Comparative study of polymorphic phase transition by differential thermal analysis, high temperature X-ray diffraction, and temperature programmed electrical conductivity measureme…

5 AUTHORS, INCLUDING:

J.M.M. Millet

Claude Bernard University Lyon 1

209 PUBLICATIONS **2,971** CITATIONS

SEE PROFILE

Gérard Thomas

École Nationale Supérieure des Mines de Sai…

134 PUBLICATIONS **889** CITATIONS

SEE PROFILE

jean-marie Herrmann

French National Centre for Scientific Research

128 PUBLICATIONS **8,976** CITATIONS

SEE PROFILE

Jacques Charles Védrine

Pierre and Marie Curie University - Paris 6

338 PUBLICATIONS **6,993** CITATIONS

SEE PROFILE

Comparative Study of Polymorphic Phase Transition by Differential Thermal Analysis, High Temperature X-ray Diffraction, and Temperature Programmed Electrical Conductivity Measurements. Case Study of Mixed Iron and Cobalt Molybdate

H. Ponceblanc,[†,‡] J. M. M. Millet,[†] G. Thomas,[§] J. M. Herrmann,[⊥] and J. C. Védrine*,[†]

Institut de Recherche sur la Catalyse, CNRS, 2 Avenue Albert Einstein, F-69626 Villeurbanne Cedex, France, Laboratoire de Chimie-Physique des Processus Industriels, Ecole Nationale Supérieure des Mines de Saint-Etienne, 42023 Saint-Etienne, France, and Laboratoire de Photocatalyse, Catalyse et Environnement, URA au CNRS, Ecole Centrale de Lyon BP 163, 69131 Ecully Cedex, France (Received: March 2, 1992; In Final Form: July 16, 1992)

A comparative analysis of the results, obtained by differential thermal analysis (DTA), high temperature X-ray diffraction (XRD), and temperature programmed electrical conductivity measurements (TPEC), in the study of the polymorphic transition (α to β form) of a mixed ferrous and cobaltous molybdate is reported. In order to progress in the interpretation of the curves obtained using TPEC, the results obtained with these techniques, used at different heating rates, have been compared. This comparison enables one to evidence the occurrence of the phase transition on the surface and in the bulk of the sample particles.

Introduction

Thermal analysis is historically the first physical method used to detect and characterize phase transitions of a chemical solid system changing with temperature.[1] It remains the simplest and the most commonly used technique for such studies. However, the detection of solid–solid phase transitions is often difficult when they present very low thermicity. In such cases, other techniques like X-ray diffraction and electrical conductivity measurements may lead to a better detection. X-ray diffraction is usually not used in a dynamic mode. However technical improvements allow the recording of sample patterns relatively rapidly at different temperatures.

The method of following the variations of the electrical conductivity of a solid as a function of the temperature has been used to study solid–solid transitions. However, most of the time, this technique is more suitable for metal systems. Only a few examples can be found on its use for oxide systems since changes in electrical conductivity are rather minor between two oxide polymorphs.[2] The phase transition of the low temperature phase α-CoMoO$_4$ to the high temperature phase β-CoMoO$_4$ has been studied using a large number of physical methods. Using differential thermal analysis, many authors agree on a temperature transition range varying from 400 to 450 °C, depending on the thermal pretreatment of the samples.[3,4] Only a few authors compared different methods to determine this phase transition, for instance DTA and X-ray diffraction,[5] thermoelectric power and electrical conductivity measurements,[6] and DTA and dilatometry measurements,[7] whereas only Ingrain and Thomas[8] studied this transformation using four different methods. In a recent work, we have studied the phase diagram of the binary system CoMoO$_4$–FeMoO$_4$ and the effect on Fe^{3+} on the phase equilibria of this system.[10] We have been able to show that this system exhibited two solid solutions α and β with a linear variation of the α/β phase transition temperature with the molar fraction x in Co$_{1-x}$Fe$_x$MoO$_4$, from CoMoO$_4$ to FeMoO$_4$, since the latter phase presents the same two polymorphic types. This system had never been investigated before, and, by contrast to CoMoO$_4$, little information is available on the phase transformation of α-FeMoO$_4$ to β-FeMoO$_4$.[9] This is presumably due on one hand to the low thermicity of the reaction and on the other hand to the high oxidizability of the ferrous compound, when the temperature is raised. To overcome these difficulties, temperature programmed electrical conductivity measurements were performed to determine the phase diagram.[10] Furthermore, we have tried to use differential thermal analysis

