm 0.0005$ )	$\alpha$ ( $\pm 0.2'$ )	$T_N(^{\circ}\text{K})$
0	4.1747	90°3.5'	545
3	4.1781	90°2.6'	
7	4.1830	90°0.8'	
15	4.1921	90°	473
20	4.1967	90°	403
25	4.2032	90°	337
30	4.2084	90°	310
35	4.2148	90°	245

controlled after dissolution in diluted sulfuric acid. All the cations were first determined complexometrically. Zinc and nickel were masked with potassium cyanide, the zinc was unmasked selectively by adding formol and then determined complexometrically in an ammoniacal medium.

The homogeneity of the solid solutions was verified crystallographically: the selected samples contained only one phase, the solid solution, the unit cell parameter of which followed the Vegard law.

It was verified that the exhydroxide NiO-ZnO mixed oxide was a homogeneous cubic solid solution. Referring to the results of Table I, the unit cell parameter allows one to estimate the zinc concentration to be 15%.

### III. Results and Discussion

#### 1. Néel temperature of the Different Solid Solutions

The thermomagnetic analysis curve obtained for pure nickel oxide is reproduced on Fig. 1. It is consistent with the results of Singer (2). but there is frequently a sensible indetermination on the ordinate values attributed to traces of ferromagnetic nickel. Since only the abscissa of the transition points had to be considered, it was not necessary to calculate the ferromagnetic correction for each different temperature. However, the above discrepancy becomes important for the NiO-

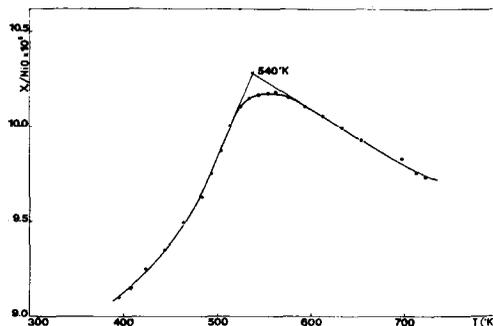


FIG. 1. Thermomagnetic analysis of pure NiO.

ZnO solid solutions heated under a low pressure of helium or nitrogen. In this case, the magnetic analyses were carried out under a low pressure of oxygen. With this precaution the perturbations practically cancelled out.

For all the solid solutions the curves obtained are similar to that reproduced on Fig. 1. The observed maxima are rather flat, particularly for copper-containing solids. Therefore, it is difficult to deduce a precise magnetic transition temperature  $T_N$  as for pure nickel oxide. Below  $T_N$  will be taken as the abscissa of the intersection point of the two tangents at the increasing and decreasing inflection points, as indicated on Fig. 1. This arbitrary rule naturally introduces a difference from the value obtained by other methods, in some cases up to 20 degrees, but it makes the comparison of all our solids easier.

The " $T_N$ " computed by this way are given on Tables I and II.

#### 2. Structure of the Samples

For easier comparisons between samples, the rhombohedral sample parameters are reported in a pseudocubic unit cell, the distortion being only equal to a few minutes. The lattice constants are given on Tables I and II.

The results are consistent with those of Schmahl et al. (18) for NiO-CuO solid solutions and with those of Kedesdy and Drukalsky (19) for NiO-ZnO solid solutions. However, these authors neglected the rhombohedral distortion affecting pure nickel oxide, and the solid solutions containing low concentrations in  $\text{Zn}^{2+}$  or  $\text{Cu}^{2+}$  ions. The increasing sizes of the unit cells in NiO-ZnO (0.0285

TABLE II  
UNIT CELL PARAMETERS AND NÉEL TEMPERATURE  
OF NiO-CuO SOLID SOLUTIONS PREPARED AT  
1100°C

CuO mole %	$a(\text{Å})$ ( $\pm 0.001$ )	$\alpha$ ( $\pm 0.5'$ )	$T_N(^{\circ}\text{K})$
5	4.1785	90°3'	570
12	4.1815	90°2'	530
20	4.1890	90°	501
25	4.1920	90°	480

Å for 25% Zn) and in NiO-CuO (0.0173 Å for 25% Cu) are related to the ionic radii differences (0.05 Å between  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$ , 0.03 Å between  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions).

