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Experimental study of the spreading, due to substitution defects, of the first order transitions in the mixed system $\text{Pb}_3\text{P}_x\text{V}_{2(1-x)}\text{O}_8$ - $\text{Pb}_3\text{V}_2\text{O}_8$

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Résumé. — Des résultats expérimentaux sur le système $\text{Pb}_3\text{P}_x\text{V}_{2(1-x)}\text{O}_8$, obtenus par goniométrie très précise des rayons X, sont présentés. Ils montrent clairement qu'il n'y a pas estompement de l'ordre des transitions quand x varie entre 0 et 1 mais étalement des températures critiques et du taux de transformation, c'est-à-dire du rapport volumique des phases haute et basse température. L'interface entre ces deux phases est décrit.

Abstract. — Experimental results by means of very precise X-ray goniometry on $\text{Pb}_3\text{P}_x\text{V}_{2(1-x)}\text{O}_8$ system are given. They clearly show that there is no smearing of the order of transitions, x varying from 0 to 1, but a spreading of the critical temperature and of the rate of transformation, i.e. the volumic ratio between the high and low temperature phases. The interfaces between the two phases are described.

1. Introduction.

Much attention has been focused upon experimental studies of tricritical points where phase transitions change from first to second order with an external parameter such as hydrostatic pressure, electric field, composition in mixed system, etc. One of the reasons is because it was theoretically shown that the critical behaviours near these points could be, for some cases, exactly described by mean field theories. In the phase diagram of $\text{Pb}_3\text{P}_x\text{V}_{2(1-x)}\text{O}_8$ system two different tricritical points were experimentally reported, one for $x = 0.25$ [1] and the other for $x = 0.72$ [2, 3]. As both pure compounds $\text{Pb}_3\text{V}_2\text{O}_8$ ($x = 0$) and $\text{Pb}_3\text{P}_2\text{O}_8$ ($x = 1$) have highly first order transitions, it was thought that the existence of substitution could drastically modify the critical properties. More generally, the influence of quenched defects (defects which cannot diffuse freely to the thermal equilibrium, such as substitution defects) on critical properties of pure systems have been theoretically studied in the context of second order transitions by several authors. For first order transitions Imry and Wortis [4] have demonstrated that discontinuities can be smeared in some cases by impurities.

The purpose of this study is to give experimental results which show there is no smearing in the order of

the transitions of $\text{Pb}_3\text{P}_x\text{V}_{2(1-x)}\text{O}_8$. It is shown that, when increasing x from 0 or decreasing x from 1, the discontinuities are as strong as for the pure systems $x = 0$ or $x = 1$, and the volumic ratio between the high and low temperature phases decreases smoothly with temperature, the stronger the effect is, the more different from 0 or 1, x is. This point explains the incorrect assertion of tricritical points in the phase diagram of the system. This effect of spreading is in relation with the singular shape of the phase diagram. We also report D.C.A. (Differential Calorimetric Analysis) and birefringence experiments which demonstrate that only precise X-rays measurements can give, for this system, an accurate determination of the order of the transitions. The interfaces between the high and low temperature phases are deduced from strain compatibility.

2. Description of the mixed system.

$\text{Pb}_3\text{P}_2\text{O}_8$ ($x = 1$) is monoclinic $C2/c$ at room temperature (β' phase) and was previously thought to become rhombohedral $R\bar{3}m$ at 180°C (γ phase). But many subsequent experiments show clearly that the behaviour of $\text{Pb}_3\text{P}_2\text{O}_8$ above 180°C is not consistent with rhombohedral symmetry [5]. Specially X-ray diffraction on single crystals and powders reveals persistence of

monoclinic superstructure lines and badly condensed doublets up to about 300 °C, with appearance of extra weak lines above 180 °C [6]. Since the exact nature of this intermediate phase γ' is much debated question (see Appendix A) and since the $\gamma' \rightarrow \beta'$ transition is easily detected by our X-ray diffraction experiments even for $x \neq 1$ (whereas γ' , if it is a real crystallographic phase, is only a very weak distortion of γ) in this article we will only refer to the $\gamma \rightarrow \beta'$ transition although it is in fact the $\gamma' \rightarrow \beta'$ transition.

