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Observation of a Mean-Field Peierls Transition In $Co_{0.83}$ $Pt(C_2O_4)_2[mddot]6H_2O$ And $Zn_{0.81}$ $Pt(C_2O_4)_2[mddot]6H_2O$

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OBSERVATION OF A MEAN-FIELD PEIERLS TRANSITION IN $Co_{0.83}Pt(C_2O_4)_2 \cdot 6H_2O$ AND $Zn_{0.81}Pt(C_2O_4)_2 \cdot 6H_2O$

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The amplitude modes of the charge density wave are observed in CoOP at 50 cm^{-1}, in ZnOP (protonated) at 53 cm^{-1}, and in ZnOP (deuterated) at 51 cm^{-1}, and studied as a function of temperature. In both materials the coupling coefficient which represents the order parameter of the Peierls distortion decreases in approaching room temperature from below. In ZnOP the behaviour is shown to be of the Landau type with a transition at 320 K. From a comparison with electrical conductivity measurements this transition is identified as a mean-field Peierls transition with $T_{3d} \approx T_p^o \approx 320$ K. The striking difference to KCP, where $T_{3d} \approx 100$ K and $T_p^o \approx 600$ K, is explained in terms of an enhanced interchain coupling in CoOP and ZnOP.

INTRODUCTION

The one-dimensional conductors of the Pt chain salts are known for a rich variety of structural and electronic

properties[1,2]. The prototype material $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$ (KCP) exhibits - resulting from a strong electron-phonon interaction - a periodic lattice distortion and a charge density wave, with an incommensurate superstructure (of period 6.7 times the Pt-Pt distance) and a Peierls gap in the electronic energy[3]. In this material and in the related cation deficient salt $K_{1.75}Pt(CN)_4\cdot 1.5H_2O$ (K(def)TCP) we have observed previously the amplitude modes of the charge density wave by means of Raman scattering[4,5]. For both of them the results were in good agreement with those obtained by inelastic neutron scattering[6,7]. The present paper is devoted to the related bis-oxalatoplatinate compounds $Co_{0.83}Pt(C_2O_4)_2\cdot 6H_2O$ (CoOP) and $Zn_{0.81}Pt(C_2O_4)_2\cdot 6H_2O$ (ZnOP) for which inelastic neutron scattering measurements are not possible for reasons of crystal size. Based on electrical resistivity, optical reflectivity and X-ray diffraction[2] an interesting interplay between electronic properties and structural ordering is anticipated which differs in several respects from what is known for KCP. In particular the three-dimensional ordering temperature was found to be much higher in CoOP and ZnOP whereas the activation energy for the electrical conductivity was observed to be smaller than in KCP. We will argue that this is the consequence of a different interchain coupling strength leading to mean-field behaviour in CoOP and ZnOP but to strong fluctuation effects in KCP.

EXPERIMENTAL

The crystals of CoOP and ZnOP, of size 2 mm x 0.5 mm x 0.5 mm, had been grown by the slow evaporation technique[8]. They were carefully encapsulated as described before[4]. An argon ion laser at 4880 Å for CoOP and 4579 Å for ZnOP with incident power of 1 mWatt on a round spot of 50 μm was used. We have verified by means of Stokes - anti-Stokes measurements, taken at different temperatures, that the overheating effect is negligible (less than a few degrees) for ZnOP, and is 30 degrees for CoOP at all temperatures. Despite of the overheating effect, the incident power could not be reduced for CoOP because of the need of a reasonable signal to noise ratio. The instrumental linewidth was 3.1 cm^{-1}. The crystal structure[8,9] of CoOP and ZnOP is orthorhombic (D_{2h}^{20} - Cccm) with two Pt atoms per unit cell in the c direction and with an intra-chain Pt-Pt spacing

of 2.841 Å for CoOP and of 2.832 Å for ZnOP. For the experimental arrangement we used the backscattering geometry, a Spex double monochromator, a Spex "Third Monochromator" and photon counting detection.

