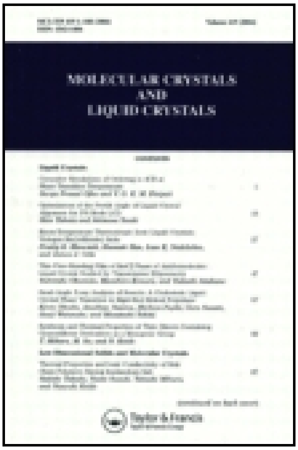

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CHARGE DENSITY WAVES OR WIGNER PARA-CRYSTAL IN 1-D BIS (OXALATO) PLATINATE SALTS ?

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Abstract Further structural evidence is presented, with particular reference to some 1-D (oxalato) platinates, for the existence in these systems of a superstructure of electrons (or holes) which is locally commensurate with the underlying lattice but statistically incommensurate along the chains.

INTRODUCTION

For over a decade the superstructure observed by diffraction techniques in quasi-1D Pt chain compounds has been attributed to a charge density wave state whose stabilization in 3 dimensions leads eventually to an insulating state. We have shown however two years ago that in 1-D bis (oxalato) platinate salts $Mt_x[Pt(C_2O_4)_2].6H_2O$, abbr. Mt-OP, forming an isostructural series when Mt is a bivalent cation and x ≈ 0.82, there is below a given transition temperature a characteristic combination of displacive modes having specific symmetries (Fig.1a), [1]. The ONE/TWO ratio between the periods of the longitudinal and transverse modes has been related to an ordering of the excess electrons (or holes) in the Pt chains. This ordering, which is locally commensurate with the underlying lattice, but statistically incommensurate, leads to the formation along the chains of micro-domains arranged around mean boundary planes which may be perpendicular or inclined with respect to the chain axis ; consequently the valence states will have a certain amount of separate identity. Based on this model the calculated satellite spectrum in Co-OP, where the wave vector $\vec{\Omega}$ is parallel to the conduction axis $\vec{c}$, has been shown to reproduce the extinction rules among the satellites and the overall variation of the satellite intensities [1].

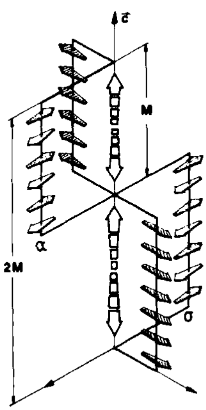


FIGURE 1a

RESULTS

We present here new experimental observations which may be decisive for discriminating between the two viewpoints. The results, illustrated by examples, can be stated as follows :

I - the displacive mode waves have non-sinusoidal character ;

II - the ordering process always takes place along crystallographic planes ;

III - the satellite superlattices (SSL) show crystal polymorphism. Two or more SSL phases can coexist in the same host crystal ; the coexisting phases may not have the same dimensionality ;

IV - Similar extinction rules hold for the various SSL.

Statement I is substantiated by 2 examples where Mt=Fe and Mg. In Fe-OP a SSL phase D has been obtained where harmonics reaching order 4 could be unambiguously indexed. (Fig.4a and 4b. In figure 4b we present the reconstructed reciprocal lattice of the Weissenberg photograph of figure 4a ; shown is the (hol) layer of a twinned fundamental monoclinic lattice and its associated superlattice with terms reaching the fourth order). Similarly third order satellite layers are visible on an oscillation photograph of Mg-OP (Fig.6). The magnitude of the high order harmonics is not compatible with a simple sinusoidal wave.

Statement II means that we have always found $\vec{\Omega}$ parallel to a vector of the reciprocal fundamental lattice. Except for Co-OP, Zn-OP, where $\vec{\Omega}$ is usually perpendicular to the (001) plane, the ordering planes of the phases we examined are listed in table I. An illustration of what we mean by "ordering plane" (domain frontier or boundary previously introduced [1][2]) is shown in Fig.1b, as reproduced from a study by H.J. Leamy and G.H. Gilmer on the roughening transition [3]. Along such a plane is represented the interchain fluctuation existing below the transition temperature. An intrachain fluctuation of the type first introduced by K. Fujiwara also exists along the chain [4]. As already pointed out both fluctuations may result in a weakening of the satellites so that the absence of high order does not necessarily mean the presence of a sinusoidal wave [1][2].