$\text{Pb}_3\text{V}_2\text{O}_8$ ($x = 0$) is isomorphous to $\text{Pb}_3\text{P}_2\text{O}_8$ in the paraelastic phase $R\bar{3}m$ but exhibits two structural transitions $\gamma \rightarrow \beta \rightarrow \alpha$; β is ferroelastic $P2_1/c$ and possibly antiferroelectric, α is ferroelastic and ferroelectric $A2$ [7].

The study of mixed compounds with $0.7 \leq x \leq 1$ was made by Torres who, on the basis of degeneracy of D.C.A. signals, predicted that the first order transition for $x = 1$ should become second order for $x = 0.7$ [2]. By fitting spontaneous strain and birefringence curves, a change in slope had been deduced at 160 °C which was interpreted as a crossover from a tricritical ($T \leq 160^\circ$) to a classical first order region ($160^\circ \leq T \leq 180^\circ$) [8]. Subsequently birefringence experiments *versus* temperature showed a decrease of jump Δn at T_c , beginning at $x = 0.80$ and vanishing at $x = 0.72 \pm 0.02$, the first reported tricritical concentration [3]. Recently a second tricritical point was predicted for $x = 0.25$ at $\gamma \rightarrow \beta$ by means of dielectric measurements on single crystals and D.C.A. on powders [1]. In a previous article we showed that the $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ transitions are highly first order in the whole range of concentrations where they appear [9]. Here we report a complete study of the phase diagram by means of X-ray, D.C.A. and birefringence measurements.

3. Experiments.

All the compounds $0 \leq x \leq 1$ were synthesized by mixing and melting PbO , V_2O_5 and $\text{NH}_4\text{H}_2\text{PO}_4$ (Merck for analysis) in the appropriate proportions; small single crystals of about 2 mm \times 2 mm \times 0.5 mm were separated from the bulks before grinding. Large single crystals were prepared at C.N.E.T. Bagnaux by the Czochralski method (about 0.5 cm \times 0.5 cm \times 0.5 cm). X-ray diffraction diagrams on powders and single crystals have been obtained on a prototype two axis goniometer [10] with a rotating anode generator of 12 kW. The precision of angle is 10^{-3} °. The structural transitions have been studied from 5 K up to 600 K. For the low temperature studies, the samples are set in a He cryostat, cooled by gaseous conduction; the thermal stability is 0.03 K, the measuring precision is 0.1 K. High temperature studies on powders have been performed in a Rigaku furnace with stability of 1 K and precision of 2 K, and the single crystals were set in a prototype furnace with same performance. D.C.A. was

performed with a calorimeter DSC 111 (Setaram). Temperature programming was from 2 K min^{-1} to 1 K h^{-1} .

4. Results and discussion.

4.1 PHASE TRANSITIONS AND TRICRITICAL POINTS.

— The prototype goniometer allowed the very precise determination of crystallographic parameters and discontinuities at transitions. The spontaneous strain tensor components e_{11}^s and e_{13}^s are the macroscopic quantities quadratically coupled to the order parameter. Their temperature dependences are shown in figure 1a for $\gamma \rightarrow \beta \rightarrow \alpha$ for some compositions with $x \leq 0.3$. The transitions are highly first order as long as they occur, the jumps at T_c being almost concentration independent. The curves are linear in practically the whole range of temperatures, because the transitions are so first order that the system doesn't reach the weak fluctuations regime described by the Landau theory.

The strain components for the $\gamma \rightarrow \beta'$ transition are compared (Fig. 1b) for two extreme compositions $x = 1$ and $x = 0.7$. The discontinuities at the pseudorhombohedral-monoclinic transition are even higher for $x = 0.7$ than for $x = 1$. It can be seen on the e_{13}^s *versus* T curves (Fig. 1c) that the slope change, at $T_0 = 433$ K (160 °C) for $x = 1$, which has been attributed to a departure from a tricritical to a first order regime [8], as well exists for $x = 0.7$ at $T_0 = 180$ K.