### 3. Comparison between Magnetic and Crystallographic Transition

The temperatures  $T_N$  against the  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  concentrations are plotted in Fig. 2.

The results for the NiO-CuO solid solutions are consistent with those of Shimomura and Tsubokawa (8). No results for NiO-ZnO solid solutions have previously appeared.

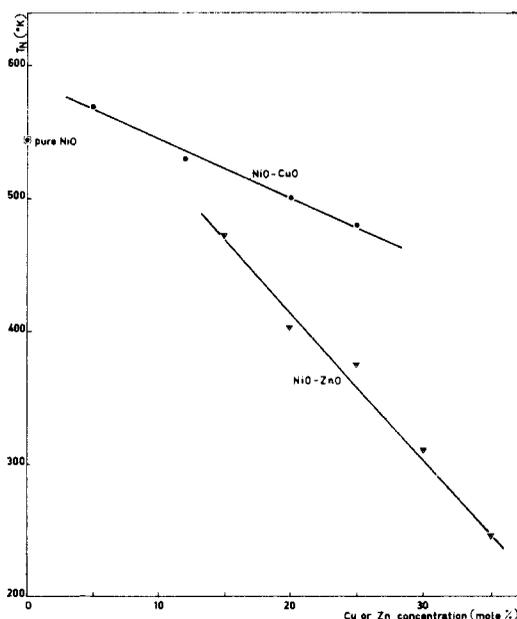


FIG. 2. Néel temperature of NiO-CuO and NiO-ZnO solid solutions.

There is a linear correlation between  $T_N$  and the concentrations, the deviations from the mean straight line being consistent with experimental uncertainty.

$\text{Zn}^{2+}$  ion insertion results in a larger decrease of the Néel point than for  $\text{Cu}^{2+}$  ions: for 25% foreign ion concentration, the decrease is 160°C for NiO-ZnO solutions and only 65°C for NiO-CuO. These differences are probably related to the electronic structure of ions: the exchange interactions are less disturbed by  $\text{Cu}^{2+}$  ions (with one unpaired electron) than by  $\text{Zn}^{2+}$  ions (with complete  $d$  orbitals).

The structure of these solids is independent of antiferromagnetism since the phases containing from 15 to 35% Zn and those from 20 to 35% Cu are perfectly cubic but antiferromagnetic at room temperature. Obviously, the exchange interactions are present in these solid solutions but they are no longer able to distort the lattice. This conclusion is consistent with the Shimomura and Tsubokawa results (8), but of course it is possible to claim with Rooksby (9) that this deformation is always present but in some cases too small to be detected. Nevertheless, it is hard to believe that the very high reactivity enhancement at the Néel point observed for NiO-ZnO and NiO-CuO solid solutions would be related to structural distortions corresponding only to a few seconds of arc.

### 4. Reactivity Enhancement at the Néel Temperature

#### (a) NiO-CuO System

The 25 at % CuO solid solution ( $S = 0.2 \text{ m}^2/\text{g}^{-1}$ ) was easily reducible by hydrogen near the Néel temperature estimated to be 207°C by our method and between 172 and 192°C by ESR measurements (14). It was possible to obtain the diagram shown in Fig. 3 where the reduction rate  $k_e$  (curve I) and the induction period  $t_i$  (curve II) are plotted versus temperature. If  $\alpha(t)$  ( $0 < \alpha < 1$ ) is the reduction ratio,  $k_e$  can be defined as the slope of the quasilinear part of the sigmoidal curve. By prolonging this linear segment,  $t_i$  is the intersection with the time axis. A very sharp maximum of  $k_e$  appears between 177 and

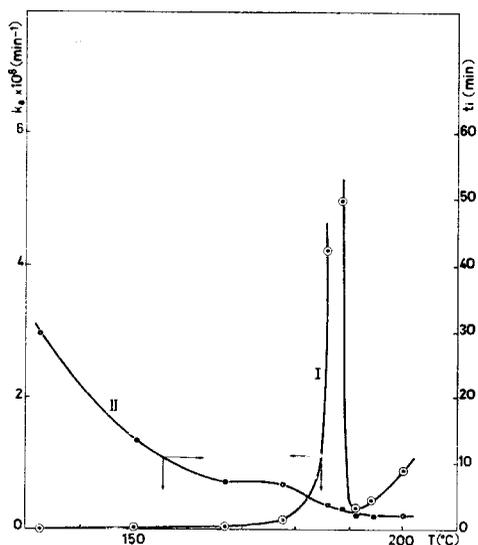


FIG. 3. Reduction by hydrogen at different temperatures of 25% Cu NiO-CuO. Curve I = reduction rate  $k_e$ ; curve II = induction period  $t_i$ .

