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Researches of Conductive Transition Metal Complexes

Ikuji TSUJIKAWA

Department of Chemistry, Faculty of Science, Kyoto University,
Kitashirakawa-oiwake-cho, Sakyo-ku, Kyoto, 606

遷移金属錯体を超伝導物質の探索の対象としてとり挙げ研究してきた。主な探索物質は以下の通りである。(1)部分酸化マグナス緑色塩 $Pt_6(NH_3)_{14}Cl_{10}X_6$ ($X=ClO_4$, BF_4, PF_6 etc)，(2)遷移金属混合原子価錯体 $Cs_2Au_2X_6$ (X=Cl, Br, I)，(3)層間化合物 RE_xTaS_2 (RE=La, Ce)。

(1)，(2)の系では高い電気伝導度を示す物質を得ることが出来たが，超伝導の出現までには至っていない。(3)の系は新しい層間化合物であり多くの多形が現われる。これまでに，α 相 La_xTaS_2 および δ 相 Ce_xTaS_2 で超伝導転移が観測され，T_c はそれぞれ2.8 K と1.7 K であった。

We have tried to realize conductive complexes even at low temperature and superconducting complexes due to d electron. Our search of conductive transition metal complexes are mainly as follows: (1) Partially oxidized Pt mixed valence complexes $Pt_6(NH_3)_{14}Cl_{10}X_4$ ($X=ClO_4$, BF_4, PF_6, etc.), (2) Au mixed valence complexes $Cs_2Au_2X_6$ (X=Cl, Br and I), (3) RE_xTaS_2 (RE=La and Ce). In the cases of (1) and (2), we have obtained highly conductive complexes, but their conductive properties are semiconductive at low temperature. In the case of (3), different preparation methods provided several phases (α, β, γ, δ and ε). The superconductivity was detected in La_xTaS_2 (phase α, $T_c=2.8$ K) and Ce_xTaS_2 (phase δ, $T_c=1.7$ K) by the AC susceptibility measurement.

KEYWORDS: mixed valence, metal-insulator transition, transition metal complex, superconductivity, rare earth, intercalation

§1. Introduction

We have tried to realize conductive complexes even at low temperature and superconducting complexes due to d electron. Our search of conductive transition metal complexes will be mentioned as follows: (1) Ligand substitution complexes, namely complexes partially oxidized by ligand substitution and by simultaneously insertion of counter ion of the Magnus green salt $[Pt(NH_3)_4][PtCl_4]$ (MGS), (2) Some other complexes with d electron conduction, (3) As related topic RE_xTaS_2 (RE=La and Ce) will also be discussed.

§2. Partially Oxidized Pt Mixed Valence Complexes

A new family of Pt mixed valence complexes: $Pt_6(NH_3)_{14}Cl_{10}X_4$ ($X=ClO_4$, BF_4, PF_6, ReO_4 and SbF_6)(hereafter abbreviated as POC, POB, POP, PORe and POSb) was synthesized from the Magnus green salt (MGS) by the partial oxidation with an oxidant of H_2O_2 or by electrochemical method.[1,2] On partial oxidation, the 1/6 of Cl^- ligands in MGS are randomly replaced by NH_3 ligands and simultaneously counter ions X are introduced. These complexes comprise of one-dimensional chains with direct contact between Pt atoms and consequently a quasi-one-dimensional band made up of $5d_{z^2}$ orbital of Pt is formed. The average valence of Pt becomes +2.33. Because of this partial oxidation, the distances between Pt atoms along a chain become shorter from 3.25 Å for MGS[3] to 2.81, 2.85, 2.89 and 2.88 Å for POC, POB, POP and POSb, respectively. They are comparable to or shorter than that of $K_2[Pt(CN)_4]Br_{0.3}\cdot xH_2O$(KCP)[4] and closer to the value for Pt metal of 2.77 Å.