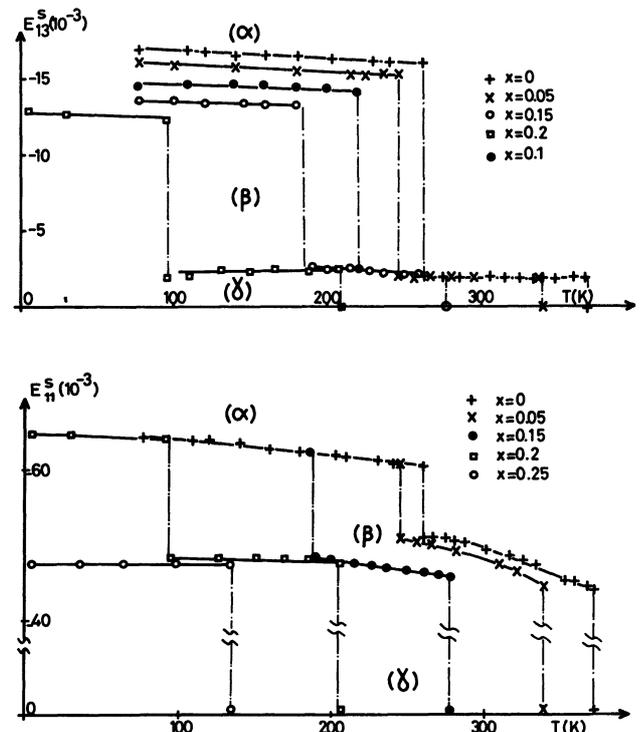


Fig. 1a. — Spontaneous strain tensor components e_{11}^s and e_{13}^s *versus* temperature for different compositions $x \leq 0.3$.

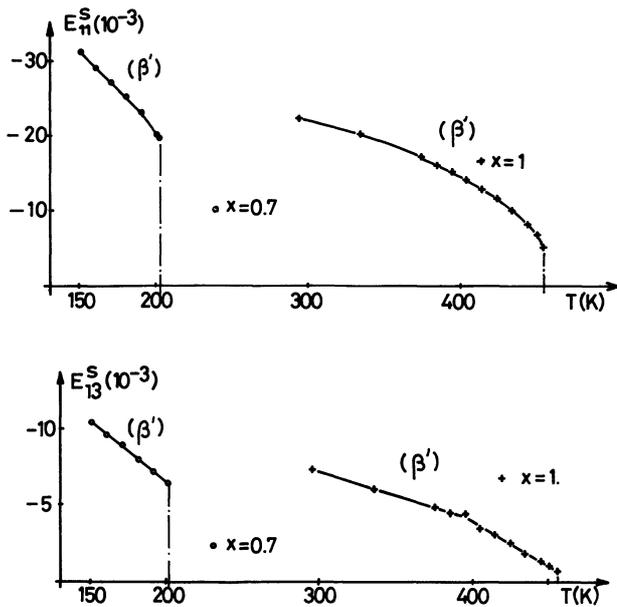


Fig. 1b. — Spontaneous strain tensor components e_{11}^s and e_{13}^s versus temperature for $x = 1$ and $x = 0.7$.

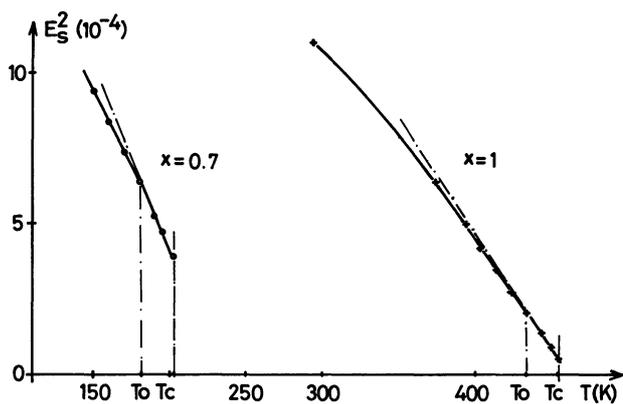


Fig. 1c. — Spontaneous strain tensor modules e_s^2 versus temperature for $x = 1$ and $x = 0.7$.

Moreover for both compositions $T_c - T_0$ has the same value (20°), so the two compounds are equally far from a tricritical point. This cross over was obtained by Guimaraes [8] by fitting e_s versus T with a fourth order in the η Landau coefficient b' , zero for $T < 433$ K and temperature dependent above 433 K. Torres showed [5] that if b' is assumed to be temperature dependent as in reference [8], the whole curve versus T can be fitted from 293 K (20°C) to 453 K (180°C) by a first order regime as well.