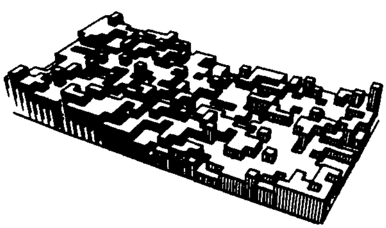
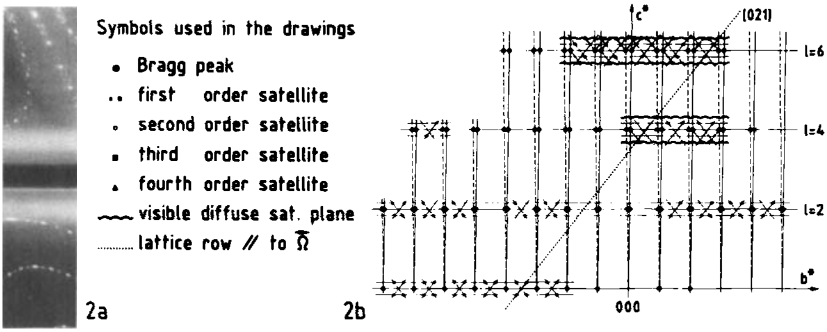
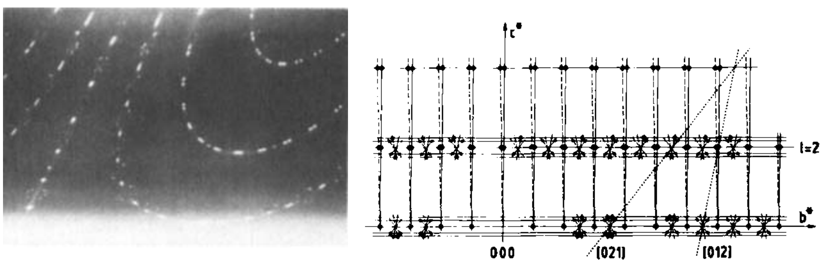


Figure 1b. Surface roughening after Leamy and Gilmer [3].

Statement III is illustrated by results obtained in Fe-OP and Mg-OP. As previously reported [1], in Fe-OP one obtains generally below the transition temperature a SSL

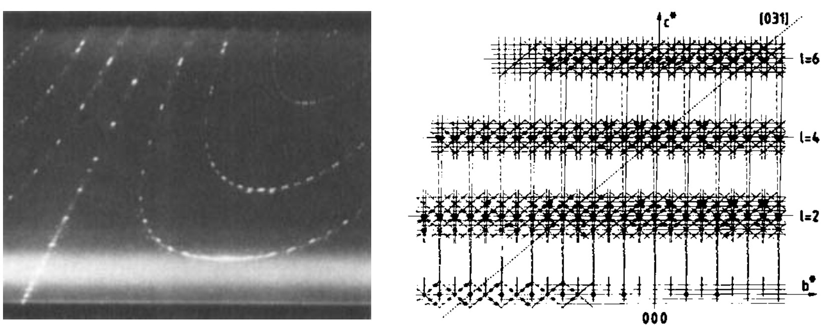


FIGURES 2a, 2b : Superlattice phase A in Fe OP. (0kl) layer



3a 3b

FIGURES 3a, 3b : Superlattice phases A and B in Fe OP. (0kl) layer

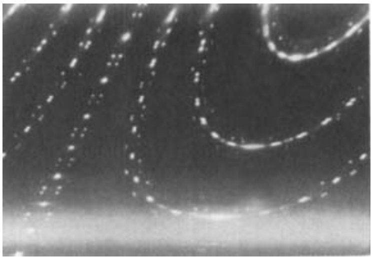


4a 4b

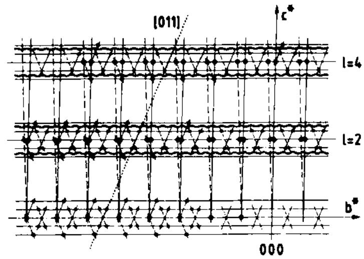
FIGURES 4a, 4b : Superlattice phase D in Fe OP. (0kl) layer