and high temperature X-ray diffraction, and it appeared interesting to compare these techniques to the latter one, for the study of the polymorphic transition of a mixed cobalt–iron molybdate, in a detailed way.

Experimental Section

(a) Sample Preparation. A Fe$_{0.12}$Co$_{0.88}$MoO$_4$ mixed cobalt–iron molybdate was prepared by coprecipitation from cobalt nitrate Co(NO$_3$)$_2$·6H$_2$O, ferrous chloride FeCl$_2$·4H$_2$O and ammonium heptamolybdate (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O mixture, under controlled atmosphere, as previously described.[10] The initial pH was equal to 7 and decreased progressively to 5 by the end of the reaction. The precursor obtained was calcined at 450 °C for 10 h and at 900 °C for 2 h under pure nitrogen flow. The low temperature α phase was obtained by grinding the sample. The prepared solid contained some Fe^{3+} cations (Fe^{3+}/(Co + Fe) = 0.026) and a small excess of molybdenum compared to the other cations ((Fe + Co)/Mo = 0.91) according to the chemical analysis.[10] The excess of molybdenum may be due to the presence of MoO$_3$ which is lost when the solid is calcinated at 900 °C.[10]

(b) Differential Thermal Analysis. The differential thermal analysis (DTA) was performed using a Setaram MTD 85 analyzer equipped with platinum/rhodium thermocouples (30/6). A 20-mg amount of the sample was placed in a 25-mm^3 platinum crucible. Analysis was achieved at a heating rate of 1, 5 and 10 °C·min^{-1}, under a deoxygenated and a dehydrated nitrogen flow (1 dm^3·h^{-1}). Alumina, pretreated at 1200 °C, was used as a reference.

(c) Temperature Programmed X-ray Diffraction. The temperature programmed X-ray diffraction (XRD) analyses were performed using a D500 Siemens diffractometer, equipped with an "Anton Paar" diffraction chamber and coupled with a DEQ PDP11/23 computer. Patterns were recorded using a copper radiation generator ($\lambda_{K\alpha}$ = 1.5418 Å) and a linear counter. The α-phase sample was placed on the platinum bar of the chamber, then evacuated, and contacted with deoxygenated and dehydrated nitrogen. A diffractogram of the sample was recorded at room temperature; then the temperature of the platinum bar was increased by 20 °C at the rate of 5 °C/min for a second experiment. A new diffraction pattern was recorded every 20 °C, after a temperature stabilization period of 2 or 45 min. The recording of each pattern with diffraction angles 2θ varying from 12 to 42° lasted 32 min. The experimental equipment and the method used to record X-ray patterns at high temperature have been detailed elsewhere.[12,13] From this series of patterns, obtained at different temperatures, an estimation of the α/β polymorphic transition reaction yield λ[14] was defined as

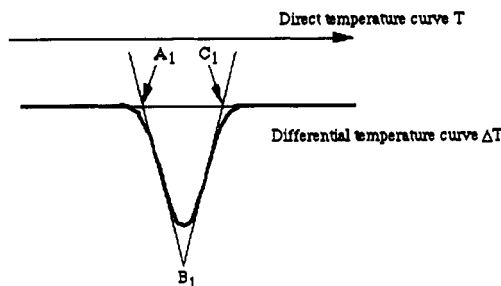$$\lambda = 1 / \left(\frac{I_1}{I_2} \frac{I_2^{\circ\circ}}{I_1^{\circ}} + 1 \right)$$