The Raman spectra for CoOP and ZnOP are presented in Fig. 1 for a number of temperatures between helium and

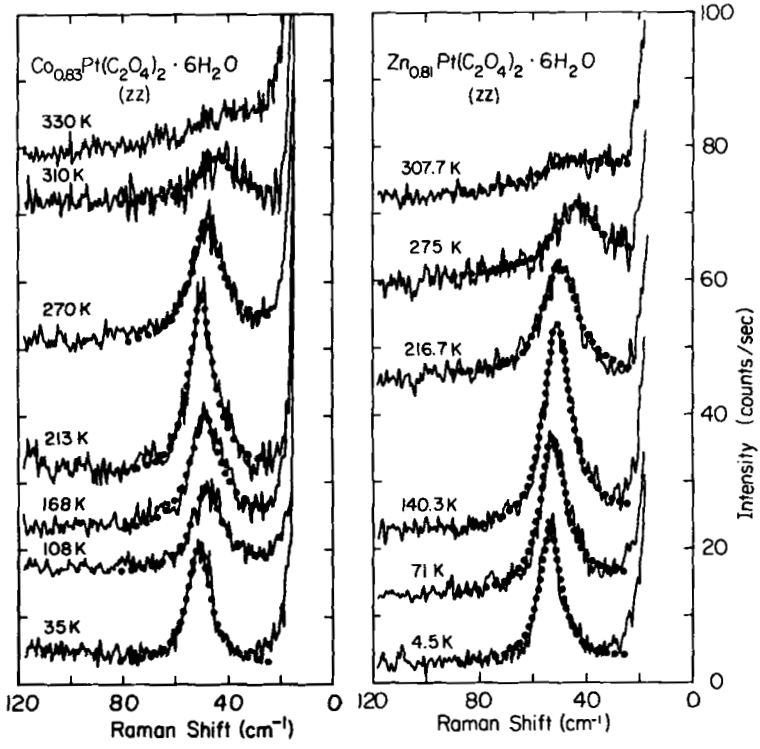

FIGURE 1 Raman spectra of CoOP and ZnOP for different temperatures. The temperatures given for CoOP have been corrected for overheating, which is practically negligible for ZnOP. Dots represent oscillator fits (see text)

room temperature. Shown is the (zz) configuration which identifies the line as of Γ_1^+ (A_g) representation. As observed previously[4] for KCP, the zz component is the only non-vanishing Raman tensor component for this line (yy, zy and yz being zero). From this it is concluded that this line represents the amplitude mode of the charge density wave for the reasons given previously[4]. This assignment is supported by the temperature behaviour of the mode as seen below. The results of Fig. 1 have been analysed by fitting the data with a harmonic oscillator expression

$$I(\omega) = [n(\omega) + 1] \cdot a^2 \, \mathrm{Im} \, (\omega_o^2 - \omega^2 - 2i\omega\gamma)^{-1} \quad (1)$$

where $n(\omega)$ is the Bose-Einstein distribution function, a the coupling coefficient, ω_o the eigenfrequency and γ the damping coefficient. The fits of a, ω_o and γ were carried out after subtraction of a small linear background, and the results are shown by the superimposed dots in Fig. 1.

We also have studied deuterated ZnOP (as compared to protonated). The results are quite similar except that the eigenfrequency of the amplitude mode is 51 cm^{-1} for deuterated ZnOP as compared to 53 cm^{-1} for protonated ZnOP (at low temperatures). The fact that the deuteration effect in ZnOP is smaller than that previously observed[4] in KCP indicates that in ZnOP the water molecules (located between the Pt chains) are less involved in the eigenvector of the charge density wave as compared to KCP.

Figs. 2 and 3 give the resulting fitting parameters for CoOP and ZnOP, respectively. It is noticed that the eigenfrequencies are slightly higher than those reported before for KCP[4]. We believe that this originates from the stiffer Pt chain as a result of the smaller Pt-Pt distances (2.841 Å for CoOP and 2.832 Å for ZnOP as compared to 2.888 Å for KCP), as explained below. The temperature dependence of the eigenfrequency is found to be small except for some decrease close to room temperature.