In a previous paper the martensitic-like behaviour of the transitions for $x < 0.3$ was emphasized [9]. In fact the phenomenon exists whatever $0 \leq x \leq 1$ is: the transformations in the system are a shear mechanism with orientation relationships between the high and low temperature phases and very large phase coexistences

and hysteresis. The latter point is revealed in figures 2a, 2b where the volumic ratios of phases versus T and x are plotted. It can be seen that substitution on $\text{Pb}_3\text{P}_2\text{O}_8$ or $\text{Pb}_3\text{V}_2\text{O}_8$ makes the transitions spread over a greater and greater temperature range up to give a non-zero volumic ratio down to 5 K for x near 0.685 and x near 0.22. Therefore the critical temperatures were chosen at the beginning of transformation on cooling. They are plotted in the phase diagram (Fig. 3); it is characterized by a very strong decrease of T_c with vertical tangents at 0 K. It is because of this large increase of slopes $\frac{dT_c}{dx}$, up to infinity, and the existence of local fluctuations of the substitution defects

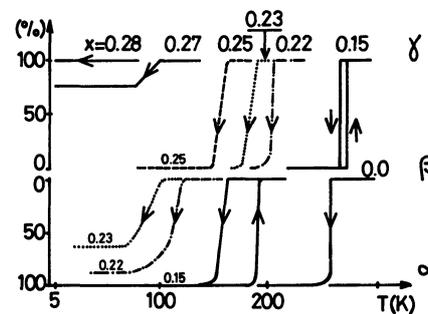


Fig. 2a. — Evolution of the volumic ratios of the phases versus temperature for single crystals with $x \leq 0.3$.

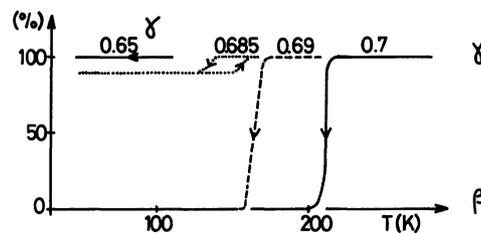


Fig. 2b. — Evolution of the volumic ratios of the phases versus temperature for single crystals with $x \geq 0.68$.

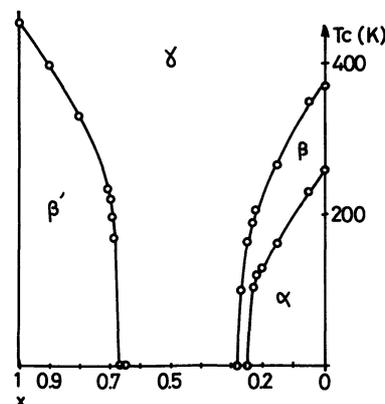


Fig. 3. — Phase diagram of the $\text{Pb}_3\text{P}_2\text{O}_8\text{-Pb}_3\text{V}_2\text{O}_8$ system.

density throughout crystals that the transitions spread over more and more. So the crystals with concentrations near the vertical boundaries have non zero volumic ratio down to 5 K.

For $0.7 \leq x \leq 1$ we studied the first order transition by D.C.A. on the same single crystal used in X-ray experiments. We obtained the same results as Torres [2]: a drastic weakening of signals, but too strong to be accounted for only by the phase coexistence. A hypothesis for the explanation of the contradiction between X-ray and D.C.A. measures is to assume that vanadium substitution acts as a pressure so that $\frac{dT_c}{dP}$ and $dT_c/d(1-x)$ may be compared. As $dT_c/d(1-x)$ hugely increases in the phase diagram, through Clapeyron relation $\left(\frac{\Delta P}{\Delta T}\right)_{T=T_c} = -\frac{\Delta H}{T\Delta V}$ (ΔV is about the same, whatever $0.7 \leq x \leq 1$ is) the apparent weakening of latent heat may be explained. Moreover it could be a general property for phase diagrams with vertical or sharp boundaries. Experiments are in progress to measure $\frac{\Delta P}{\Delta T}$, at $T = T_c$, for different compositions in order to test this hypothesis.