Figure 1. Schematic representation of a DTA signal corresponding to a phase transition.

where $I_1{}^\circ$ and I_1 are the intensities of the main diffraction peak of the α phase (2,2,0). The former one was measured before the transformation ($T < 400\ °C$), whereas the latter one was obtained at the temperature of the recorded spectrum. I_2 and $I_2{}^{\circ\circ}$ represent the intensities of the main diffraction peak of the β phase (2,2,0); the former was measured at the temperature of the recorded spectrum, whereas the latter was obtained after the end of the transformation ($T > 500\ °C$). Assuming that the diffraction peak (3,1,1) of the β phase, whose relative intensity represents 16%, with respect to the highest line of a pure β-CoMoO$_4$,[15] was superimposed to the main diffraction peak of the α phase (2,2,0), I_1 represents the corrected intensity:

$$I_1(\text{corrected}) = I_1(\text{measured}) - 0.16(I_2)$$

(d) Temperature Programmed Electrical Conductivity Measurements. The temperature programmed electrical conductivity measurements (TPEC) of the sample were measured in a static cell as previously described.[11] A 400-mg amount of the powdered sample was placed between two platinum electrodes under a constant mechanical pressure of 1×10^5 Pa. The experiments can be carried out under different atmospheres (air, reduced pressure of oxygen, vacuum) without affecting the transition temperature. In the present study, a primary dynamic vacuum of 8 Pa was used and maintained during all the experiments. The temperature of both electrodes was given by two soldered thermocouples whose wires were also used, when short-circuited, as conductors for electrical measurements. The electrical resistance of the samples was measured, according to the range investigated, with a Kontron multimeter (Model DMM 4021) or with a digital teraohmmeter (Guildline Instruments, Model 9520). Most of the measurements were carried out with a heating rate r of 5 $°C/min$, but r could vary between 1 and 10 $°C/min$. The samples behaved as bulk conductors and the apparent electrical conductivity σ ($\Omega^{-1}\cdot cm^{-1}$) was calculated from the conductance $1/R$ and by taking into account the geometric factor t/S, in which t is the thickness of the compressed powder (about 0.5 cm) and S the section area of the electrodes (diameter 1 cm): $\sigma = (1/R)(t/S)$. More accurate values of the electrical conductivity were obtained using the apparent volumic weight μ and the mass m of the sample: $\sigma = (1/R)(1/S^2)(m/\mu)$.

Results

(a) Analyses of the Signals Obtained by the Different Techniques. First we will describe the different points that can be determined on the experimental curves obtained using the different techniques. The differential thermal analysis curves are characterized by three points A_1, B_1 and C_1, which can be defined as previously described[17] and are shown in Figure 1. Points A_1 and C_1, which do not precisely correspond to the beginning and to the end of DTA signals, are nevertheless chosen for their reproductibility. Point B_1 which corresponds to the temperature at which the maximum exchanged heat occurs in the transformation is conventionally considered as the transition temperature. A phase transition can be characterized by XRD by following as a function of the temperature the advancement rate λ of the reaction, calculated as described in the Experimental Section. On the curve showing this evolution, three points A_2, B_2, and C_2 can be defined as shown in Figure 2. A_2 represents the temperature above which
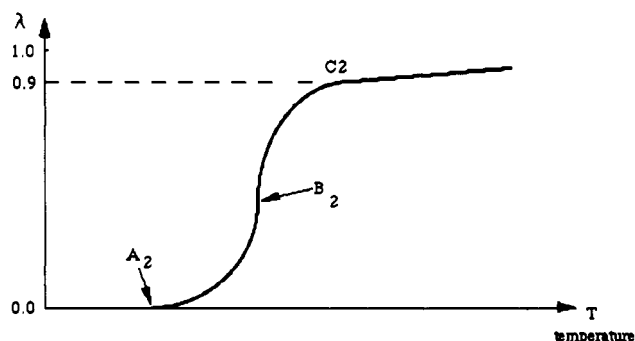

