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Observation of Four Crystalline Phases of the One Dimensional Conductor $Zn_{0.81}[Pt(C_2O_4)_2]\cdot 6D_2O$ by Neutron Diffraction

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Four different crystalline phases of $Zn_{0.81}[Pt(C_2O_4)_2]\cdot 6D_2O$ have been observed and partially characterized by single crystal neutron diffraction measurements. A crystal in the previously reported orthorhombic α-form was pulled along its c-axis at room temperature and was found to transform to a monoclinic β-form. Two new coexisting phases, monoclinic γ-Zn-OP and orthorhombic δ-Zn-OP were found when the sample was cooled to 200 K. Further crystallographic work is necessary in order to establish the detailed nature of the new phases.

INTRODUCTION

The partially oxidized bis(oxalato)platinate salts[1] form an interesting series of one-dimensional conductors which are in many respects complementary to the extensively studied tetracyanoplatinate salts, e.g. $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$, KCP(Br). The bis(oxalato)platinate salts are cation deficient and have the formula $M_x[Pt(C_2O_4)_2]\cdot yH_2O$, (M-OP), where M is a cation. For divalent cations, e.g. Co^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+} and Cu^{2+}, $0.81 < x < 0.84$ and $y \sim 6$ whereas for monovalent cations, e.g. NH_4^+, Rb^+ and K^+, $1.6 < x < 1.81$ and y is between 1 and 4. One interesting aspect of these compounds is that the partially filled conduction band along the Pt-atom chain gives rise to the Peierls instability resulting in a phase transition from a high temperature metallic

state to a low temperature insulating or semiconducting state. This results in a superstructure which is basically one-dimensional; but the particularly interesting aspect of the bis(oxalato)platinate salts is that other superstructures,[1,2] which are basically three-dimensional and have been termed "non-Peierls" superstructures also occur. Such superstructures often lead to atypical Peierls transitions, e.g. in Co-OP.[3]

A serious problem in interpreting the physical measurements on bis(oxalato)-platinate salts and in comparing results obtained by different groups is that the reported basic crystal structures for compounds of similar but not identical chemical composition are often quite different.[1] These differences may arise from at least three different origins, namely:

i) *Undetected changes in chemical composition* It is well established that by changing the crystal growth techniques or by varying the acidity of the growth solution, varying amounts of cations and water molecules can be incorporated into the crystal lattice of the M-OP-salts.[4-6] Therefore strictly speaking one should talk not about one compound, but distinguish between phases having different compositions, with each having its own structure and physical properties. Moreover, since the change in composition accompanying the formation of a different phase may be very small, variations in x and y may be easily undetected in the absence of detailed chemical analysis.

ii) *Uncontrolled parameters during crystallization* The growth of crystals of a particular phase may depend crucially upon parameters which are unknown and therefore uncontrolled during crystallization. Subtle changes in these parameters between different groups of workers may be very difficult to identify and may be responsible for the preparation of different phases.

iii) *Physical conditions* The effects of mechanical treatment and temperature upon the crystal structures of partially oxidized complexes have been studied relatively little and not at all for the bis(oxalato)platinate salts. If mechanical hysteresis is significant, the history of a sample is important and should be recorded.

In order to study (iii), i.e. the effect of physical conditions on the crystallographic properties of the partially oxidized bis(oxalato)platinate salts we have performed a neutron diffraction study on a single crystal of $Zn_{0.81}[Pt(C_2O_4)]\cdot 6D_2O$, Zn-OP($D_2O$), and we have found several crystallographic phases as well as hysteresis effects after both mechanical and thermal treatment.