TABLE I

Superlattice phase	Fe OP (A)	Fe OP (B)	Fe OP (C)	Fe OP (D)	Mg OP (α)	Mg OP (β)	Cu OP
Plane of crystallization	(021)	(012)	(001)	(031)	diffuse	(011)	($\bar{3}$01)



5a



5b

FIGURES 5a, 5b : Superlattice phases α and B in Mg OP. (0kl) layer

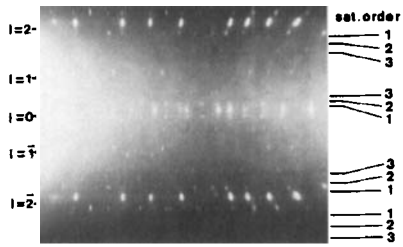


FIGURE 6 : Mg OP: oscillation / $\vec{c}$

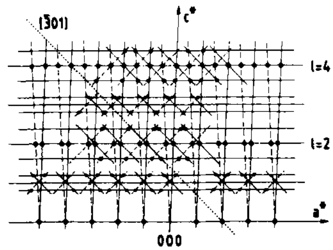


FIGURE 7 : Cu OP. (h0l) layer

phase A with $\vec{\Omega}$(A) parallel to [021] (Fig.2a,2b). Sometimes the SSL phase A appears in association with another SSL phase B, with $\vec{\Omega}$(B) parallel to [012], both phases being related to the same twinned monoclinic fundamental lattice (Fig.3a,3b). Phase A has been also observed in association with a phase C, $\vec{\Omega}$(C) being // to [001] of an orthorhombic lattice. In Mg-OP two superlattices α and B are seen to coexist at least between T_c = 283K and 77K (Fig.5a,5b). The 3-D SSL phase B which appears below T_c has a wave vector $\vec{\Omega}$(B) parallel to [011] ; it is distinct from the phase α displaying only diffuse satellite planes and which is therefore ordered in one dimension only.

In connection with statement III it may be of interest to point out some of its consequences regarding the physical properties of these systems. It has been claimed in this conference by Carneiro et al. that there is evidence for a devil's staircase structure in some compounds showing a chaotic behaviour of the conductivity in the Mt-OP series [5]. For example in Mg-OP, where only chaos is observed, they assume that a competition between 2 instabilities, namely the Peierls instability and the ordering of the cations, with wave vector q_{Mt}, leads to a stepwise devil's staircase behaviour because $q_{Mt} << k_F$ [6]. Apart from the fact that the mentioned differences cannot be considered as a proof for the *existence* of such a structure, it is difficult to see how q_{Mt} might be arbitrarily different from k_F in the *same* phase. As suggested by our results, there exists in Mg-OP a competition between 2 superlattice phases rather than between 2 ordering periods, which are essentially correlated. Mixed physical properties will result in Mg-OP from the coexistence in the same system of SSL phases with different dimensionality.

Statement IV, which would require lengthy comments, is briefly illustrated by the (hol) layer of Cu-OP (Fig.7), showing the same "optic" displacive mode α (Fig.1a) as in the (hol) layer of Co-OP, [1] ; likewise the (okl) layers of Fe-OP(A) (Fig.2b), and Fe-OP(D) (Fig.4b), show the same "acoustic" modes σ (Fig.1a) as the (okl) layer of Co-OP [1].

CONCLUSION

The experimental facts which we have gathered, characterized by the presence in the 3-D regime of high order satellite harmonics, lattice polymorphism, systematic extinction rules in the satellite spectrum and a specific pattern of displacive modes are difficult to reconcile with a simple sinusoidal CDW modulation. They rather satisfy criteria typical of lattice order. The concept we have previously introduced of an electronic lattice order which is locally commensurate with the underlying lattice, but statistically incommensurate along the chains, appears more suitable for meeting the various structural requirements ; such a system implies, as pointed out also by H. Nagasawa, a certain degree of mixed discrete valency [7]. By analogy with the case of magnetite Fe_3O_4, where the mobile charges become ordered below a sharp Verwey transition, a similar description in terms of a Wigner (para or quasi)-crystal appears here equally possible for defining the type of prevailing order together with the spatial and temporal fluctuations which are present in the structures reported here [8].

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