

## Growth of High Quality $\text{Per}_2\text{M}(\text{mnt})_2$ Single Crystals; Evidence of $\beta$ -Phase in $\text{Per}_2\text{Pt}(\text{mnt})_2$

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*The conditions for obtaining single crystals of  $\text{Per}_2\text{Pt}(\text{mnt})_2$  via an electrochemical process are described. The occurrence of a lower conductivity  $\beta$ -phase cannot be avoided. Thermal dependence of resistivity and thermopower of  $\beta$ - $\text{Per}_2\text{Pt}(\text{mnt})_2$  is reported and results discussed in comparison with previously known  $\beta$ -phase members ( $M=\text{Cu}$  and  $\text{Ni}$ ) of the  $\text{Per}_2\text{M}(\text{mnt})_2$  family.*

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### 1. INTRODUCTION

Perylene-based conductors with metallic conductivity over a large temperature range are known since 1980<sup>1,2</sup>. In particular, the members of  $\alpha$ - $\text{Per}_2\text{M}(\text{mnt})_2$  ( $\text{mnt}=\text{maleonitriledithiolate}$  and  $M= \text{Au}, \text{Co}, \text{Cu}, \text{Fe}, \text{Ni}, \text{Pd}$  and  $\text{Pt}$ ) exhibit metal-to-insulator(M-I) phase transitions, ascribed as Peierls instabilities, with critical temperatures ranging from 8 K (Pt) to 73 K (Co).

More recently, magnetoresistance measurements on  $\alpha$ - $\text{Per}_2\text{M}(\text{mnt})_2$  ( $M= \text{Au}, \text{Pt}$ ) under high-magnetic field revealed not only that the low temperature CDW could be suppressed in an anisotropic fashion, but also the emergence of a cascade of field induced charge density wave transitions, resulting in an unconventional phase diagram.<sup>3,4</sup> The growing interest in this system and large demand for samples, makes it mandatory to use the most fiducial procedures to get crystals suitable for different studies.

Besides crystal quality, it is necessary to be aware that for identical starting chemical mixtures of perylene,  $\text{M}(\text{mnt})_2$  salts and solvents, compounds with different stoichiometries can be obtained or polymorphism can occur. In fact besides the common 2:1 perylene: $\text{M}(\text{mnt})_2$  stoichiometry, the 1:1 (with inclusion of solvent)<sup>5</sup> and 4:3 were obtained for  $M=\text{Co}$ <sup>6</sup> and a 1:1 compound is also known for  $M=\text{Pt}$ <sup>7</sup>. The existence of a  $\beta$ -phase, with the

same 2:1 stoichiometry, was shown by Gama *et al.*<sup>8</sup> for M=Cu and Ni. In this paper, we present evidence for the existence of the  $\beta$ -phase for M=Pt too.

## 2. CRYSTALLISATION

Although the earlier samples of  $\text{Per}_2\text{M}(\text{mnt})_2$  were obtained by oxidation of perylene with iodine in the presence of  $n\text{-Bu}_4\text{N}[\text{M}^{\text{III}}(\text{mnt})_2]^{1,9}$ , we will discuss hereafter only the electrocrystallisation process, the most widely used procedure for obtaining molecular conductors, which however depends on numerous factors<sup>10</sup>.

In our systematic study, some factors remained constant for simplification. First, the electrodes were always made of platinum, wire for the anode, and wire, grid or foil for the cathode. Electrodes were polished with alumina and used alternately as anode and cathode in acidulated water, rinsed with distilled water and dried prior to use. Second, the type of cell, although varying in shape and volume, was always a two-compartment cell separated by a porous fritted disc. Finally, the solutions were always de-aerated with nitrogen or argon.

The choice of galvanostatic or potentiostatic method was in favour of the first, as the later yields larger amounts of material but as microcrystalline powder, e.g. for M = Cu and Ni but favouring the  $\beta$ -phase. After the choice of constant current, the main variables remained the solvent, concentrations, temperature and current density. Solvents in which perylene and  $n\text{-Bu}_4\text{N}[\text{M}(\text{mnt})_2]$  are both soluble, revealed in general a limitation of perylene solubility. Acetonitrile and THF in which perylene has larger solubility than in dichloromethane yielded formation of dendritic crystals. Dichloromethane and 1,1,2-trichloroethane were the single solvents in which better macroscopic results were obtained: bundles of long crystals, easily separable and with shiny faces. No improvements resulted from mixtures of solvents such as dichloromethane with acetonitrile or THF.

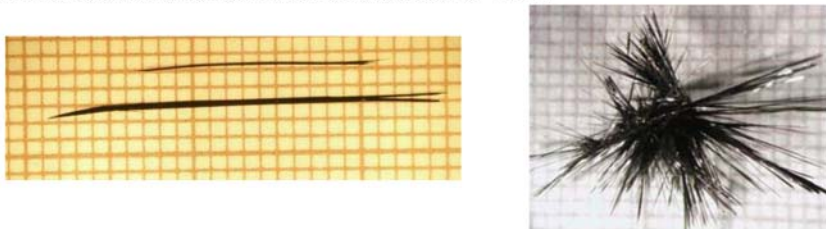


Fig 1. Large  $\alpha\text{-Per}_2\text{Pt}(\text{mnt})_2$  crystals obtained (division=1 mm) (left) and bundles as grown on the electrode (right).