Figure 2. Schematic representation of the advancement rate λ of a phase transition as a function of the programmed temperature.
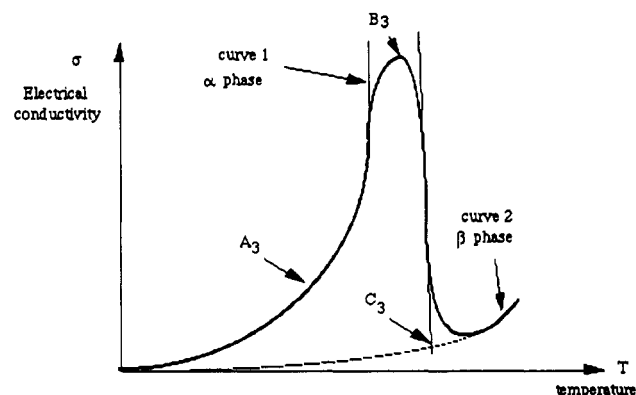

Figure 3. Schematic representation of the variation of the electrical conductivity of a cobalt molybdate powdered sample as a function of the programmed temperature during the transition from the α phase to the β phase.

the β phase can be detected by XRD. Point B_2 represents the temperature at which an inflection point is observed on the λ curve, and point C_2 is arbitrarily chosen as the temperature at which $\lambda = 0.90$.

Before analyzing the signal obtained by TPEC, the principle of the use of the technique to study the phase transition may be outlined. It is generally assumed that the electrical conductivity σ of oxides varies as a function of residual partial pressure P_{O_2} and temperature T, according to the equation

$$\sigma(P_{O_2},T) = CP_{O_2}{}^{1/n}\ \exp(-\Delta H_c/RT)$$

where ΔH_c represents the enthalpy of conduction and C is a constant which only depends on various characteristics of the powdered sample (charge and mobility of the charge carriers, number of contact points between grains, etc.). The exponent n is generally an integer; for a given gas, its value is indicative of the nature of the solid defects which generate charge carriers. Its algebraic sign determines the type of semiconduction (n or p). In the case study of the molybdates phase transition, it has been established that both α- and β-CoMoO$_4$ are p-type semiconductors at atmospheric pressure whereas the former becomes an n-type semiconductor and the latter remains p type when oxygen residual pressure is decreased below 13 Pa.[8,16] Hence, in our experimental conditions (under vacuum), the σ against temperature curves relative to α and β forms are sufficiently distinct to allow the observation of the phase transformation when the temperature is increased, as shown in Figure 3, whereas at atmospheric pressure this transformation cannot be observed.

Thus, as shown in Figure 3, when the temperature is raised, σ values of the sample are placed on curve 1 (α phase) until the polymorphic transition takes place. When this occurs, σ values decrease (curve 2, β phase). The temperature corresponding to the maximum of the resulting curve is generally considered as the temperature of the polymorphic transition α/β.

On the curve showing the variations of σ versus T (Figure 3), three special points A_3, B_3 and C_3 can be distinguished. Their significance can be explained as follows: A_3 corresponds to the
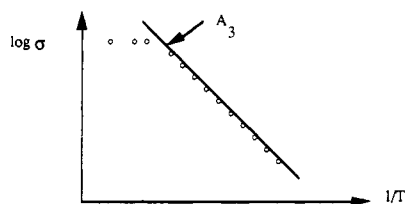
Figure 4. Arrhenius plot of the conductivity showing the beginning of the phase transition of a cobalt molybdate powdered sample (O, experimental points).

