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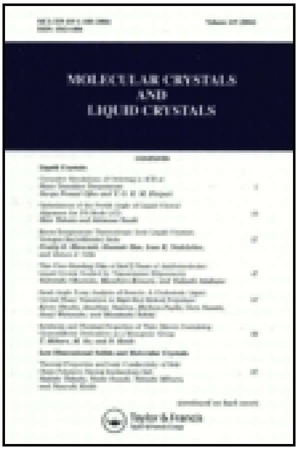

Molecular Crystals and Liquid Crystals

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A STUDY OF CHAOS ASSOCIATED WITH THE PHASE TRANSITION IN $Mg_{0.8}[Pt(C_2O_4)_2]\cdot 6H_2O$

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Abstract A study of the phase transition in $Mg_{0.8}[Pt(C_2O_4)_2]\cdot 6H_2O$ (Mg-OP) by a combination of electrical conductivity differential scanning calorimetry and X-ray techniques has been carried out. Evidence of chaotic behaviour and long lifetime metastable states is presented.

INTRODUCTION

The partially-oxidised bis(oxalato)platinate salts of divalent metal cations $M_{0.8}[Pt(C_2O_4)_2]\cdot 6H_2O$ (M-OP) (where M = Mg, Co, Zn, Mn, Ni or Fe) have been extensively studied during the past decade.[1-10] Structural studies have revealed that the series is virtually isostructural having unit cell dimensions a, 16.6 ± 0.2; b, 14.33 ± 0.06; c, 5.675 ± 0.025 A; V_c, 1344 ± 15 A^3. In all but Mn-OP a common high temperature orthorhombic phase (space group C_{ccm}) has

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been demonstrated but at temperatures, within 20 K of room temperature, a phase transition occurs which breaks the symmetry of the space group. The series can be divided into two classes on the basis of the low-temperature space group. Class A, which comprises Co-OP, Zn-OP and Ni-OP, undergoes an antiphase sliding of the bis(oxalato)platinate chains to yield the orthorhombic space group P_{ccn} in which the two chains within the unit cell are non-equivalent. This is the room-temperature structure of Ni-OP and has been fully resolved.[3] In the class B compounds (Mg-OP, Fe-OP and Mn-OP) an in-phase sliding of the bis(oxalato)platinate chains results in a monoclinic unit cell.[2,7] In Mg-OP the monoclinic angle (α) is 89°.[7] The crystal also becomes twinned preventing the determination of the space group of the monoclinic phase. Mn-OP is in this twinned monoclinic phase at room temperature.[9] In both classes, satellite reflections develop during the course of the transition indicative of the development of a superstructure.

The differences between the low-temperature phases of the two classes are reflected in differences between their transport properties. In the class A compounds there is a dramatic fall in conductivity in the vicinity of the phase transition which constitutes a metal-insulator transition. In the class B compounds the changes are very much less marked, the metal insulator transition being very smeared.

The room-temperature crystal structure of the title compound, Mg-OP, was determined by Krogmann.[10]

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Dubois[7] later made a detailed X-ray examination of the phase change and of the development of the satellite reflections that accompany it. His studies revealed that the transition centred on 283 K and that the satellite reflections developed fully over a few degrees. He reported that the wavevector of the superstructure was incommensurate both with the basic lattice and with the 1-D Peierls distortion of the platinum atom chain. Some preliminary investigations of the conductivity and its variation with temperature were reported and compared with that of the cobalt salt.[1,4] Recent careful measurements of the behaviour of the conductivity and thermopower of Mg-OP in the region of the phase transition by Mizuno et al[5] revealed very unusual behaviour which was attributed to a chaotic transition.[6,8] This chaotic transition was characterised by two unusual features. Firstly, the phase transition produced a small rise in conductivity (cf. the class A compounds where the conductivity falls sharply with temperature) and secondly, at constant temperature within the transition region, the conductivity changed with time over a period of 1-3 hrs. This chaotic behaviour was explained in terms of three competing ordering forces within the crystal: the basic lattice, the 1-D Peierls distortion and the 3-D (non-Peierls) superstructure. These forces are all mutually incommensurate.