THE EXPERIMENT

Zn-OP(D_2O) was prepared by a method similar to the one previously reported for $Zn_{0.81}[Pt(C_2O_4)_2]\cdot 6H_2O$, (Zn-OP($H_2O$))[7] but using D_2O as solvent. Zn-OP(H_2O) has been reported to be orthorhombic (space group *Cccm*) with unit cell dimensions $a = 16.52$ Å, $b = 14.36$ Å and $c = 5.665$ Å.[7] The highly conducting axis is along c with the Pt-Pt distance of 2,83 Å. A single crystal of

Zn-OP(D_2O) of dimensions $0.4 \times 0.3 \times 5\,mm^3$ was used in order to avoid the large incoherent neutron scattering from protons in Zn-OP(H_2O). The experiment was performed at one of the DR3 reactor's triple axis spectrometers operated in its zero-energy transfer mode with wavelength $\lambda = 2.387$ Å ($E = 14.35$ meV). Only Bragg reflections in the (*ac*) plane were investigated. This means, of course, that we have not made a full determination of the unit cells in the new phases, but enough, we feel, to illuminate the issues mentioned above.

First the crystal was placed with one end in wax and Figure 1 shows the neutron intensities for scans through the (002) and (200) reflections at room temperature. The upper part of Figure 1 shows the results for a "$\Theta:2\Theta$" scan

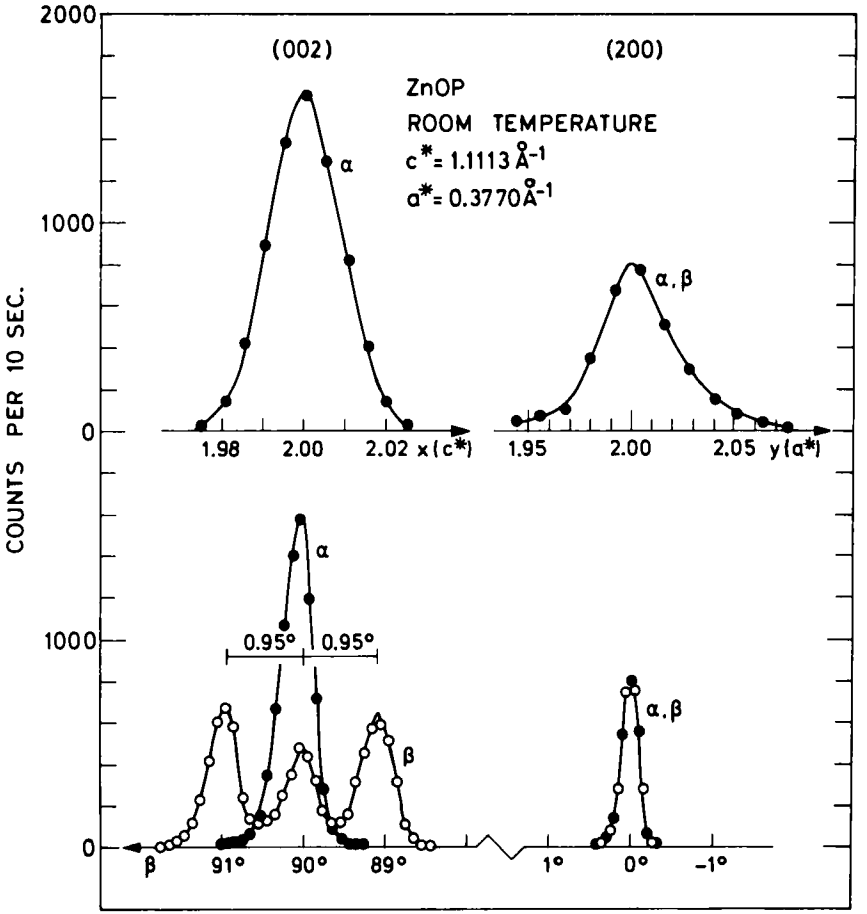

FIGURE 1 α- and β-modifications of Zn-OP(D_2O) at room temperature. α-phase: solid circles show Θ–2Θ scans (upper part) through the (002) and (200) reflections and ϕ-scans (lower part). β-phase: open circles show the splitting of the (002) reflection.

whilst the lower part shows a "ϕ" scan (rotating the crystal at fixed 2Θ). The results give $c^* = 1.113$ Å^{-1}, $a^* = 0.3770$ Å^{-1} and $\beta = 90°$ corresponding to an orthorhombic α-phase $a = 16.67$ Å and $c = 5.654$ Å. These values are close to those determined for Zn-OP(H_2O) at room temperature.