The DC conductivities of pressed pellets of POC, POB, POP and POSb were measured under hydrostatic pressure in the range of 4.2 K to r.t. by the four probe method. The activation energy E_a of these complexes becomes considerably smaller than that of MGS ($E_a=190$ meV).[5] They are listed in Table I. The conductivity values of the partially oxidized complexes are alike each other and rather high in spite of the measurement on the powder compressed pellets, which comes from the fact that the Pt atoms are partially oxidized and the distance between the Pt atoms becomes shorter.

The temperature dependence of the conductivity depends on the symmetry of the counter anions. The conductivity of the complex with the tetrahedral anion such as POC and POB is semiconductive over all temperature region. On the other hand, in the case of the complex with the octahedral anion such as POP and POSb, broad conductivity maximum appears at about room temperature and its temperature shifts to the lower temperature side with increasing pressure.

The ESR measurement was undertaken for POC, POB and POP. The g factors observed are characteristic of d_{z^2}-like hole state, with an admixture, due to spin-orbit interaction, of the degenerate $5d_{xy,yz}$ states. The log (Intensity × T) vs T^{-1} plots are shown in Fig. 1, where experimental points lie on straight lines for all of these complexes. This indicates that the ground state consists of non magnetic Pt^{2+} and Pt^{4+} ions and paramagnetic Pt^{3+} ions are produced by thermal activation. Figure 2 shows the temperature dependence of the line width ΔH_{pp}. For these complexes, the minima of width appear

Table I. Conductivity at room temperature and activation energy in semiconductive region for compressed pellets.

	POC	POB	POP	POSb
d(Pt–Pt)/Å	2.81	2.85	2.89	2.88
P=1 bar				
$\sigma_{r.t.}/Scm^{-1}$	1.1	1.4	1.4	5.2
E_a/meV	26–34	20–30	10–28	5–17
high-pressure	(1.2 GPa)	(0.9 GPa)	(1.3 GPa)	(1.2 GPa)
$\sigma_{r.t.}/Scm^{-1}$	3.4	2.7	5.0	11.9
E_a/meV	20–30	15–25	~10	5–10

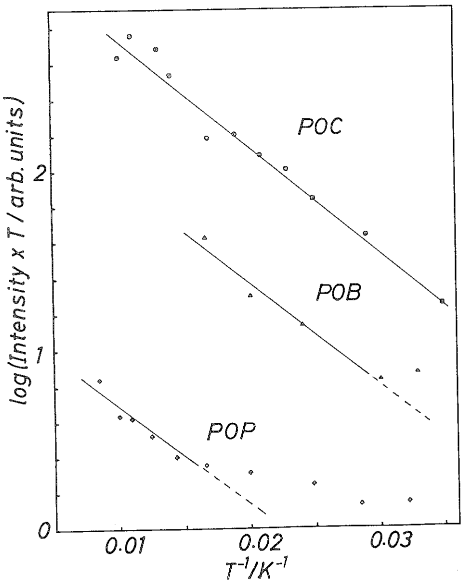

Fig. 1. Intensity of ESR signal for POC, POB and POP.

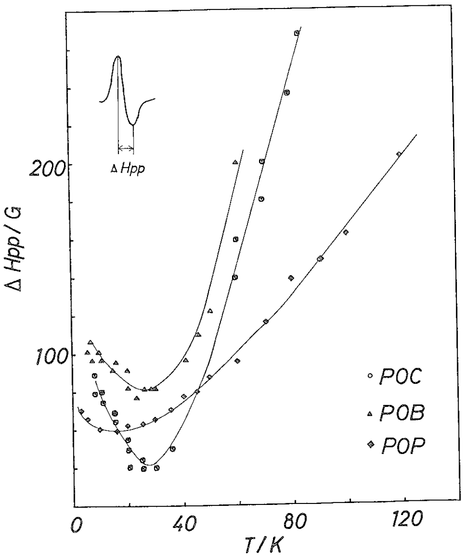

Fig. 2. Line width of ESR signal for POC, POB and POP.

around 15 K-30 K. It might be explained by the consideration that with increasing temperature the motional narrowing takes place at first caused by Pt^{3+} hopping and next the width increases due to phonon scattering. In KCP the width minimum appears at about 90 K[6] and it cannot be understood why in our complexes the temperature of the width minima is lower by more than 60 K than that of KCP.