190°C, i.e., exactly where the ESR technique detects the Néel point. This effect is indeed artificially amplified by heat transfer phenomena because of the high reaction exothermicity (14). Therefore, only the existence of the maximum is of interest and not its magnitude.

The relative increase of  $k_e$  at the magnetic transition temperature is due mainly to an enhancement of the growing speed of the metallic nuclei which obeys the same Arrhenius law on both sides of the narrow Néel transition range (14). A similar variation in the growing speed of the metallic nuclei has been observed for the reduction of pure nickel oxide in the vicinity of its Néel point (11). As there is no discontinuity in the variation of  $t_i$  (Fig. 3, curve II), it seems that the formation speed of the metallic nuclei does not change very much. Consistent with a reactivity variation confined in a narrow temperature domain, it can also be noted that the two parts of the Arrhenius diagram  $\log k_e$  vs  $1/T$  on both sides of 177–190°C range are the same straight line (14). This is not the case for nickel oxide (11). However, during the reduction of NiO the formation of metallic nuclei is much lower than for 25% Cu NiO-CuO. The nucleation is therefore more sensitive to even small modifications

of surface state for pure NiO. This may explain the different behaviour of the two solids. Another possible explanation is structural modification of pure NiO which could result in a break in the Arrhenius diagram. To decide between these two hypotheses, it would be necessary to prepare a 1.5% Cu NiO-CuO solid solution, the structure of which would probably be similar to that of pure NiO, but the preparation method described above does not allow a sufficient degree of homogeneity for such low concentration.

It can be concluded that the enhancement of growing speed of the metallic nuclei is related to the antiferro-paramagnetic transformation.

### (b) NiO-ZnO System

1. *Results.* The 15% Zn NiO-ZnO solid solutions prepared at either 1200°C or 650°C begin to be reducible at about 285°C, i.e., clearly above the Néel point (200 and 213°C, respectively).

For reduction ratios between 0.2 and 0.4, the reduction curve  $\alpha = f(t)$  is linear for every temperature. The reduction velocity was measured at several successive constant temperature, in the interval  $0.2 < \alpha < 0.4$ , so

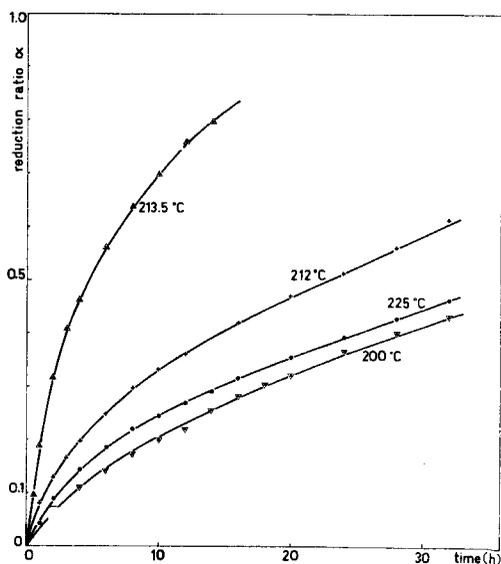


FIG. 4. Reduction at 295°C of 15% Zn NiO-ZnO pretreated by hydrogen at different temperatures.

that the activation energy could be deduced in one experiment. The value obtained was 43.2 or 41.3 kcal·mole<sup>-1</sup>, depending on the preparation temperature (1200 or 650°C). Furthermore, for a given temperature and reduction ratio the solid prepared at 650°C was about 30 times more reducible than the 1200°C solid. Therefore, the 650°C solid was chosen to test the effect of the magnetic transition, by means of two series of experiments. In the first, after a previous reduction up to  $\alpha = 0.2$  at 350°C reduction was tried at the Néel temperature (213°C). A rapid but limited (1–3%) reduction was indeed observed, but the reaction quickly stopped. In the second, the solid was heated for 3 hr. in hydrogen ( $p = 150$  Torr) at constant temperatures around the Néel point. The sample was then heated in the same atmosphere for 10 min at  $295 \pm 1^\circ\text{C}$ . Figure 4 shows that the reduction isotherms are very close together for two temperature different from the Néel point (200 and 225°C), but that the reducibility is strongly enhanced after a pretreatment at 212°C, and even more at 213.5°C.