For CoOP, the damping constant and coupling coefficient indicate an anomalous behaviour around 100 K. Measurements of the electrical conductivity by Underhill and Wood[10] show in some cases[11] a minor drop in the activation energy at this point. Further studies will be needed to elucidate this. The decrease in the coupling coefficient, representing the order parameter of the Peierls distortion and the

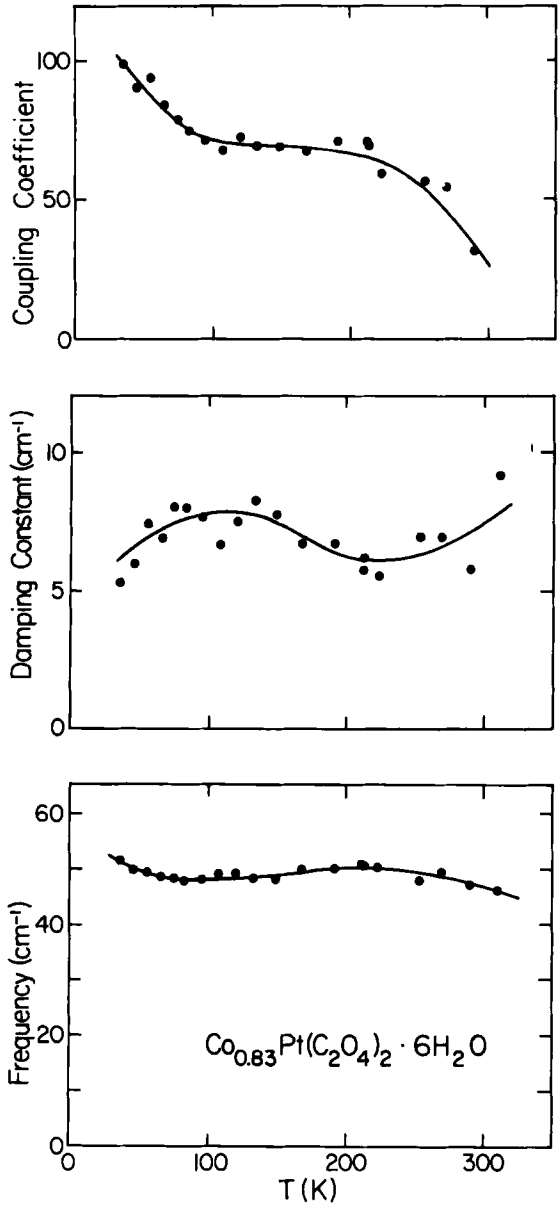

FIGURE 2 Fitting parameters: Eigenfrequency, damping constant and coupling coefficient (order parameter of Peierls distortion) of the amplitude mode of the charge density wave in CoOP versus temperature. Curves are guides to the eye.