§3. Some Other Complexes with d Electron Conduction

We have investigated the mixed valence state in $Cs_2Au^{I}Au^{III}X_6$ (X=Cl, Br and I). The crystal has a distorted perovskite structure(I4/mmm), which is similar to that of $BaBiO_3$. We have the analogy of 3D superconductor $BaPb_xBi_{1-x}O_3$ in mind. It can be correspondence: $Cs^+ \leftrightarrow Ba^{2+}$, Au^+, $Au^{3+} \leftrightarrow Bi^{3+}$, Bi^{5+}, $X^- \leftrightarrow O^{2-}$.

In order to investigate the mixed valence state of the Au ions, we have measured the X-ray photoelectron spectra(XPS) and the ^{197}Au Mössbauer spectra.[7]

In the case of XPS, as a probe for an examination of the oxidation state of the Au ions, we measured the binding energies of the $4f_{5/2}$ and $4f_{7/2}$ levels of Au ions. In the cases of X=Cl and Br, Au^{I} and Au^{III} ions are clearly distinguishable. The energy difference between the Au^{I} and Au^{III} levels in $Cs_2Au_2X_6$ is smaller than that between the Au^{I} level in Bu_4NAuX_2 and the Au^{III} level in Bu_4NAuX_4, which implies that the oxidation states of Au^{I} and Au^{III} in $Cs_2Au_2X_6$ approach the Au^{II} oxidation state. In the case of X=I, the binding energy of Au^{I} in Bu_4NAuI_2 is almost equal to that of Au^{III} in Bu_4NAuI_4. So that, the Au^{I} and Au^{III} states in $Cs_2Au_2I_6$ could not be distinguished.

In the case of ^{197}Au Mössbauer spectra, as a probe for an examination of the oxidation state of the Au ions, we measured the isomer shift and the electric-quadrupole splitting at 16 K. In this measurement, the Au^{I} and Au^{III} states could be distinguished for all the compounds $Cs_2Au_2X_6$ (X=Cl, Br and I).

For these compounds, we have observed the structural phase transition at about 600 K, where the crystal structure changes from the tetragonal perovskite structure to the cubic one. In the cubic phase, the oxidation state of Au may be Au^{II}.

Recently, in the case of X=Br, we could synthesize the cubic perovskite phase at atmospheric pressure. The oxidation state of the Au ion is considered to be Au^{II} from the measurement of the ^{197}Au Mössbauer spectra, XPS and ESR. Figure 3 shows the X-ray powder diffraction pattern for the tetragonal and cubic phases of $Cs_2Au_2Br_6$. The conductivity value of the cubic phase is rather high ($\sigma \sim 10^{-2}$ scm^{-1}) in spite of the halogen bridged complex. The conductivity measurement under the hydrostatic pressure is in progress.

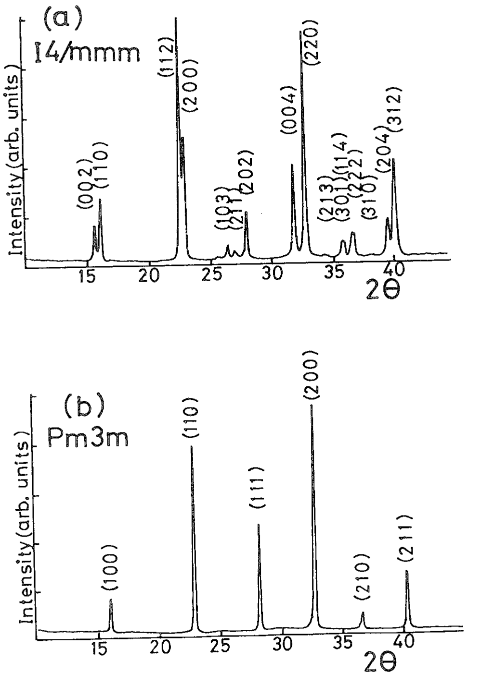

Fig. 3. X-ray powder diffraction pattern for $Cs_2Au_2Br_6$. (a) Tetragonal phase. (b) Cubic phase.