During the treatment by hydrogen at 212–213.5°C, the specific area changes only weakly (10 instead of 12 m<sup>2</sup>·g<sup>-1</sup>). More there are no microcrystalline metallic nuclei, since by magnetic analysis (Fig. 5), no ferromagnetism is detected at 293°K. Referring to the variation of magnetic susceptibility between 77 and 293°K (Fig 6), the untreated sample (curve I) and the 213°C pretreated one (curve II) behave as paramagnetics. The hypothesis of the

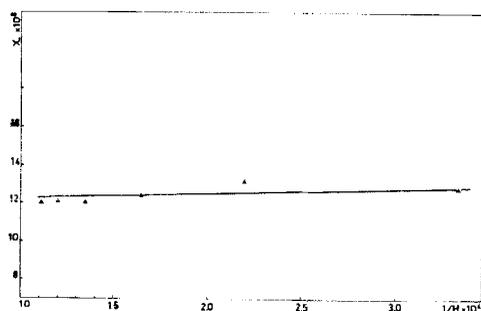


FIG. 5. Magnetic susceptibility variation versus magnetic field of 15% Zn NiO-ZnO pretreated at 213°C.

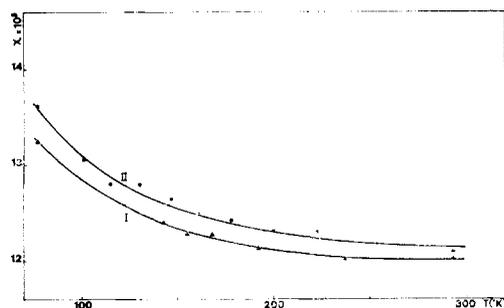


FIG. 6. Thermomagnetic analysis of 15% Zn NiO-ZnO, with (curve II) and without (curve I) pretreatment by hydrogen at  $212 \pm 4^\circ\text{C}$ .

presence of an 15% Zn Ni-Zn alloy with a Curie point below 293°K has to be rejected. It is difficult to exclude the possible creation of superparamagnetic metallic nuclei without any magnetization measurements at very low temperatures (4.2°K for example). However, their presence is highly improbable because of the very small differences in the magnetic susceptibilities observed at 77°K (Fig. 6, curves I and II). The only clear variation observed after the hydrogen pretreatment concerned the colour of the samples. Initially black, they turn grey after a pretreatment at 200 or 225°C, but green at 213°C.

2. *Discussion.* The black colour of dispersed nickel oxide after being in the presence of oxygen is attributed to a nonstoichiometry due to excess of oxygen (20). The same interpretation is very reasonable for 15% NiO-ZnO heated in oxygen at 650°C. The reducibility enhancement observed with NiO-CuO solid solutions near the Néel point is again found for NiO-ZnO. However, because of the low reactivity of this solid, the reduction process is limited here to the elimination of excess oxygen.

This modification of the 15% NiO-ZnO state has important consequences for its reduction in metal, as visible Fig. 4. It is not the result of a different dispersion of the oxide, or of metallic nuclei creation favoring the reduction process. It must be noted that the reduction activation energy is practically the same for NiO-ZnO than for pure zinc oxide ( $39 \pm 2$  kcal·mole<sup>-1</sup>) (21). A thermodynamic

limitation explains this result. The ZnO reduction equilibrium is very unfavorable ( $K_p = 10^{-6.6}$  at 327°C (21)). It is highly probable that the water vapour produced at the very beginning of NiO-ZnO reduction results in partial and selective reoxidation of zinc atoms into zinc oxide. The reduction of this so formed ZnO is probably necessary to regenerate the (NiO-ZnO) metal interface. This stage in the reaction has the same activation energy as the reduction of pure ZnO, and is by the way the stage which determines the rate of the whole process. Moreover, the selective reoxidation phenomenon of zinc which hinders the reduction is certainly increased by the presence of excess oxygen in the oxide to be reduced. The elimination of the excess oxygen from the solid is favoured by an hydrogen treatment at the Néel temperature and increases finally the reduction rate at higher temperature (Fig. 4). Both nucleation rate and metallic growing rate can be changed by these effects.