The metal insulator transition in the class A compound Ni-OP has been discussed in terms of the ordering of the cations in columns parallel to the bis(oxalato)platinate chains.[3] This results in a

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sinusoidal modulation of the platinum chain which in turn gives rise to 3-dimensional ordering and the development of a superstructure. In these and other anion-deficient salts the band-filling and therefore k_F is determined by the occupancy of the cation sites. Therefore it is a natural consequence of the divalent charge on the cations that the wavevector of the Peierls distortion and the c component of the cation ordering are commensurate at 2 k_F and k_F respectively. Thus in Ni-OP and the other class A compounds the superstructure is seen to be commensurate with the Peierls distortion.

If the same model is to be applied to Mg-OP it is difficult to understand the observation of Dubois[7] that the superstructure is incommensurate with the Peierls distortion. One way of breaking the interdependence of the band-filling and cation occupancy (and thus the wavevectors of the Peierls distortion and the superstructure) is to postulate the presence of other cations within the lattice. Since the method of preparation and chemical analysis precluded the presence of a second metal cation the most likely candidate is the proton, presumably associated with the water of crystallisation. In the standard method for the preparation of Mg-OP the salt is crystallised from a solution of $H_{1.6}[Pt(C_2O_4)_2]$ and $MgSO_4$. It is evident therefore that protons are present during crystal growth and could be incorporated into the lattice. The incorporation of protons has been demonstrated in a number of 1-D platinum chain compounds in the past. In order to test this idea crystals were produced by four different methods and the results obtained on crystals from each preparation compared.

EXPERIMENTAL

Preparation of Mg-OP Crystals

Method 1: The previously published method. A solution of $H_x[Pt(C_2O_4)_2]$ (1 mol) and $MgSO_4$ (0.8 mol) was allowed to evaporate in air for 14 days. The pH of the mother liquor was 1.5.

Method 2: A solution of $Mg[Pt(C_2O_4)]$ was produced by the double decomposition of $Ag_2[Pt(C_2O_4)_2]$ and $MgCl_2$ followed by filtration. To the resulting yellow solution a few drops of chlorine water were added whereupon the solution became dark blue. The solution was warmed on a steam bath for a few minutes to remove excess chlorine and to dissolve the precipitate. The solution was allowed to evaporate for 14 days. The pH of the mother liquor was 5.

Method 3: A solution of $Mg[Pt(C_2O_4)_2]$ was produced as described for method 2. The pH was adjusted to pH 7 by the addition of MgO. After filtering to remove excess MgO the solution was transferred to an H-shaped electrolysis cell. A constant current of 1 μA was passed via Pt electrodes through the solution under an atmosphere of argon. After one month large single crystals were obtained in the anode compartment. The pH of the mother liquor was 7.

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Method 4: Mg-OP obtained by method 1 was recrystallised from de-ionised water. The pH was not measured but may be assumed to have been approximately 7.

RESULTS AND DISCUSSION

Structure and Superstructure

The unit cell dimensions of crystals from all four preparations were measured by means of oscillation and zero-level Weissenberg photographs and found to agree with those previously reported. Preliminary studies of the superstructure of crystals from methods 1 and 4 indicate that those from method 4 (in which proton incorporation would *not* be expected) exhibit different superstructures within the same crystal. Crystals from method 1 (in which proton incorporation might be expected) have a superstructure which is *commensurate* with the Peierls distortion in the chain direction but *incommensurate* perpendicular to the chain direction.

Electrical Conductivity

The room temperature conductivity was measured for a number of crystals from each preparation. Within the normal spread of results observed for this compound the crystals prepared by the different methods did not differ significantly from one another or from previously reported values.

The variation of conductivity with temperature for crystals prepared by each method was carefully measured in the vicinity of the transiton (295-265 K) using a microcomputer controlled conductivity apparatus.

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Evidence of time dependency was sought by taking four readings over a period of one hour at each temperature. Typical results are shown in Figure 1. It is clear that the conductivity behaviour in the transition region is affected by the method of preparation and that a range of behaviour is observed. This varies from that observed for crystals prepared by method 4 in which the transition can be detected only by very careful examination to the very obvious evidence of the transition in crystals from method 1. It was found that both the magnitude of the change in conductivity and its time dependency at constant temperature during the transition was greatest in the crystals prepared at the lowest pH and that these effects decrease with increasing pH of the mother liquor from which the crystals were grown. At lower temperatures all the crystals examined behaved as intrinsic semiconductors with an activation energy for conduction (Δ) in the range 50-60 meV irrespective of the method of preparation.