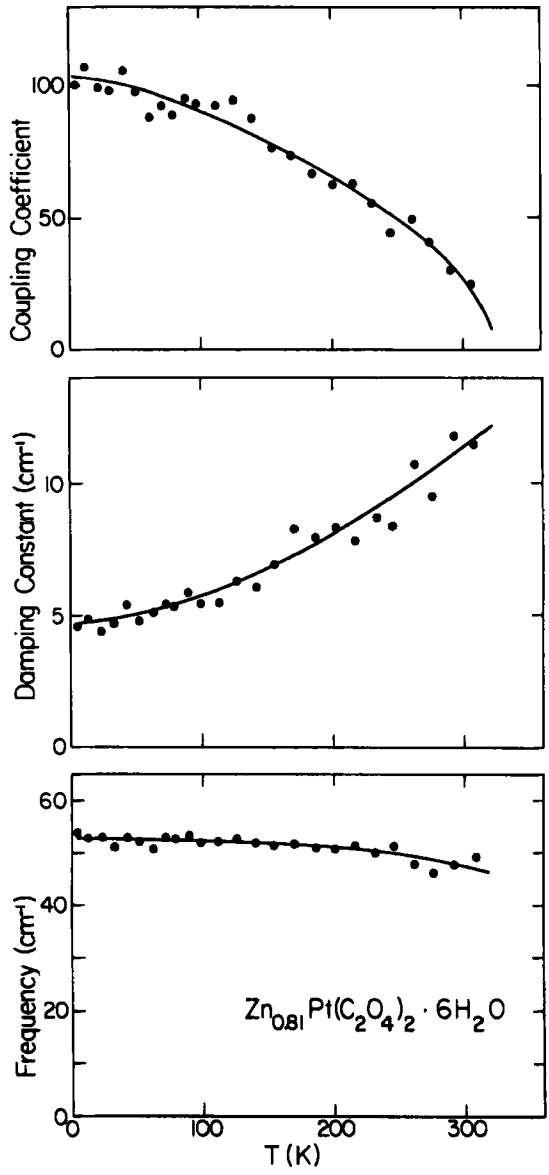

FIGURE 3 Fitting parameters: Eigenfrequency, damping constant and coupling coefficient (order parameter of Peierls distortion) of the amplitude mode of the charge density wave in ZnOP (protonated) versus temperature. Curves are guides to the eye.

slight increase in the damping constant on approaching room temperature are in agreement with the transition inferred from electrical conductivity measurements[12] which has been confirmed by X-ray scattering experiments[9].

In ZnOP, where our results are believed to be more reliable because of better signal to noise ratio, the behaviour of the damping constant and the coupling coefficient are seen in Fig. 3 to vary concurrently. If the square of the coupling coefficient is plotted versus temperature, as shown in Fig. 4, a straight line is obtained

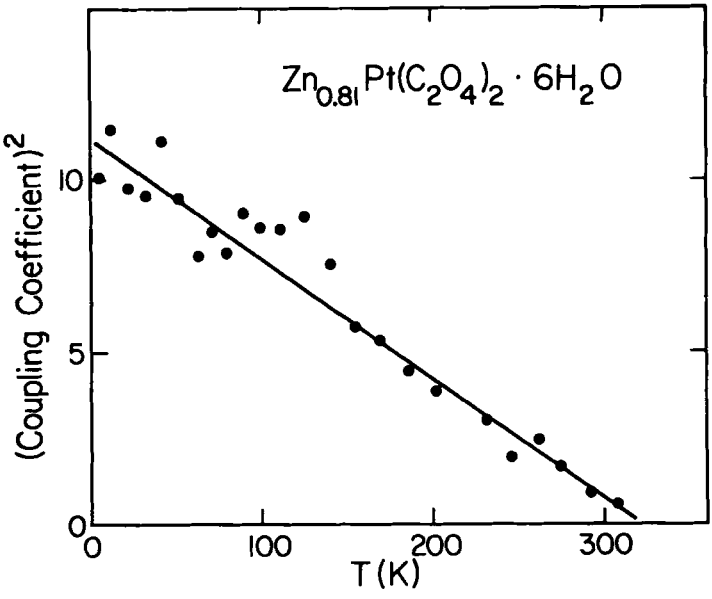

FIGURE 4 Square of coupling coefficient of the amplitude mode of ZnOP versus temperature

which indicates a mean-field behaviour for the order parameter and a phase transition at 320 K. This transition appears to be related to the rapid change from activated to temperature-independent behaviour observed in electrical conductivity measurements between 250 K and 300 K [13,14,2] and to the diffuse X-ray scattering results[15]. It has been associated with the three-dimensional ordering temperature T_{3d} of the Peierls instability, and below, we will give

further support to this interpretation. If the inverse damping constant γ^{-1} is plotted versus temperature a linear relationship is found over the whole temperature range, similarly to what had been reported for the amplitude modes of the charge density wave in the two-dimensional structures 2H-$TaSe_2$ and 1T-$TiSe_2$ [16].