The single crystals used in the birefringence experiments [3] were prepared by the Czochralski method so that the fluctuations of x are much greater than in the small crystals, prepared from cooling baths, which we used in X-ray diffraction. Moreover these fluctuations in the large crystals are certainly not local deviations around an average value but rather a gradient throughout the bulk. This certainly created a huge phase coexistence making the assertion of a tricritical point $x = 0.72$ incorrect. The results of our own birefringence experiments performed at C.N.E.T. Bagnex go to the same effects: we have performed birefringence experiments on three single crystals prepared by the Czochralski method $x = 0.15$, $x = 0.71$, $x = 0.695$. For the compounds $x = 0.15$ it is unambiguously known [9, 5] that the transitions $\gamma \rightarrow \beta \rightarrow \alpha$ are highly first order. However our birefringence experiments display no discontinuities. This result clearly reveals impossibility to deduce the order of transitions in this system from only birefringence experiments. For the other two

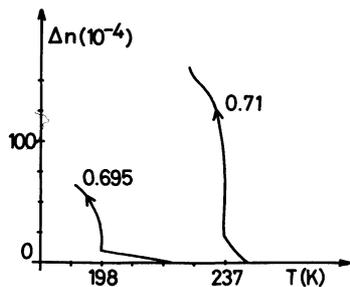


Fig. 4. — Birefringence versus temperature for single crystals with $x = 0.71$ and $x = 0.695$.

samples, birefringence could only be studied in the vicinity of T_c as the appearance of domains avoided meaningful measurements far below T_c . Although rather inconclusive, these experiments (Fig. 4) seem to go against the existence of a tricritical point at $x = 0.72 \pm 0.02$.

4.2 GRINDING EFFECTS. — When small single crystals are ground into powder there is an increase of spreading of transitions. This phenomenon, which is more important for the rich vanadium compounds, is observed even for the pure compounds $x = 0$ (Fig. 6). Moreover the phase coexistence remains down to 5 K and appears to be slightly grain size dependent (Fig. 6). Thermal evolution of the phase volumic ratios are given in figure 5a and 5b, for various x values. These grinding effects probably originate in local variations of strains created by grinding, as it is suggested by the important hysteresis observed for powder samples. This huge phase coexistence on powder samples induced an

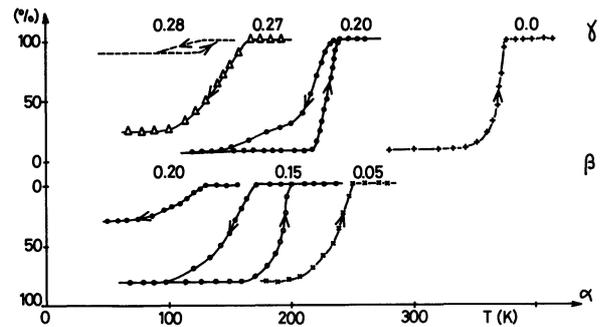


Fig. 5a. — Evolution of the volumic ratios of the phases versus temperature for powder samples with $x \leq 0.3$.

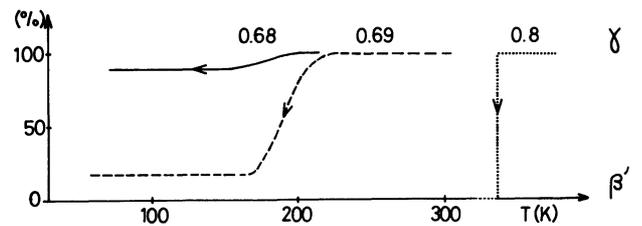


Fig. 5b. — Evolution of the volumic ratios of the phases versus temperature for powder samples with $x \geq 0.68$.

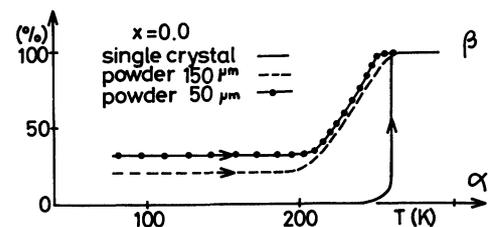


Fig. 6. — Grinding effect on the evolution of the volumic ratio of the phases in the transitions of $x = 0.0$.

incorrect determination of the space group ($P2_1$ instead of $A2$) reported in the literature. This led to an inaccurate description of the $\beta \rightarrow \alpha$ transformation, see Appendix B. Likewise D.C.A. signals exhibit drastic weakening and broadening when grinding, specially for the $\beta \rightarrow \alpha$ transition on cooling run, for which no signal is detected (Fig. 7). This explains the incorrect assertion of a tricritical point for $x = 0.25$ [1] partially based on the weakening of D.C.A. signal on powder samples.