Time Dependent Conductivity in the Transition Region of Mg-OP (preparation 1)

The results obtained during this investigation confirm that Mg-OP exhibits no time dependent conductivity at constant temperature above or below the transition region, but that the conductivity is time-dependent in the vicinity of the transition. A more detailed investigation of this time dependency was made by cooling a crystal from preparation 1 from 290 to 260 K in steps of 2 K. The crystal was held at each temperature (better than ± 0.1 K) for 2 hrs taking

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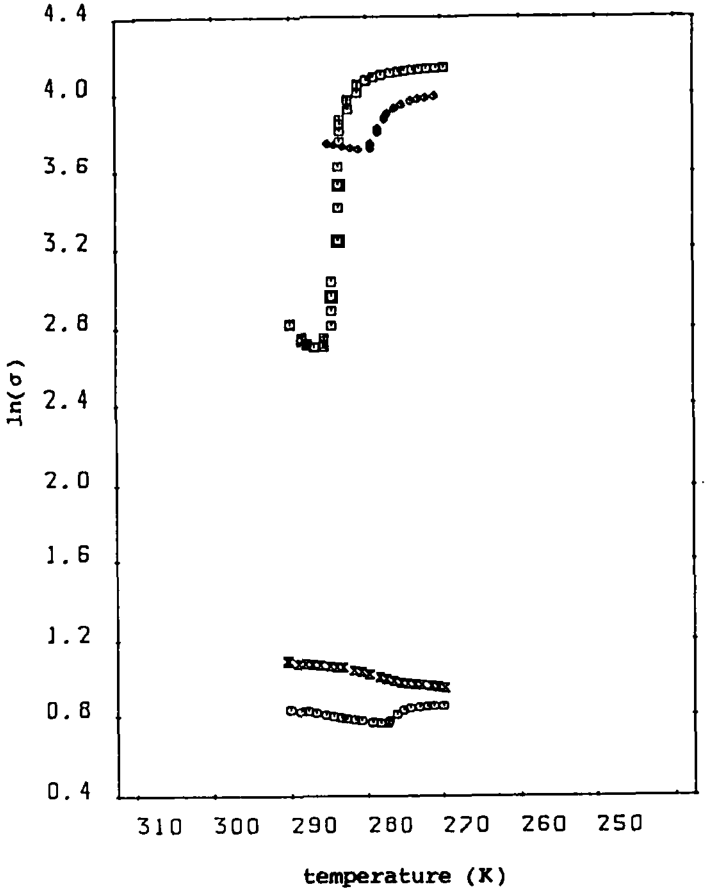

FIGURE 1 The variation of conductivity with temperature for crystals of Mg-OP prepared by different methods (in all cases 4 readings have been taken over a 1 hr period at each temperature)

Key ▫▫▫▫ crystal prepared by method 1
●●●● crystal prepared by method 2
oooo crystal prepared by method 3
xxxx crystal prepared by method 4

readings every 10 minutes. The time dependency of the conductivity was modelled by the exponential relationship:

$$\sigma(T,t) = \sigma(T,\infty) + (\sigma(T,0) - \sigma(T,\infty))\exp(-t/\tau)$$

where t = time in minutes, T = thermodynamic temperature and τ is the time constant,

i.e. the conductivity at temperature T approaches its asymptotic value ($\sigma_{(T,\infty)}$) exponentially with time constant τ. The data was analysed using the non-linear least-squares procedure incorporated in the GENSTAT[11] statistical package. In this way initial estimates of τ and $\sigma_{(T,\infty)}$ were refined. Because of the interdependence of the two derived parameters (τ and $\sigma_{(T,\infty)}$) it is very difficult to interpret data obtained at the extremities of the transition region. Data from the middle of the transition region yielded values for the time constant ranging from 14 to 41 minutes, but all save one were within two standard deviations of 20 minutes. This is a very long time constant for the disappearance of a metastable state. In a recent paper Milhaly and Milhaly reported the decay of a metastable state in orthorhombic $TaSe_3$ in which, using a logarithmic (as opposed to exponential) model, they observed a similar timescale and temperature independence of the time constant.[12]

Dynamic Studies

A series of experiments were performed in which the crystal was heated or cooled at a constant rate whilst the conductivity was monitored. Thus, no attempt was made to allow the sample to come to equilibrium and

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this should allow the observation of more short-lived metastable states and of the 'Devil's Staircase' effect. Crystals were heated or cooled at 1, 2, 3 or 4 K min^{-1} and readings of conductivity were made approximately every 0.5 K over the temperature range 290 - 260 K.