DISCUSSION

In the mean-field theory for the one-dimensional coupled electron-phonon system the frequency of the amplitude mode ω_+ is related to the bare phonon frequency ω_Q ($Q = 2k_F$) by [17,4]

$$\omega_+ = \sqrt{\lambda}\,\omega_Q \tag{2}$$

where $\lambda = N(\epsilon_F)g_Q^2/\omega_Q$, k_F denoting the Fermi wavevector, $N(\epsilon_F)$ the density of states at the Fermi level and g_Q the electron-phonon coupling. For deuterated KCP neutron scattering[6] indicates that $\omega_Q = 8$ meV (64 cm^{-1}) and Raman scattering[4] yields an amplitude mode at 38 cm^{-1}. Combining these two values with Eq.(2) results in a parameter $\lambda = 0.35$ for KCP which is in good agreement with other, less direct determinations[18]. The gap parameter Δ_o given by the equation

$$\Delta_o = \alpha \epsilon_F e^{-\frac{1}{\lambda}}, \tag{3}$$

where α is a numerical factor which depends on the band structure, can be determined by identifying Δ_o with the activation energy deduced from the low temperature electrical conductivity. In this way the values $\Delta_o = 0.072$ eV (KCP [12]), 0.05 eV (CoOP [10,12]) and 0.054 eV (ZnOP [13]) have been found. Using Eq. (3) the different value of Δ_o for KCP as compared to the value for the oxalates may be attributed to an enhanced effective mass (as observed in ZnOP[13]) and thus a lower Fermi energy in the latter compounds. Therefore the parameter λ should be essentially the same in the three compounds, and, using Eq. (2), one has to conclude that the harder amplitude modes in the oxalates (50 cm^{-1} in CoOP, 53 cm^{-1} in ZnOP as compared to 44 cm^{-1} in protonated KCP) are simply a consequence of a stiffer lattice, i.e. a higher bare frequency ω_Q. This is rea-

sonable in view of the smaller Pt-Pt distance in these materials as compared to KCP (see above). (The argument is not changed if one assumes that the factor $\alpha\epsilon_F$ has the same value in the three materials since then Eq. (3) together with the value $\lambda = 0.35$ for KCP and the quoted gap values would imply a value $\lambda = 0.31$ for CoOP and $\lambda = 0.32$ for ZnOP, which could not account for a 20% change in ω_+).

Mean-field theory for the one-dimensional chain connects the gap value Δ_o to the transition temperature T_p^o by the BCS relation

$$k_B T_p^o = 0.567 \ \Delta_o. \tag{4}$$

From this and the above values for Δ_o one obtains T_p^o = 470 K for KCP, 330 K for CoOP and 360 K for ZnOP. The three-dimensional ordering in KCP has been established to occur around 100 K [19], and the difference between T_{3d} and T_p^o has been attributed to strong one-dimensional fluctuations. On the other thand, by associating the critical temperature deduced from the Raman data on ZnOP and CoOP (320 K) with the three-dimensional ordering in these materials, we have to conclude that $T_{3d} \approx T_p^o$. This suggests that, in CoOP and ZnOP, the one-dimensional fluctuations are suppressed by the three-dimensional ordering. Theoretically the two temperatures are indeed expected to essentially coincide if the interchain coupling is strong enough. Horovitz et al. have shown[20] within a tight-binding scheme (neglecting interchain Coulomb interaction but allowing for interchain hopping) that this is the case if the inequality

$$t_\perp \gtrsim 2k_B T_p^o \tag{5}$$

holds, where $t_\perp$ is the transverse hopping integral. We estimate $t_\perp$ from the observed electrical conductivity anisotropy ($\sigma_\perp/\sigma_\parallel \approx 10^{-4}$ in KCP[3] and 10^{-2} in CoOP[21]) by assuming that $\sigma_\perp/\sigma_\parallel = (t_\perp/t_\parallel)^2$ and that the longitudinal hopping integral is of the order of 1 eV (which appears to be appropriate for the Pt salts). This yields $t_\perp \approx 0.01$ eV (120 K) for KCP and 0.1 eV (1200 K) for CoOP implying that the inequality Eq. (5) is fulfilled for CoOP but not for KCP. Therefore strong fluctuations are indeed expected to occur for KCP ($T_{3d} \ll T_p^o$) whereas CoOP will exhibit mean-field behaviour ($T_{3d} \approx T_p^o$). This explains in a

natural way why KCP has a higher Δ_0 but nevertheless a lower T_{3d} than the oxalates.