The chosen concentration of perylene in dichloromethane was ca.  $1.6 \times 10^{-2}$  M, close to saturation, and the double (or slightly exceeding) of the

concentration for  $n\text{-Bu}_4\text{N}[\text{M}(\text{mnt})_2]$  while the temperature was kept constant at  $30^\circ\text{C}$ . Dilute solutions gave rise to very thin crystals. As the process is limited by diffusion, and no forced agitation was used, concentrations as high as possible are favourable, then the relatively high temperature (merely  $10^\circ\text{C}$  below the normal boiling point of the solvent). Currents were used in the range  $0.5 - 5\mu\text{A}$ , corresponding to current densities  $1\text{-}10\mu\text{A}\cdot\text{cm}^{-2}$ . Finally, but not less important, special care was placed in the purification of starting materials and solvents. Using these optimised conditions with current densities in the lower range it was possible to obtain  $\alpha\text{-Per}_2\text{Pt}(\text{mnt})_2$  crystals as large as those shown in fig.1 .

However, in spite of the optimised conditions previously referred, and all care in reproducing the experimental conditions, the formation of  $\beta$ -phase crystals in some batches could not be avoided. Macroscopic observation of crystal habit is not indicative of  $\alpha$ - or  $\beta$ -phase, except for deemed shine in the second. Electrical transport measurements can discriminate samples from the two phases. For  $\text{M} = \text{Cu}$  and  $\text{Ni}$ , there are about 50% occurrence of each of them, whereas for  $\text{M} = \text{Au}$  and  $\text{Pt}$ , a large majority of batches yield only  $\alpha$ -phase specimens. However, occasionally a batch is found where the behaviour is quite different.

### 3. ELECTRICAL TRANSPORT RESULTS

Several samples of  $\text{Per}_2\text{Pt}(\text{mnt})_2$  from different batches showed negative slopes over the entire temperature range, both in electrical resistivity and thermopower, a clear distinct behaviour of  $\alpha$ -phase results.

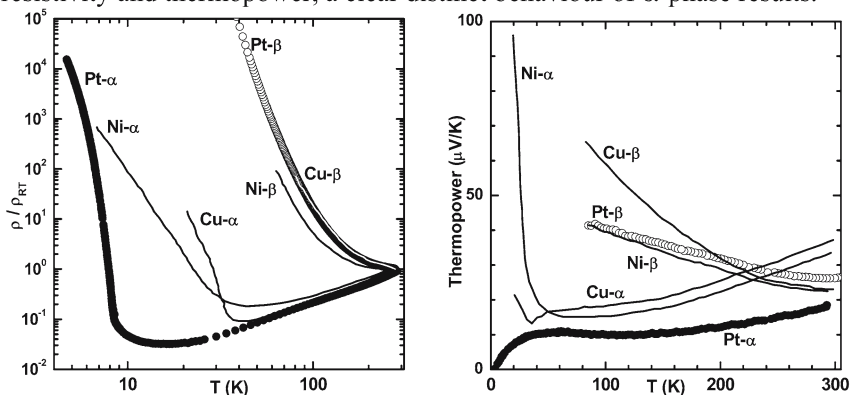


Fig. 2- Thermal dependence of electrical resistivity (left) and thermopower (right) for  $\beta\text{Per}_2\text{Pt}(\text{mnt})_2$ . For comparison, data on  $\alpha$ -phase of  $\text{M} = \text{Pt}$  is also shown as well as on  $\alpha$ - and  $\beta$ -phases of the analogues with  $\text{M} = \text{Cu}$  and  $\text{Ni}$ .

Room temperature conductivity of these samples ranges from 14 to 38  $\text{S cm}^{-1}$ , i.e., 20 to 50 times lower than the typical value for the  $\alpha$ -phase and of the same order of magnitude of  $\beta$ -phase samples of  $\text{M} = \text{Cu}$  and  $\text{Ni}$ . Thermoelectric power has a room temperature value of  $27 \mu\text{V K}^{-1}$ , and has a temperature dependence very similar to the  $\text{Ni}$  analogue, whereas the values for the  $\text{Cu}$  one increases steeper with decreasing temperature.

#### 4. CONCLUSION

We have shown that the existence of  $\beta$ -phase in the  $\text{Per}_2\text{Pt}(\text{mnt})_2$  with properties comparable to the  $\text{Cu}$  and  $\text{Ni}$  analogues previously described. The formation of this  $\beta$ -phase remains uncontrolled, although its formation seems to be more unfavourable than in the  $\text{Ni}$  and  $\text{Cu}$  compounds.

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