In order to be able to cool the crystal, it was transferred to another (closed) sample holder. The crystal was fastened by first fixing one end to the mounting with low temperature varnish and then pulling the crystal over into the correct orientation for the experiment and fastening the other end in the same way. The strain introduced by pulling the crystal along its c-axis in this way was sufficient to change the character of the (002) reflection dramatically. Although the (200) reflection was unchanged, approximately $\frac{2}{3}$ of the crystal has changed to a twinned monoclinic β-phase with the crystallographic angle $\beta = 89.05°$ as shown in the ϕ-scan on Figure 1. The crystal quality appeared unchanged during the α–β transformation as evidenced by the unchanged widths of the intensities in the figure.

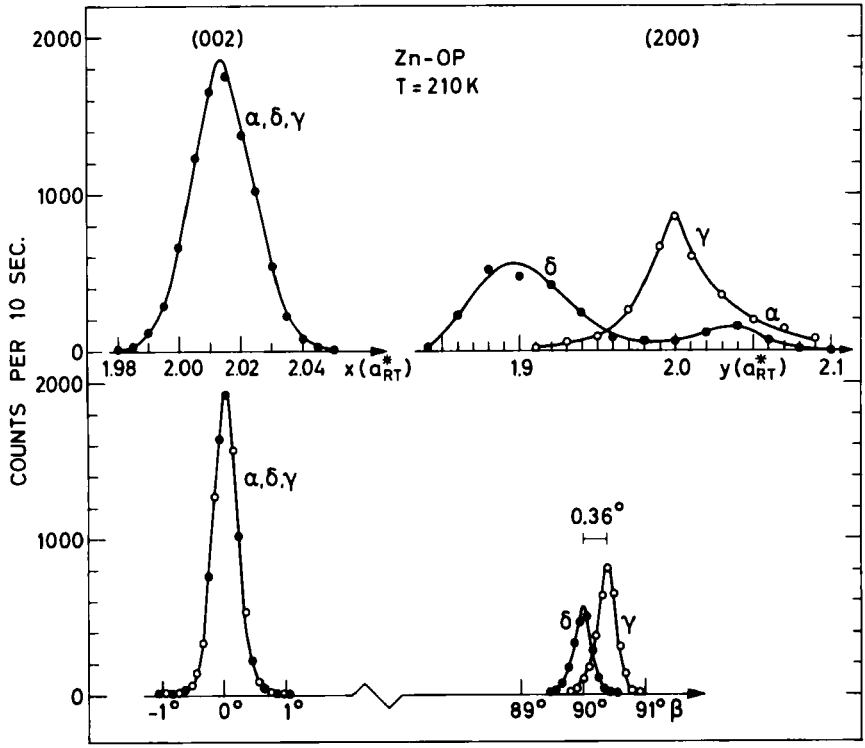

FIGURE 2 α-, δ- and γ-phases of Zn-OP(D_2O) at $T = 210$ K. Θ:2Θ scans (upper part) and ϕ-scans (lower part) through the (002) and (200) reflections.

On cooling, the crystal transformed back to pure α-phase at a temperature above 273 K; but at 210 K yet a totally different pattern was observed. The (002) reflection was unchanged except for thermal contraction, whereas a complicated structure was observed in the (200) direction as shown in Figure 2. Apart from a small portion still in the thermally contracted α-phase, most of the crystal appears to be in either one of two distinctly new phases, the monoclinic γ-*phase* with $a^* = 0.3761$ Å^{-1} and $\beta = 90.36°$ or the orthorhombic δ-*phase* where $a^* = 0.3582$ Å^{-1}. Unlike to the twinned β-phase the γ-phase appears to be in one domain.