TABLE I: Comparison of the Values of Phase Transition Temperature Determined by the Different Techniques at Different Heating Rates for the Compound Fe$_{0.12}$Co$_{0.88}$MoO$_4$ [a]

experimental techniques	heating rate (r) (°C/min)	point A (°C)	point B (°C)	point C (°C)
no. 1 DTA	1	399	411	432
	5	402	420	440
	10	469	500	529
no. 2 XRD	0.1*	375	418	480
	1*	400	430	530
no. 3 TPEC	1	284	414	450
	5	333	416	455
	10	390	415	467

[a] Values marked with an asterisk indicate heating rates were changed by changing the temperature stabilization period from 2 to 45 min.

temperature of the beginning of the reaction; it can be more precisely defined from a curve log $\sigma = f(1/T)$ (Figure 4) since it corresponds to the beginning of a deviation from the van't Hoff law ($\sigma = \sigma_0 \exp(-\Delta H_c/RT)$) which characterizes the initial pure phase. The second point B_3 has, in a previous work,[8] conventionally been considered as the temperature of the transformation; this point will be discussed further. The last point C_3 corresponds to the end of the transformation observed by this technique.

(b) Experimental Results Obtained with the Three Techniques in the Study of a Mixed Iron and Cobalt Molybdate. The mixed iron and cobalt molybdate studied by the three techniques was Fe$_{0.12}$Co$_{0.88}$MoO$_4$. Its specific area measured with the BET method was 1.5 m^2·g^{-1} with a mean particle size of about 1–2 μm.

The α/β phase transition of this compound has been studied using DTA, XRD, and TPEC. The temperatures which correspond to points A, B, and C obtained with the different techniques and with different heating rates are presented in Table I. The determination of the temperature does not present any difficulties, except in the case of the DTA analysis, since the signals recorded for this type of solid transformation were always very sluggish, even after great amplification. Consequently accurate measurements remain very difficult. This is in good agreement with the very low variation of enthalpy for the phase transformation of CoMoO$_4$ (3.6 kJ·mol^{-1}) and of FeMoO$_4$ (0.8 kJ·mol^{-1}).[18]

The effects of the variation of the heating rate on the curves obtained by the three techniques can be visualized in Figure 5. Furthermore, the effects of the variation of the heating rate r on the TPEC values measured at a fixed temperature of 380 °C are shown in Figure 6. The value measured at equilibrium is obtained after heating the sample from 20 to 380 °C at a rate of 10 °C/min and waiting for a stabilization period of 7 h. It is in good agreement with the value obtained by extrapolation to rate zero of the curve in Figure 6.

Discussion

From these results three observations can be made.

(i) Whatever the heating rate, the beginning of the signal variation was always observed by TPEC (points A_3) at a lower temperature than that observed by DTA (points A_1) and by XRD (points A_2). The different sensitivities of the techniques must be considered: DTA and XRD give information about transformations in the bulk of the particles, whereas TPEC is rather sensitive to modifications of their surface due to the contact points between grains. Moreover, it is generally admitted that the de-
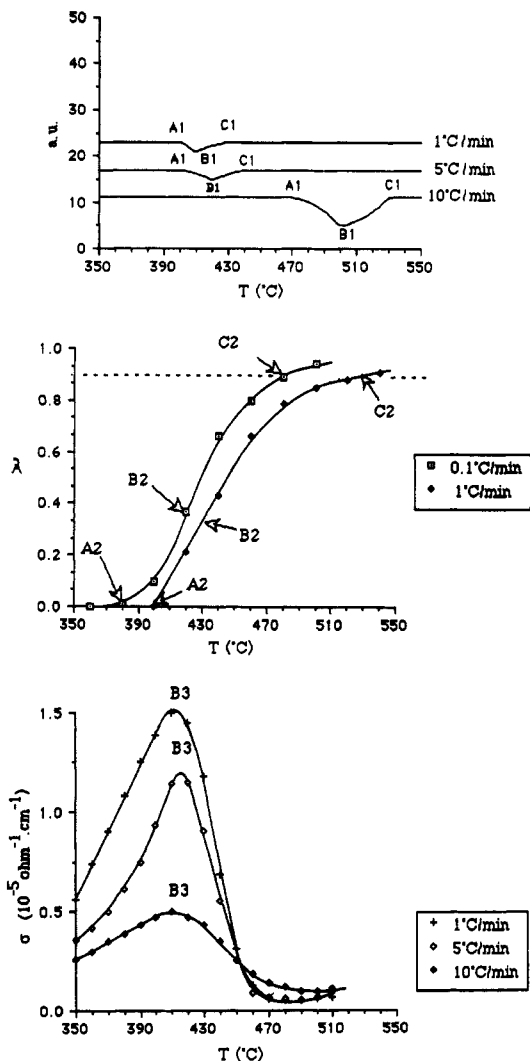