#### IV. Conclusion

Our study leads to new information on the following points.

1. The incorporation of zinc oxide in nickel oxide results in an important decrease of its Néel temperature.

2. There are many other solid solutions with the same characteristics as those described by Shimomura (8), i.e., cubic but antiferromagnetic at room temperature.

3. The reduction by hydrogen of 25% Cu NiO-CuO solid solution near its Néel temperature has shown that the magnetic transition definitely increases the reactivity, even if there is no simultaneous structural transition.

4. A confirmation is given by the 15% Zn NiO-ZnO phase. In this case, the antiferro-paramagnetic transformation makes the elimination of excess oxygen by hydrogen easier. There results an important modification of the reduction kinetics for temperatures higher than the Néel point.

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#### References

1. J. B. GOODENOUGH, "Magnetism and the Chemical Bond", p. 99, Wiley, New York, (1963).
2. J. R. SINGER, *Phys. Rev.* **104**, 929 (1956).
3. M. W. VERNON AND M. C. LOVELL, *J. Phys. Chem. Solids* **27**, 1125 (1966).
4. C. J. TOUSSAINT, *J. Appl. Cryst.* **4**, 293 (1971).
5. M. W. VERNON, *Phys. Status Solidi* **K1**, 37 (1970).
6. A. J. SPRINGTHORPE, *Phys. Status Solidi*, **K3**, 24 (1967).
7. L. C. BARTEL AND B. MOROSIN, *Phys. Rev.* **B3**, 1039 (1971).
8. Y. SHIMOMURA AND T. TSUBOKAWA, *J. Phys. Soc. Japan* **9**, 19 (1954).
9. H. P. ROOKSBY, *Trans. Brit. Ceram. Soc.* **56**, 581 (1957).
10. G. NURY AND H. FORESTIER, "Proceedings of the International Symposium on the reactivity of Solids," Göthenburg I, 189 (1954).
11. A. ROMAN AND B. DELMON, *C.R. Acad. Sci.*, **269**, B, 801, (1969) and **271** B 77, (1970).
12. J. A. HEDVALL, "Einführung in die Festkörperchemie", p. 183, Friedr. Vieweg-Sohn Braunschweig (1952).
13. P. GRANGE, H. CHARCOSSET, AND Y. TRAMBOUZE, *J. Thermal Analysis* **1**, 311 (1969).
14. P. GRANGE, Thesis, Lyon, (1970).
15. M. HOUALLA, P. TURLIER, R. FRETY, R. BARDET, H. URBAIN, AND Y. TRAMBOUZE, *Ann. Chim. (Paris)* **8**, 175 (1973).
16. G. EL SHOBAKY, P. C. GRAVELLE, S. J. TEICHNER, Y. TRAMBOUZE, AND P. TURLIER, *J. Chim. Phys.* **64**, 310 (1967).
17. H. CHARCOSSET, R. FRETY, Y. TRAMBOUZE, AND M. PRETTRE, "Proceedings of the Sixth International Symposium on the Reactivity of Solids", p. 171, Wiley-Interscience, New York (1969).
18. N. G. SCHMAHL, J. BARTHEL, AND G. F. EIKERLING, *Z. Anorg. Allg. Chem.*, **332**, 230 (1964).
19. H. KEDESZY AND A. DRUKALSKY, *J. Amer. Chem. Soc.* **76**, 5941 (1954).
20. P. C. GRAVELLE AND S. J. TEICHNER, *Adv. Catal. Relat. Subj.*, **20**, 245 (1969).
21. W. VERHOEVEN AND B. DELMON, *Bull. Soc. Chim.*, 3073 (1966).