In order to study the possible relation between the δ- and γ-phases, we measured in more detail the intensity contours around the (200) reflection. We found that the δ- and γ-phases are really the outer extremes of a continuous distribution of coexisting crystallographic phases. This is shown in Figure 3 by the ridge of neutron intensity between the extreme δ-phase (200) reflection at $(X, Y) = (-0.005, 1.995)$ and the γ-phase (200) reflection at $(X, Y) = (0, 1.90)$.

On warming the crystal to room temperature the diffraction pattern contained components from all four of the above phases demonstrating that hysteresis occurs. At this point the crystal had lost its high crystallographic quality and gave broad intensities, but no sign of water loss could be seen.

SUMMARY

Since we have determined only two independent reflections, the unit cells of the α, β, γ, and δ phases of Zn-OP(D_2O) are not uniquely determined. However, some useful insight into their nature may still be gained, and we believe that our conclusions below are basically correct, although they are based on the assumption that the symmetry of Zn-OP(D_2O) is always either orthorhombic or monoclinic. With this assumption our results may be used to characterize the unit cells of the four phases which are shown in Figure 4.

The α-phase of Zn-OP appears to be isostructural with MG-OP and Co-OP and from our low temperature studies we get the thermal expansion coefficients in the a and c directions in Zn-OP(D_2O) to be 12×10^{-5} K^{-1} and 4.5×10^{-5} K^{-1} respectively, which is close to the reported values for KCP(Br).[8]

The β-phase of Zn-OP(D_2O) was formed by a monoclinic distortion of the α-phase due to a slight stretch of the crystal along the c-axis. The twinning of the crystal is indicated in Figure 4 by the two different orientations of the deformed unit cell.

The existence of the monoclinic γ-phase of Zn-OP(D_2O) to which the α-phase transforms upon cooling might be directly related to the Peierls transition in the same way as in TTF-SCN,[9] but more measurements are needed to establish this.