Mean-field behaviour in the oxalates is not only evidenced by the coincidence of T_{3d} and T_p^o but also by the Landau behaviour of the coupling constant a as described above (Fig. 4). On the other hand the amplitude mode frequency plotted against temperature (Figures 2 and 3) indicates a very weak softening by approaching T_{3d} in contrast to both simple soft-mode theory[22] and experiments in two-dimensional systems[16]. However it is well-known[23] that the simple soft-mode behaviour will break down if lower-lying modes contribute to the order parameter susceptibility (e.g. if a "dynamic central peak" appears in the spectral function in addition to the "soft" mode). There is indeed a lower lying mode in an incommensurate charge density wave system, the phase mode. The nonlinear coupling between amplitude and phase mode will inhibit the complete

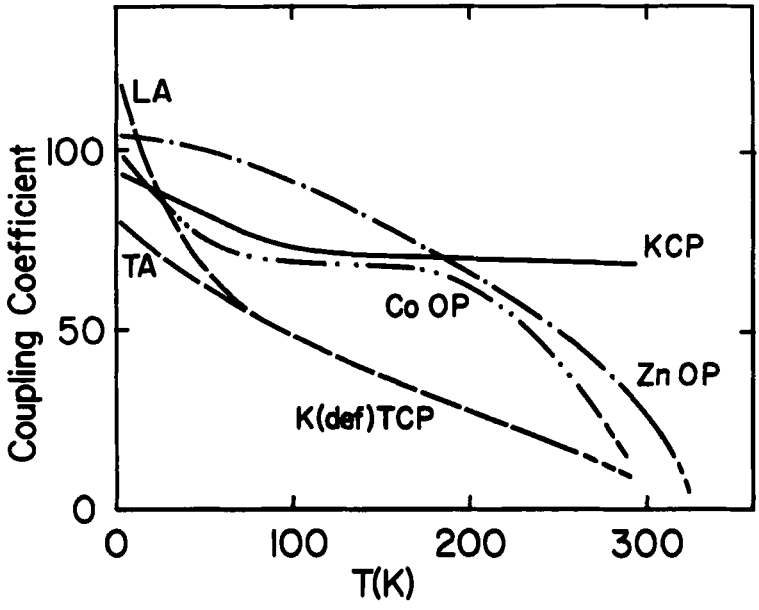

FIGURE 5 Comparison of temperature behaviour of coupling coefficient of amplitude mode (order parameter of Peierls distortion) for the different members of the Pt chain salt family.

softening of the amplitude mode. Furthermore this coupling could be responsible for the strong increase of the damping constant with temperature similarly to the mechanism proposed for KCP by Kurihara[24].

It is instructive to compare the present results for CoOP and ZnOP with those obtained for the tetracyanoplatinates KCP [4] and K(def)TCP [5,25]. Fig. 5 shows the coupling coefficient, which is proportional to the order parameter, as a function of temperature for the four cases. In KCP it decreases up to $T_{3d} \approx 100$ K and remains practically constant above this temperature where it may represent a "root mean-square order parameter"[3] of the strongly fluctuating one-dimensional regime. The results for K(def)TCP, although less reliable in the temperature dependence than those of CoOP and ZnOP because of more scatter in the data, are quite similar to those of the oxalates and indicative for a Peierls transition at room temperature, in agreement with the interpretation of electrical conductivity data advanced by Epstein et al.[26]. More details about K(def)TCP will be published elsewhere[25].

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