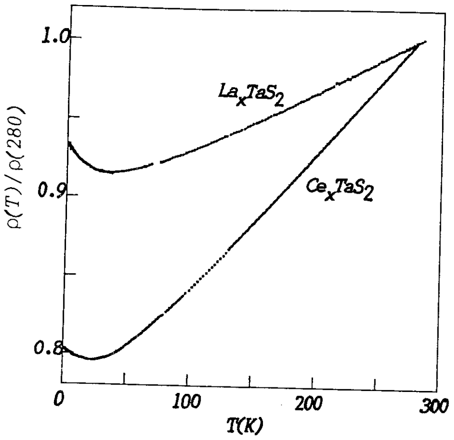

Fig. 4. Resistivity for RE$_x$TaS$_2$ (RE=La and Ce, phase γ) as a function of temperature. The resistivity at 280 K is 1.1×10^{-3} Ωcm for La$_x$TaS$_2$ and 1.3×10^{-3} Ωcm for Ce$_x$TaS$_2$.

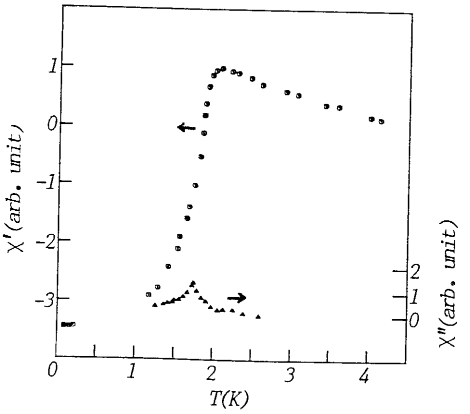

Fig. 5. Susceptibility for Ce$_x$TaS$_2$ (phase δ). χ'' has a maximum at 1.7 K.

§4. RE$_x$TaS$_2$ (RE=La, Ce)

New intercalated systems RE$_x$TaS$_2$ (RE=La, Ce) were prepared and their transport and superconducting properties were investigated.[8] Different preparation methods provided five phases (α, β, γ, δ and ε) which could be classified according to their structure forms. The resistivity was investigated for La$_x$TaS$_2$ (phase γ) and Ce$_x$TaS$_2$ (phase γ) with needle shape. Results are shown in Fig. 4. Both compounds have the similar room temperature resistance and the temperature dependence of resistivity which has a broad resistance minimum at 35 K for La$_x$TaS$_2$ and 23 K for Ce$_x$TaS$_2$. The occurrence of the minimum can be associated with the Kondo effect, but, in this case it is unlikely because La$_x$TaS$_2$ has non paramagnetic impurities. Another possibility is, as observed in 1T–TaS$_2$,[9] the hopping conductivity in the carrier localization state that could result in such resistance minimum. Futher investigations (*e.g.* magnetoresistance) are indispensable to elucidate the mechanism that causes this phenomenon.

AC susceptibility measurement was carried out for La$_x$TaS$_2$ (phase α) and Ce$_x$TaS$_2$ (phase α, β and δ). La$_x$TaS$_2$ shows the superconductivity with the transition temperature (T_c) of 2.8 K, which is defined as the temperature where the susceptibility has half value of the perfect diamagnetism. Ce$_x$TaS$_2$ (phase δ) with long interlayer distance of 17.4 Å becomes also superconducting as shown in Fig. 5. For this compound, the susceptibility was measured down to 0.1 K achieved by the adiabatic demagnetization. The signal of χ'' has a maximum at 1.7 K which corresponds to T_c. In this phase, the appreciable paramagnetic signal is observed above T_c, which behaves as the Curie-Weiss law ($\chi = C/T - \theta$). The susceptibility measurement under high magnetic field are in progress to study whether the antiferromagnetic order coexists.

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