The results are plotted in Figure 2 as a complete cycle of cooling and warming at the same rate of change of temperature. This, because of hysteresis, yields a two dimensional figure and by using the same axes throughout, the shapes of the hysteresis loops can be compared. It can be seen that increasing the rate of change of temperature produces (1) a depression of the transition temperature on cooling indicating supercooling and (2) an elevation of the transition temperature on warming suggesting superheating. The amount of hysteresis appears therefore to be dependent on the rate of change of temperature. Figure 3 shows the results obtained on 3 different crystals illustrating the variation observed from crystal to crystal.

An interesting feature of these results is the apparent overshoot of the equilibrium conductivity on heating, the extent of overshoot being dependent on the rate of warming. This could indicate a metastable state produced by heating, possibly the first example of such a phenomenon. This metastable state decays over a period of 10 minutes at 290 K (dotted lines on Figure 2) or on heating to 295 K (Figure 3a).

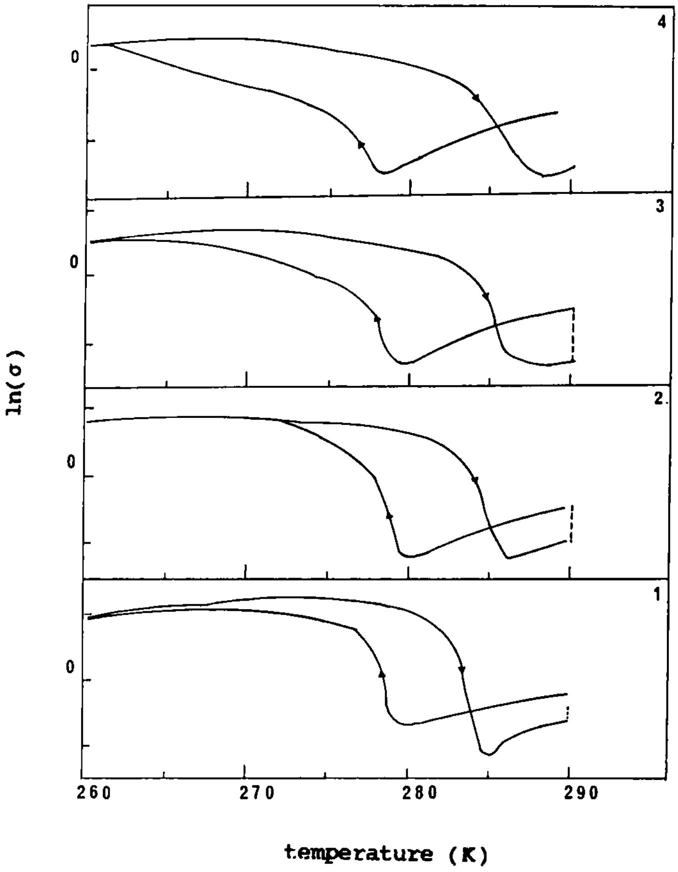

FIGURE 2 Dynamic conductivity studies on a single crystal of Mg–OP at 1, 2, 3 and 4 K min^{-1}