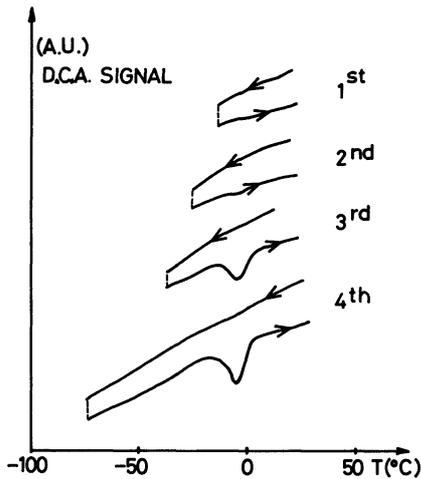


Fig. 7. — D.C.A. signal at $\beta \rightarrow \alpha$ transition for $x = 0$ as a function of the lowest reached temperature on cooling and heating runs.

4.3 INTERFACE BETWEEN THE HIGH AND LOW TEMPERATURE PHASES. — The spreading of the critical temperature is a characteristic of martensitic transitions. Classically competition between volumic, surface and elastic energies accounts for the existence of a critical size of low temperature phase embryos R_c . This size R_c is shown to decrease with temperature so that spreading appears.

Martensitic transformations in metals and alloys progress by a planar interface between the high and low temperature phases called habit plane. An important step is made when one is able to write down the crystallographic orientation relationships between the

two phases and to give the orientation of the habit plane, which is not obviously a Miller's plane. For $\text{Pb}_3\text{P}_2\text{V}_2(1-x)\text{O}_8$, as explained in reference [9], the orientation relationships are obvious since every phase can be described in a common monoclinic cell (no rotation of axes during transitions occurs, only distortions). In order to find out the habit plane we can adapt the procedure used by Sapriel for finding ferroelastic walls [15]: the macroscopic vectors in the habit plane must have the same elongation at T_c . We must here use a reference frame common for all phases i.e. the same used for spontaneous strain (Ref. [15]) $\mathbf{X} = \mathbf{c}_{\text{mono}}$, $\mathbf{Y} = \mathbf{b}_{\text{mono}}$, $\mathbf{Z} = a_{\text{mono}} \sin \beta \mathbf{i}$ (\mathbf{i} on the high temperature threefold axis), but on the contrary of Sapriel's procedure we must here use the normal strain components, as for instance the high and low temperature phases differ in e_{33} when $e_{33}^s = 0$. So we may write :

$$\begin{aligned} (e_{ij}(T_c)_{\text{H.T.}} - e_{ij}(T_c)_{\text{L.T.}}) x_i x_j = \\ = \Delta_{ij}(T_c) x_i x_j = 0 \quad (1) \end{aligned}$$

and using the same reasonnement as Sapriel, say that the equation (1) is a cone which has a singular point, the apex 0. It can't be a physical solution for habit plane unless it degenerates into plane that is :

$$\det \Delta_{ij}(T_c) = 0 \quad (2)$$

i.e. for $\bar{3}m$ F2/m species :

$$\Delta_{11} \Delta_{22} \Delta_{33} - \Delta_{13}^2 \Delta_{22} = 0. \quad (3)$$

We have applied this procedure to the compounds with $x < 0.3$ and found that if equation (3) is satisfied (see below) the habit plane for $\gamma \rightarrow \beta$ has equation on XYZ orthonormed axis

$$x (\Delta_{11}(T_c))^{1/2} \pm y (\Delta_{22}(T_c))^{1/2} = 0$$

and for $\beta \rightarrow \alpha$

$$\begin{aligned} x (\Delta_{11}(T_c))^{1/2} \pm y (\Delta_{22}(T_c))^{1/2} + \\ + z (\Delta_{33}(T_c))^{1/2} = 0. \end{aligned}$$

These planes are not crystallographic planes but of course can be approached with high Miller indices. In table I we give the numerical values of these planes.

For $\text{Pb}_3\text{V}_2\text{O}_8$, Manolikas made electronic microscopy experiments and demonstrated that both transitions

Table I. — Coefficients of the equation of the interface plane at the $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ transitions for $x < 0.3$ in the orthogonal spontaneous frame.