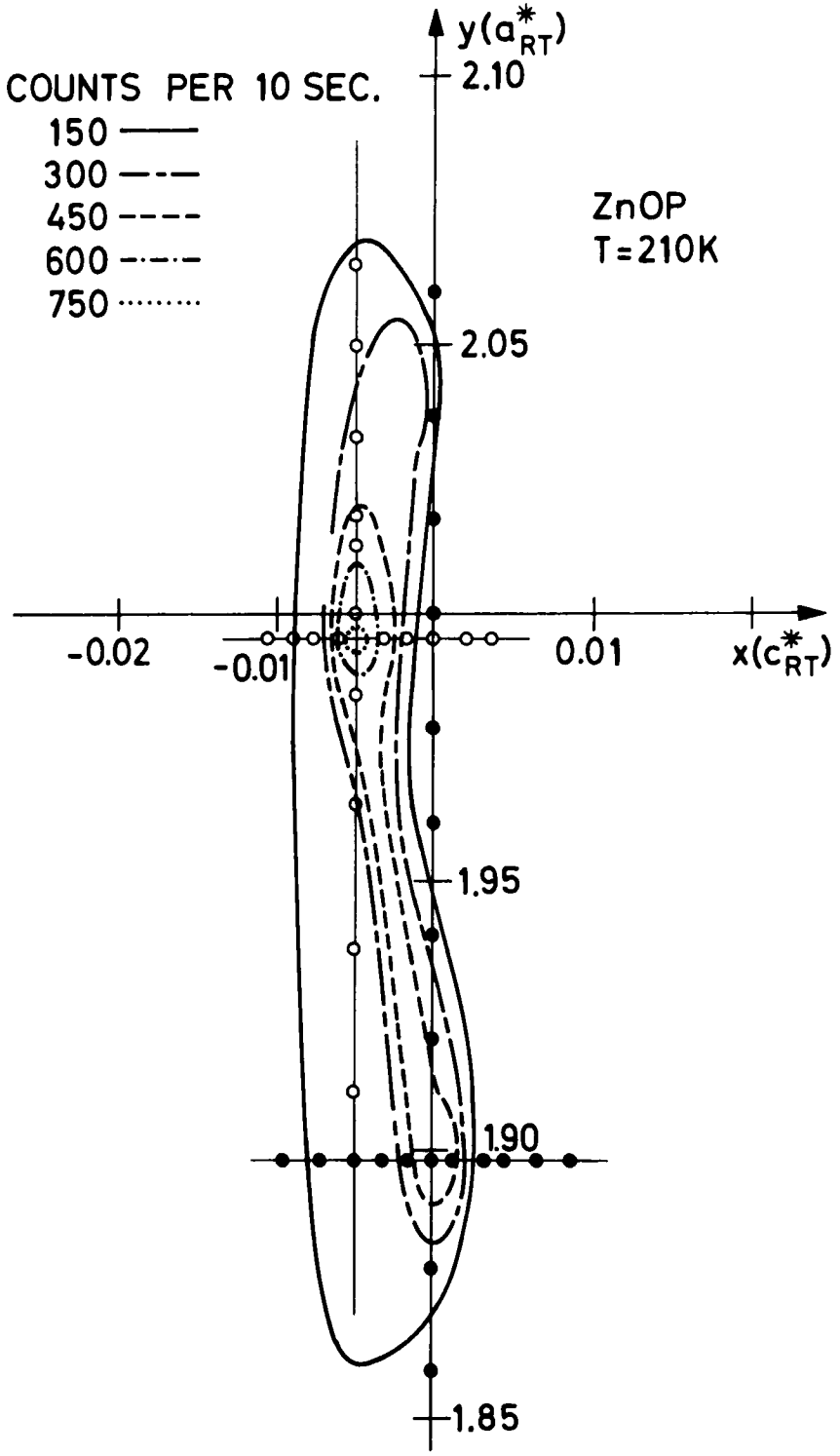

FIGURE 3 Intensity contours around the (200) reflection at $T = 210$ K demonstrating the coexistence between the monoclinic γ-phase and the orthorhombic δ-phase. The relevant measuring points from Figure 2 are indicated.