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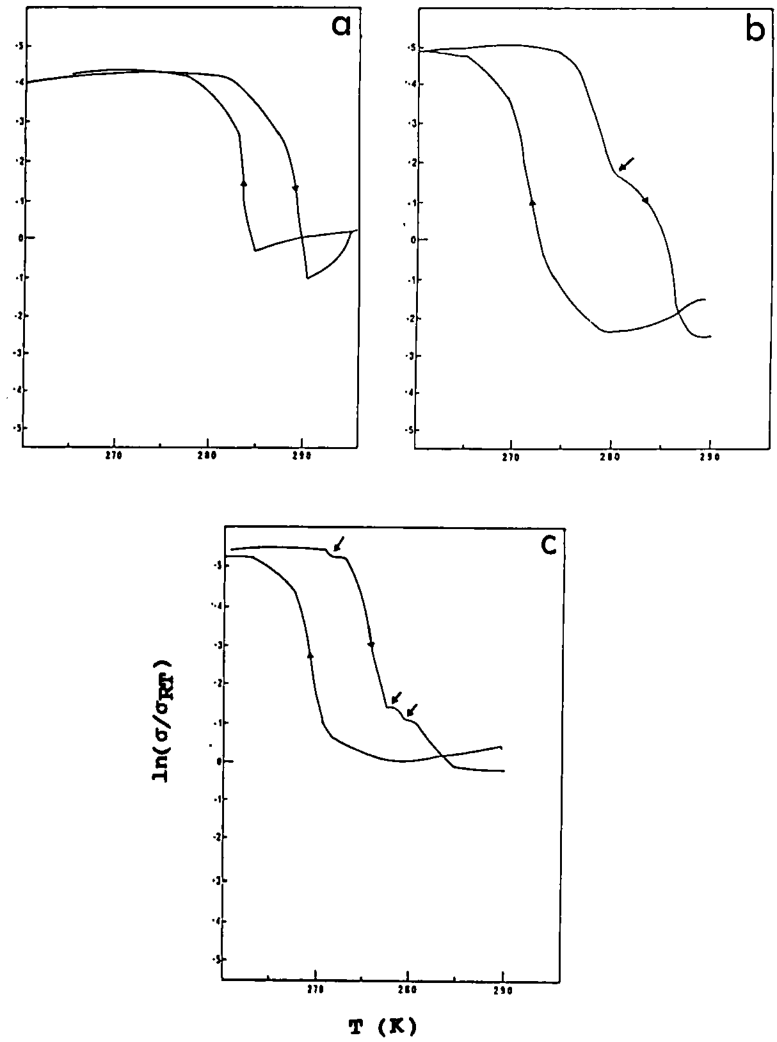

FIGURE 3 Hysteresis loops showing the variation from crystal to crystal and (arrowed) transient metastable states indicating the 'devil's staircase' a) 1 K min^{-1}, b) 2 K min^{-1}, c) 2 K min^{-1}.

The steps in the conductivity that can be seen in Figure 3b and 3c can be taken as evidence of transient metastable states associated with a 'Devil's Staircase'. Because only a few 'steps' are observed it appears that the average transient time for these states is too short to be observed under the conditions of the experiment.

Differential Scanning Calorimetry

Although dc conductivity studies yield much information about the transition in Mg-OP they can give no information about the energy changes that occur during the transition. Differential scanning calorimetry (DSC) is a convenient way of studying this aspect of the transition since it measures directly the heat change associated with the transition. A one milligram sample of Mg-OP was cycled between 290 and 275 K at 1.25, 2.5 and 5 K min^{-1}. A typical result is shown in Figure 4. The transition appears quite

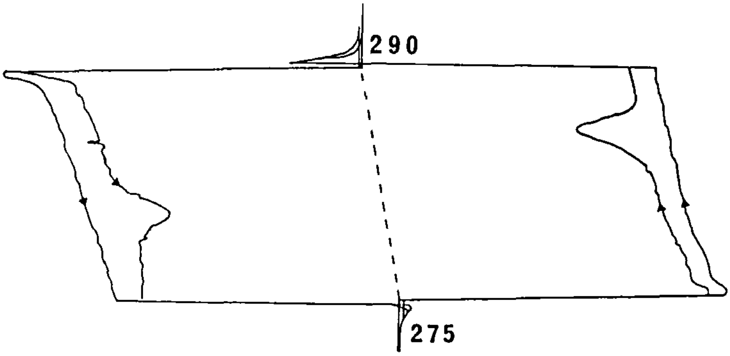

FIGURE 4 Differential scanning calorimetry at 2 K min^{-1} between 275 and 290 K.

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clearly as a peak on both the warming and cooling parts of the cycle. The peak observed on cooling is much broader than that on warming, has a 'tail' and is at a lower temperature than that of the warming cycle. Thus hysteresis is observed in both DSC and dc conductivity studies.

The position of the peaks and the amount of hysteresis is dependent on the rate of change of temperature in a very similar fashion to that found in the dynamic conductivity studies. In Figure 5 the extent of hysteresis is shown as a function of rate of change of temperature from the data obtained by both measurements. The agreement between the two sets of data is quite remarkable, especially when one considers the difference in the nature of the two techniques.

