CHEMISTRY LETTERS, pp. 177-178, 1980. © The Chemical Society of Japan 1980

$2k_F$-$4k_F$ TRANSITION IN POTASSIUM DEFICIENT PARTIALLY OXIDIZED PLATINUM SALTS, $K_{1.75}[Pt(CN)_4].1.5H_2O$

Hayao KOBAYASHI, Yoshio HANO, Takaaki DANNO,
Akiko KOBAYASHI*, and Yukiyoshi SASAKI*
Department of Chemistry, Faculty of Science, Toho University,
Funabashi, Chiba 274
*Department of Chemistry, The Research Centre for Spectrochemistry,
Faculty of Science, The University of Tokyo, Hongo, Tokyo 113

X-ray photographs of $K_{1.75}[Pt(CN)_4].1.5H_2O$ showed weak $2k_F$ reflections below 294 K, which had been overlooked in neutron and X-ray diffraction studies. These reflections suggest the $2k_F$ eightfold structure. Above Tc, the Pt chain has a $4k_F$ fourfold structure. The 294 K transition can be regarded as the first example of $2k_F$-$4k_F$ transition in the partially oxidized platinum compounds.

Recently, independent neutron[1] and X-ray diffraction studies[2] have determined the fourfold structure of the potassium deficient partially oxidized platinum salt $K_{1.75}[Pt(CN)_4].1.5H_2O$ hereafter K(def)TCP. Assuming a uniform chain, the stoichiometry of K(def)TCP implies an electronic band filling of 7/8 and Fermi vector $k_F=0.875\pi/c_o$, where c_o is the average intrachain platinum distance. The $2k_F$ diffuse scattering,[3] a Kohn anomaly[4] in an inelastic neutron scattering, the d.c. resistivity[5] and the reflectance[6] showed characteristic one-dimensional behavior. The fourfold room temperature structure of K(def)TCP can be regarded as the $4k_F$ structure.

Epstein and Miller suggested the second order mean-field transition near 305 K.[7] Our conductivity measurements[8] showed a similar anomaly (Tc~300 K) to that of Epstein and Miller. We took oscillation and Weissenberg photographs of K(def)TCP between 215 and 313 K by the use of a high-powered X-ray generator (Rigaku RU1000) with Ni-filtered Cu radiation (50Kv, 1000mA) and the X-ray films of Sakura SCRE(Fig.1). The results are summarized as follows.

1) In contrast with the lattice periodicity so far reported, the crystal of K(def)TCP has a eightfold structure ($2k_F$ structure) along the platinum chain below 294 K.

2) The intensity of the $2k_F$ reflections increases abruptly around 294 K(Tc)(Fig.2). Above Tc, the $2k_F$ reflections disappear and there remain faint $2k_F$ diffuse streaks and $4k_F$ reflections.

3) The characteristic intensity distribution of $2k_F$ reflections in the high angle region shows that the crystal lattice is sinusoidally modulated by the $2k_F$ wave ($T<Tc$). According to the development of the $2k_F$ wave, the lattice vectors varies from $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ ($T>Tc$) to $\mathbf{a}$, $2\mathbf{b}$ and $2\mathbf{c}$ ($T<Tc$).

Putting all accounts together, the 294 K transition can be regarded as a $2k_F$-$4k_F$ transition, which corresponds to the phase transition found by Epstein and Miller. The $2k_F$-$4k_F$ transition of K(def)TCP is the first example in the partially oxidized platinum compounds. Although Carneiro, Jacobsen and Williams[9] considered K(def)TCP to be metallic above 50 K, the appearance of the $2k_F$ structure clearly shows that K(def)TCP is not a simple one-dimensional metal at least below 294 K.

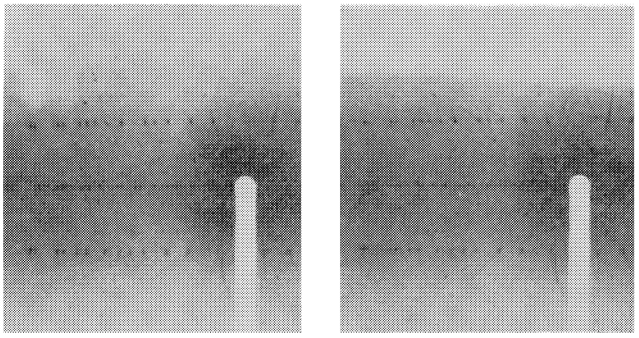

Fig.1. a) The oscillation photograph of K(def)TCP around the c axis at 318 K (above Tc).
b) The oscillation photograph of K(def)TCP around the c axis at 273 K(below Tc).

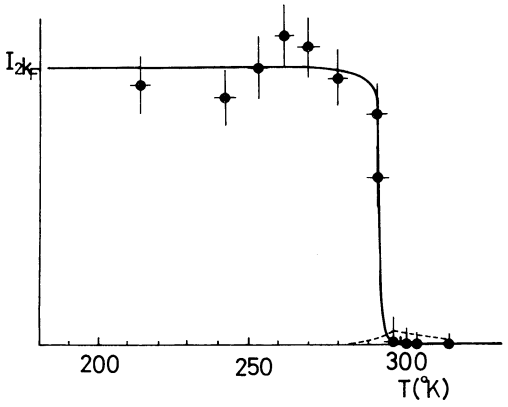

Fig.2. The temperature dependence of the averaged intensity of the $2k_F$ reflections measured by a microdensitometer. Broken line shows a rough plot of the intensity of $2k_F$ diffuse streak.

References

1) J.M.Williams, K.D.Keffer, D.M.Washecheck and N.P.Enright, Inorg. Chem. 15, 2446(1976).
2) A.H.Reis,Jr., S.W.Peterson, D.M.Washecheck and J.S.Miller, Inorg. Chem. 15, 2455(1976).
3) A.J.Schultz, G.D.Stucky, J.M.Williams, T.R.Koch and R.L.Maffly, Solid State Commun., 21, 197(1977).
4) K.Carneiro, J.Eckert, G.Shirane and J.M.Williams, Solid State Commun., 20, 333(1976).
5) T.W.Thomas, C.H.Hsu, M.M.Labes, P.S.Gomm, A.E.Underhill and D.M.Watkins, J. Chem. Soc. Dalton, 2050(1972).
6) R.L.Musselman and J.M.Williams, J. Chem. Soc. Chem. Commun., 187(1977).
7) A.J.Epstein and J.S.Miller, Solid State Commun., 29, 349(1979).
8) H.Kobayashi et al. to be published.
9) K.Carneiro, C.S.Jacobsen and J.M.Williams, Solid State Commun., 31, 837(1979).

(Received December 4, 1979)