	$(\Delta_{11}(T_c))^{1/2}$	$(\Delta_{22}(T_c))^{1/2}$	$(\Delta_{11}(T_c))^{1/2}$	$(\Delta_{22}(T_c))^{1/2}$	$(\Delta_{33}(T_c))^{1/2}$
	$\parallel c \parallel$	$\parallel b \parallel$	$\parallel c \parallel$	$\parallel b \parallel$	$\parallel a \sin \beta \parallel$
$x = 0$	0.623	1.267	0.353	0.490	0.560
$x = 0.20$			0.418	0.656	0.515
$x = 0.25$	0.680	1.334	no more transition		
		$\gamma \rightarrow \beta$	$\beta \rightarrow \alpha$		

occur with sharp front [11] ; for $\gamma \rightarrow \beta$ he was able to photograph and to determine the habit plane : he found the ratio of the two-dimensional Miller indices to be equal to ± 1.45 , value to be compared with our own finding

$$\frac{(\Delta_{22}(T_c))^{1/2} \|\mathbf{b}\|}{(\Delta_{11}(T_c))^{1/2} \|\mathbf{c}\|} = 1.43 .$$

Other evidences of the martensitic mechanism are our experiments of D.C.A. on single crystals and powders : experiments on single crystals ($x = 0.15$) reveal that the first order peak for $\gamma \rightarrow \beta$ is decomposed when passing through the transition very slowly (1 K h^{-1}) into numerous sharp little peaks with critical temperatures slightly different. This process is to be compared with Barkausen pulses in BaTiO_3 for instance : it seems likely that each pulse is associated with the nucleation and growth of the low temperature domains by creation and displacement of habit planes. The described mechanism strictly supposes that equation (3) is fulfilled. It can be seen that (Fig. 8) this equation is proved to be strictly correct for $\beta \rightarrow \alpha$ with $x \leq 0.1$, and for $\gamma \rightarrow \beta$ with x in the vicinity of the boundary concentration 0.28. As for $x = 0$ the mechanism have been verified by Manolikas, it seems that here, as for non-permissible domain ferroelastic walls described by Sapriel [15], the high and low phases manage to adapt each others ⁽¹⁾.

This procedure could of course be applied to rich phosphorus compounds but we have no experimental

⁽¹⁾ We have recently come across the paper of Boulesteix *et al.* [12] where they made a systematical resolution of equation (2) for all possible ferroelastic species. However they voluntarily neglected the possible change of volume at transitions i.e. they used spontaneous strain tensor for each species. They demonstrated that in $3\text{mF}2/\text{m}$ species, equation (2) can only have approximate solutions when using spontaneous tensor. Here we have demonstrated that because of the high first order transitions, that implies to not neglect the non spontaneous strain components, there can be for certain special values of strain components an exact solution for equation (3) (for $\gamma \rightarrow \beta$ with $x = 0.28$ and $x \leq 0.10$ for $\beta \rightarrow \alpha$). This require of course a very precise knowledge of jumps in crystallographic parameters. More generally, taking the whole strain at transitions into account can modify Boulesteix's results in such a way as making permissible solutions normally forbidden, or the opposite. We have already pointed out that important atomic shifts at $\gamma \rightarrow \beta$ occur in layers orthogonal to the threefold axis, leading to a foil aspect of single crystals after transition [9] ; in his paper Boulesteix gives a possible reason of existence of habit plane when the equation (3) is not fulfilled : because of existence of thin foils at transitions the equation could be valid in each foil « because the intersections of the cone with the plane of the foil, assumed to pass through the apex of the cone, are lines independent of the origin chosen ». Roughly speaking, in a thin foil a cone « looks like » two planes.

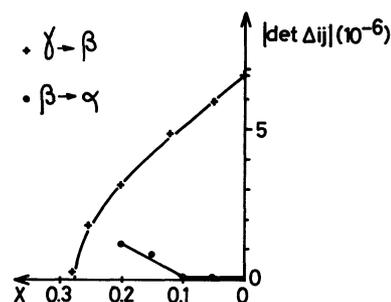


Fig. 8. — Variation of the condition of strain compatibility versus x for $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ transitions.

evidences of the existence of an habit plane : for $x = 1$ there is no decomposition of D.C.A. peak and for $x = 0.7$ the signal is too weak. As the phase coexistence on powders only occurs for x in the vicinity of 0.69 it is likely that the previously described mechanism nevertheless exists near this concentration.