GENERAL DISCUSSION AND CONCLUSIONS

The differences in the variation of electrical conductivity with temperature of the Class A and Class B compounds has been related to the development of a superstructure commensurate with the Peierls distortion (PD) in the Class A compounds and a superstructure incommensurate with the PD in Mg-OP. The incommensurate nature of the superstructure in Mg-OP was based on the studies of Dubois. The present work shows that crystals of Mg-OP can be obtained with a superstructure commensurate with the PD in the chain direction but incommensurate perpendicular to the chain direction. This is supported by recent work on the Class B compound Mn-OP which shows that the

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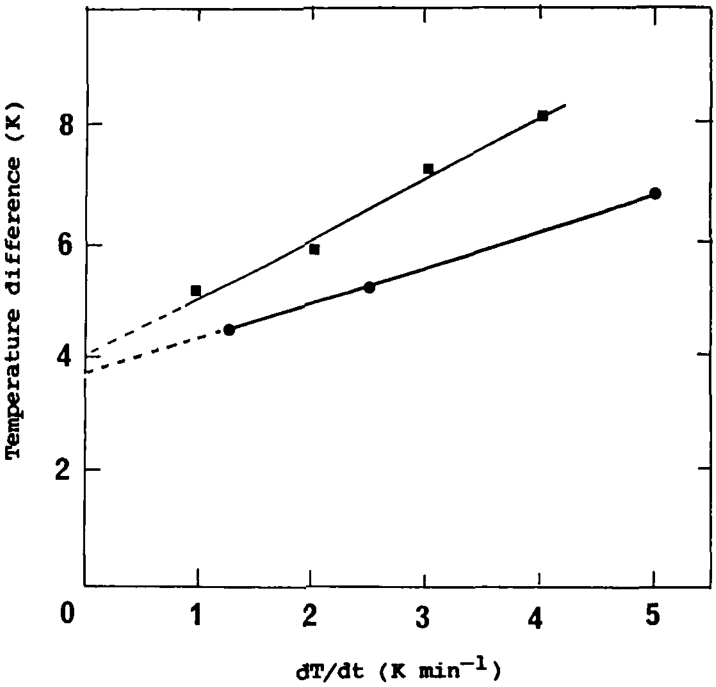

FIGURE 5 Difference in transition temperature on warming and cooling cycle obtained from conductivity studies ■ ■ ■ and differential scanning calorimetry ● ● ● .

superstructure present in this compound is also commensurate with the PD in the chain direction.

Perhaps the most significant feature is the fact that whereas the development of the superstructure has a profound effect on the conductivity in the Class A compounds it has either a relatively small effect or almost no effect at all on the conductivity in the

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Class B compounds. This difference has recently been discussed in terms of the Frenkel-Kontorowa model.[8] In this model Class A behaviour corresponds to the cations experiencing a weak potential from the Pt lattice and Class B behaviour to the cations experiencing a strong potential.

The behaviour of a Class B compound such as Mg-OP appears to involve a very smooth, smeared metal to semiconductor transition. This is the behaviour of Mg-OP crystals grown at pH 7. However, crystals grown at low pH and which might be expected to contain protons bound in the lattice as H_3O^+, show a pronounced effect at the transition temperature although the behaviour is quite different from the Class A compounds. These crystals display the chaotic behaviour described fully earlier. The development of the different superstructures in the Class A and Class B compounds must be due to subtle effects since there is no obvious reason related to the size of the cation or unit cell dimensions etc. Thus the tendency to undergo one or other of these transitions must be finely balanced. In Mg-OP crystals that display chaotic behaviour the variation of electrical conductivity with temperature can be interpreted to indicate that the system is so finely balanced that evidence of both Class A and Class B conduction behaviour is observed. On cooling the crystal to just above the transition temperature the conductivity begins to fall sharply with decreasing temperature reminiscent of Class A behaviour. However on further cooling the C_{ccm} to monoclinic transition occurs and

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the conductivity is restored to approximately the original value. Class B behaviour then follows. It is interesting to note that this behaviour is only observed in Mg-OP crystals grown from acid solution and which may therefore contain H_3O^+ in the lattice. The presence of H_3O^+ in place of Mg^{2+} in the lattice will change the wavevector of the ordered Mg^{2+} lattice resulting in a different superstructure. This could lead to a locally more ordered structure reminiscent of the Class A compounds.

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