Figure 5. Effect of the variation of the heating rate on the signals corresponding to the α/β phase transition temperature of the compound Fe$_{0.12}$Co$_{0.88}$MoO$_4$: (a, top) effect of the variation of the heating rate on the DTA signal, (b, middle) effect of the variation of the heating rate on λ curves (XRD), and (c, bottom) effect of the variation of the heating rate on the TPEC signal.
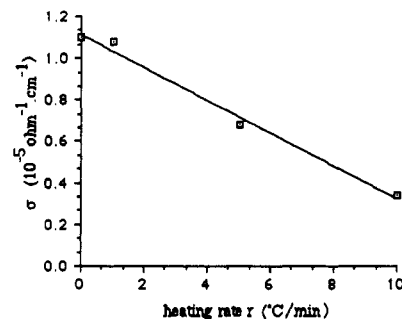

Figure 6. Effect of the variation of the heating rate on TPEC values measured at 380 °C with the compound Fe$_{0.12}$Co$_{0.88}$MoO$_4$.

tection limit by XRD of one crystallographic phase in a mixture is about 5%. This difference of sensitivity can explain that signal variations observed by TPEC always took place at temperatures lower than those observed by XRD. Two possibilities must be considered for the occurrence of a phase transformation: it can either be initiated at the surface of each particle at a given temperature or be only concerned with the bulk of a few particles. If we compare parts b and c of Figure 5, we notice that the temperature corresponding to point B_3 in Figure 5c corresponds to a reaction yield λ in Figure 5b which does not exceed 0.15. Since the conductivity percolation threshold for oxides (the percentage above which one phase, when mixed with others, im-

poses its electrical conductivity value to the overall mixture) is assumed to be about 0.40,[19] the hypothesis of the phase transformation beginning simultaneously at the surface for all the particles seems to be confirmed. Moreover, this is in agreement with the fact that the surface is more rapidly equilibrated in temperature than the bulk and is often characterized by defects (impurities, crystallographic steps, etc.) which can induce the nucleation of the β phase. From that view, the phenomenon observed by TPEC at a temperature (point A_3) 120 °C below the corresponding temperature observed by DTA (point A_1) can be considered more as a surface structural "prearrangement" point occurring before the bulk transition than the beginning of the transition itself. The lower the heating rate, the earlier this prearrangement seems to take place.

(ii) A good agreement was observed between the temperatures of points B_i for lower heating rates r. But when r was increased, the temperatures of points B_1 and B_2 increased, whereas there was no significant effects on the temperatures of point B_3. These observations show that the delay between the transformation of the surface and the bulk increases drastically when the heating rate is increased. On the other hand, the constancy of the temperature of point B_3 indicates that, above this temperature, the β phase is abundant enough on the surface to impose its conductivity, whatever the thickness of the particle transformed.

(iii) A rather limited variation of temperatures corresponding to points C_3 was observed, whereas the temperatures corresponding to points C_1 and C_2 increased drastically. The same interpretation as that proposed for point B_3 can be formulated for the nearly constant value of C_3. At this point ($450 < T < 470$ °C), the surface of all the particles is constituted by the β phase, whereas XRD analysis (Figure 5b) shows that the corresponding advancement rate λ does not exceed 0.60.