5. Conclusion.

X-ray measurements have unambiguously shown that the substitution defects do not induce any weakening of the transition discontinuities of $\text{Pb}_3\text{P}_{2x}\text{V}_2(1-x)\text{O}_8$, but a spreading in temperature with important phase coexistences. The transitions have been described by means of analogy with martensitic transformations. The described mechanism as well as the phase diagram have helped us to explain the wrong conclusions deduced from D.C.A. and birefringence results reported in the literature.

Acknowledgements.

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Appendix A.

ABOUT THE γ' INTERMEDIATE PHASE OF $\text{Pb}_3\text{P}_2\text{O}_8$.

— Two different interpretations for the same X-ray pattern in the intermediate phase γ' were reported. For Joffrin [6] the macroscopic room temperature ferroelastic domains $\text{C}2/\text{c}$ transform at 453 K (180°C) into a microstructure of same symmetry with very small monoclinic distortion and quasi rhombohedral cell-parameters. These microdomains are related three by three by the high temperature threefold axis, giving rise to the extra lines, the real monoclinic-rhombohedral transition occurring at about 573 K (300°C). Torres interpreted the same pattern by the existence between 453 K and 573 K of a superstructure $\text{C}2/\text{c}$ ($Z = 16$) so that the phase sequence should be $\text{R}3\text{m}$ ($Z = 1$) \rightarrow $\text{C}2/\text{c}$ ($Z = 16$) \rightarrow $\text{C}2/\text{c}$ ($Z = 4$) [13]. This interpreta-

tion was supported by a phenomenological study of the Landau development in the $R\bar{3}m$ symmetry. In order to clarify these points we are reinvestigating $\text{Pb}_3\text{P}_2\text{O}_8$ by means of X-ray diffraction and D.C.A. on single crystals and powder from room temperature up to 900 K. Our preliminary results confirm the persistence of monoclinism above 453 K but there are two major difficulties to the occurrence of a superstructure $C2/c$ ($Z = 16$). First, from a theoretical point of view, the superstructure is stabilized, in the phase diagram built from Landau free energy, when one invariant of order eight becomes as large as one invariant of order four, which seems to us unlikely; second, from an experimental point of view, some extra lines which must exist in the $C2/c$ ($Z = 16$) phase but not in the microdomains $C2/c$ ($Z = 4$) are not observed.

So it seems to us that the Joffrin's explanation squares better with experiences although we don't have any conclusive experimental evidences so far. Nevertheless the physical origin of such a nucleation of microdomains related by a high temperature symmetry, at the isomorph transition $C2/c$ ($Z = 4$) \rightarrow $C2/c$ ($Z = 4$), is not quite clear; whereas in incommensurate system near lock-in temperature this situation is naturally explained by nucleation of $1q$ solitons with negative surface energy separating commensurate domains. The occurrence of an incommensurate phase above 453 K should explain the observed texture, in a

similar way as in quartz. Experiments are in progress in order to test this assumption by very precise diffractometry on superstructure lines. Our preliminary results confirm that the γ' phase is in fact incommensurate.

Appendix B.

ABOUT THE $\beta \rightarrow \alpha$ TRANSITION MECHANISM IN $\text{Pb}_3\text{V}_2\text{O}_8$. — The mechanism for $\beta \rightarrow \alpha$ ($x = 0$) which was previously described, is a simultaneous condensation of two irreducible representations at two different points of the Brillouin zone, one triggering the other [14]. In fact there is no sub-group relation between β ($P2_1/c$) and α ($A2$ instead of $P2_1$), however $A2$ is a sub-group of $R\bar{3}m$, and the transition $A2 \rightarrow R\bar{3}m$ really occurs when a hydrostatic pressure is applied. Moreover the cell parameters *versus* T for the α phase are in exact prolongation of those of the γ phase. Thus, in addition to the condensation of an irreducible representation in point F leading to $R\bar{3}m \rightarrow P2_1/c$, there is certainly a zone centre Γ mode, soft enough in the trigonal phase, and normally giving rise to $R\bar{3}m \rightarrow A2$, but crossed by the other mode. This point is also supported by the fact that in both β and α phases, atomic positions are very close and no important atomic motion is required to go from one to the other [7].

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