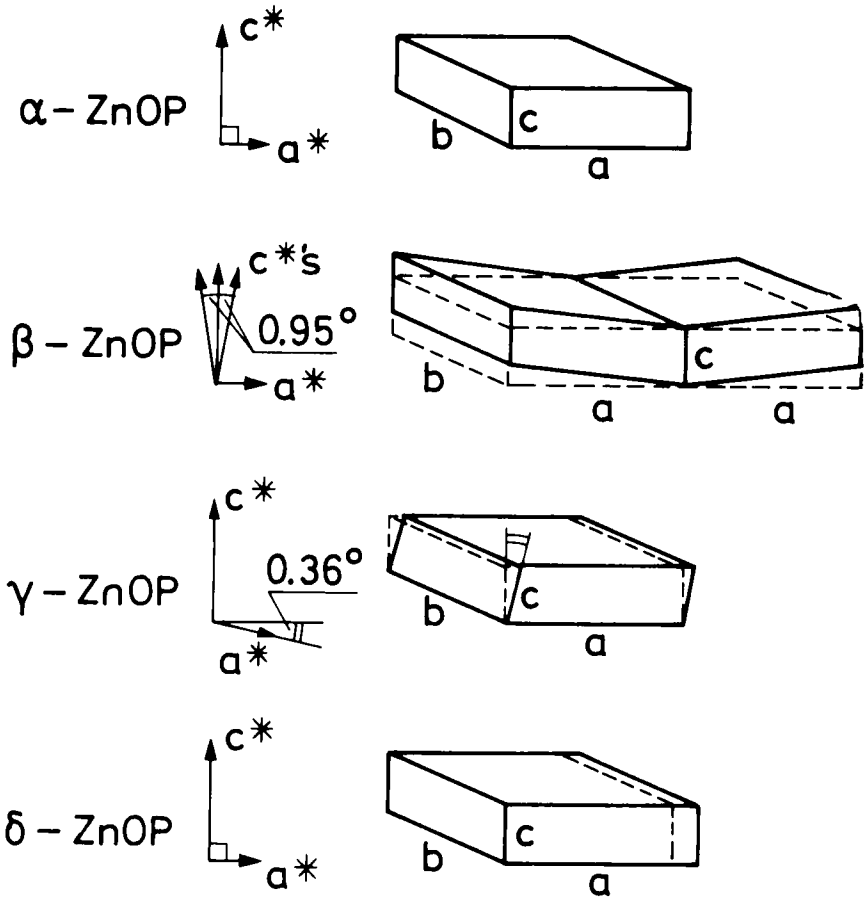

FIGURE 4 The schematic unit cells of α, β, γ, and δ-Zn-OP(D_2O).

The observation of a second orthorhombic phase in Zn-OP(D_2O), the δ-phase, is unexpected. This phase has an a-axis which is 7.5% longer than the α-phase and it seems natural to explain such a large difference as stemming from a difference in staggering angle between adjacent $Pt(C_2O_4)_2$ groups. The distribution of intermediate phases between γ and δ would then correspond to a distribution in stagger angles. This angle has been debated because of different theoretical predictions,[10,11] and because of the experimental evidence that it varies from phase to phase.[1] Therefore a full structural determination of δ-Zn-OP(D_2O) would be of interest to see how the low temperature value of the stagger angle is related to theoretical calculations.

The above experiment demonstrates that the basic structure of Zn-OP(D_2O) does depend on the mechanical and thermal history of the crystal. This may

well be a general property of the partially oxidized bis(oxalato)platinate salts, so that great care has to be taken not only during the preparation of crystals [(i) and (ii) above] but also during the subsequent handling of the crystals.

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References

1. A. E. Underhill, D. M. Watkins, J. M. Williams and K. Carneiro, "A Comprehensive Review of Linear Chain Bis(oxalato)platinate Salts (in *Extended Linear Chain Compounds,* ed. J. S. Miller, Plenum Press, in press).
2. H. Kobayashi and A. Kobayashi, "Superstructures and Phase Transitions in 1-D Inorganic Materials" (in *Extended Linear Chain Compounds,* ed. J. S. Miller, Plenum Press, in press).
3. A. Braude, A. Lindegaard-Andersen, K. Carneiro and A. E. Underhill, *Synthetic Metals,* **1,** 35 (1979).
4. A. Kobayashi, Y. Sasaki, I. Shirotani and H. Kobayashi, *Solid State Commun.,* **26,** 653 (1978).
5. K. Krogmann, *Z. Anorg. Allg. Chem.,* **358,** 97 (1968).
6. D. J. Wood, A. E. Underhill, R. Broach, S. W. Peterson and J. M. Williams, unpublished results.
7. A. E. Underhill, D. M. Watkins and C. S. Jacobsen, *Solid State Commun.,* **36,** 477 (1980).
8. K. Carneiro, G. Shirane, S. A. Werner and S. Kaiser, *Phys. Rev.,* **B13,** 4258 (1976).
9. G. A. Thomas, D. E. Moncton, F. Wudl, M. Kaplan and P. A. Lee, *Phys. Rev. Lett.,* **41,** 486 (1978).
10. J. S. Miller, *Inorg. Chem.,* **15,** 2357 (1976).
11. A. H. Reis, Jr., *Inorg. Nucl. Chem. Lett.,* **13,** 231 (1977).