Conclusion

Electrical conductivity measurements proved to be extremely sensitive and reproducible in the determination of the polymorphic transition temperatures of cobalt and iron molybdates.

In contrast with DTA and XRD data, TPEC measurements gave information about phase transformation occurring at the surface layers of the grains.

A structural prearrangement of the surface, occurring before the total phase transition, was detected by TPEC measurements at a temperature 120 °C lower than that of any signal given by the other two techniques.

The analysis of the data obtained by the three techniques showed that the phase transformation initiated at the surface of the grains of the molybdate phases and propagated into the bulk. The lower the heating rate was, the smaller the difference in the phase transformation degree between the surface and the bulk. Moreover a surface structural transformation was detected far below the transition temperature, at a temperature which corresponds approximately to the appearance of the catalytic activity of the solid.

This study thus demonstrates the interest of using TPEC. Because of its sensitivity at the surface of the particles, this technique appears well adapted to the study of phase transformation of catalysts.

References and Notes

(1) Le Chatelier, C. R. *Acad. Sci. Paris* **1887**, *104*, 1443.
(2) Mehrotra, P. N.; Chandrashekar, G. V.; Rao, C. N. R.; Subbarao, E. C. *Trans. Faraday Soc.* **1966**, *62*, 3586.
(3) Colleuille, Y. Ph.D. thesis, Lyon, 1955.
(4) Lipsch, J. M.; Schuit, G. C. A. *J. Catal.* **1969**, *15*, 163.
(5) Haber, J.; Nowok, J.; Ziolkowski, J. *Bull. Acad. Pol. Sci., Ser. Chim.* **1973**, *21*, 479.
(6) Dubey, B. L.; Lakshmi, M.; Ishwar, D. A. S.; Tiwari, B. N. *Indian J. Pure Appl. Phys.* **1978**, *16*, 1066.
(7) Yasutoshi, S.; Toshio, M.; Masahiko, I. *Yogyo Kyokaishi* **1980**, *88*, 693.
(8) Ingrain, D.; Thomas, G. *Ann. Chim. Fr.* **1981**, *6*, 515.
(9) Sleight, A. W.; Chamberland, B. L.; Weiher, J. F. *Inorg. Chem.* **1968**, *7*, 1093.
(10) Ponceblanc, H.; Millet, J. M. M.; Coudurier, G.; Legendre, O.; Védrine, J. C. *J. Phys. Chem.*, preceding paper in this issue.
(11) Herrmann, J. M. In *Les techniques physiques d'etude des catalyseurs*; Védrine, J. C., Imelik, B., Eds.; Editions Technip: Paris, 1988; Chapter 22, p 753.
(12) Ingrain, D.; Thomas, G. *C. R. Colloq. Rayons (Montpellier)* **1981**, 99.
(13) Millet, J. M. M.; Sebaoun, A.; Thomas, G. *J. Therm. Anal.* **1984**, *29*, 445.
(14) Ingrain, D. Ph.D. thesis, St.-Etienne, 1983.
(15) Courtine, P.; Cord, P. P.; Pannetier, G.; Daumas, J. C.; Montarnal, R. *Bull. Soc. Chim. Fr.* **1968**, 4816.
(16) Bindo, M.; Steinbrunn, A. *J. Chim. Phys. Phys.-Chim. Biol.* **1988**, *85*, 433.
(17) I.C.T.A., *J. Therm. Anal.* **1975**, *7*, 695.
(18) Courtine, P.; Daumas, J. C. *C. R. Acad. Sci. Paris* **1969**, *268*, 1568.
(19) Ammi, M.; Bideau, D.; Troadec, J. P.; Ropital, F.; Thomas, G. *Solid State Commun.* **1985**, *55*, 1.