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学 位 論 文 題 目 Structure and Properties of Partially Oxidized  
Salts of Metallophthalocyanine

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## Introduction

Partially oxidized phthalocyanine salts have some salient features such as their characteristic stacking structure and peculiar physical properties. In particular some of these materials show anomalous electron transport property, i.e. absence of a Peierls transition in spite of their strong one-dimensional natures. In the measurement of the dc electrical conductivity of these materials, however, the resistance jumps due to the extrinsic origin are the large problem for obtaining a reliable conductivity curve. To conquer this problem, the author constructed the microwave conductivity measurement apparatus which enables the strain-free cooling of a sample crystal.

## Construction of Microwave Conductivity Measurement Apparatus

Electrical conductivity of a single crystal at microwave region can be obtained from the change of the Q-value and resonant frequency shift by using cavity perturbation method. Since this method has high sensitivity and needs no contact of electrode, this is applicable to observe the dielectric constant of a very thin and mechanically weak sample. However, it has been reported that when the sample's conductivity is large and its resonant frequency shift is high, the microwave loss tends to become apparently larger and thus the microwave conductivity is estimated to be smaller than the true value. This phenomenon has been thought to be caused by the change of coupling constant between the cavity and the wave guide induced by the resonant frequency shift by the sample, or to be caused by the imperfect frequency specification of the apparatus. Some ideas have

been proposed to avoid such an effect by Guldbrandsen et al. and Buravov et al.

In the process of constructing a microwave conductivity measurement apparatus, the author found the followings: if the resonant cavity has only slight incompleteness that is the bottom plate is set incorrectly to the cylindrical  $TE_{011}$  cavity—even if there exist electric contact or not between the two parts—a large extrinsic microwave loss appears especially when a long conductive sample is placed in the cavity. The change of the coupling between the waveguide and resonant cavity is relatively small in contrast to the claim of Buravov et al. Furthermore, through the experiment of TTF–TCNQ, the author found that the correction of microwave loss by subtracting the loss of metal wire which is proposed by Guldbrandsen et al. is not always the effective method.

#### Microwave conductivity of DCNQI Salts

On the contrary to the anomalous behavior of some partially oxidized phthalocyanine salts, some dicyanoquinonediimine (DCNQI) salts exhibit a metal–insulator transition. From the optical spectra, the presence of an inter–chain interaction through the coordination bond between Cu and cyano groups of DCNQI in  $Cu(Me_2-DCNQI)_2$  and one–dimensional character of alkali–metal salts of DCNQI have been pointed out. Temperature dependence of their microwave conductivity was measured to know the typical response of these materials and to compare them with those of phthalocyanine salts in their insulating phase.

#### Microwave conductivity of $MPcX_z$

The temperature dependence of microwave conductivity was measured on the single crystals of phthalocyanine salts:  $NiPc(AsF_6)_{0.5}$ ,  $PtPc(ClO_4)_{0.5}$ ,  $PtPc(AsF_6)_x$ ,  $CoPc(AsF_6)_{0.5}$ . They exhibited a metal–insulator transition. In contrast to the salts of  $NiPc$ ,  $H_2Pc$ , and  $CuPc$ , the

feature of conductivity of  $\text{CoPc}(\text{AsF}_6)_{0.5}$  was semiconducting and the room-temperature conductivity was an order of magnitude smaller than the other metallic phthalocyanine salts. These features of  $\text{CoPc}(\text{AsF}_6)_{0.5}$  quite resemble to that of  $\text{CoPcl}$  in spite of the difference of the band-filling factor and the repeating unit of electrostatic potential.

#### Properties of $\text{CoPc}(\text{AsF}_6)_{0.5}$

Crystal structure and physical properties of  $\text{CoPc}(\text{AsF}_6)_{0.5}$  were measured. The crystal belongs to the tetragonal system with the space group of  $P4/mcc$ , the lattice constant being  $a=14.234(2)$ ,  $c=6.296(2)$  Å, and  $Z=2$ . Both the infrared and visible spectra suggest that Co is not oxidized but the Pc ring is mainly oxidized contrary to the analogous material  $\text{CoPcl}$ . Optical conductivity  $\sigma(\omega)$  along the stacking axis shows a strong peak at 0.29 eV and a weak one at 1.2 eV. The former peak indicates the existence of a bandgap of ca. 0.2 eV in the  $\pi$ -band and the latter is the evidence for the band formation in a Co chain through the direct overlap of  $3d_z^2$ -orbitals. Magnetic susceptibility is the superposition of the Curie-Weiss part with a Curie constant of  $0.056 \text{ emu mol}^{-1}$  and the nearly temperature independent part. The latter components is interpreted as a Bonner-Fisher type paramagnetism with an effective exchange interaction  $J/k_B=230 \text{ K}$  (antiferromagnetic) in the Co chain, which is consistent with the value of  $J$  estimated from the optical transition at 1.2 eV.

Though the Pc ring is considered to act as the conducting pathway like other phthalocyanine salts, the optical property along the conducting axis does not resemble the salts based on the non-magnetic phthalocyanines that have conducting pathways in the Pc chains. This result arouses an interest in the possible role of the magnetic interaction between two chains in the  $\text{CoPc}$  salt. The solid properties of  $\text{CoPc}(\text{AsF}_6)_{0.5}$  such as crystal structure, dc and high-frequency electrical conductivity, magnetic susceptibility, and optical property and quite similar

to those of CoPcI.

### Ferromagnetic Interaction of in Solid CoPc(OBu)<sub>8</sub>

In the process of studying the conducting CoPc salt, concentrating on the magnetic interaction between the unpaired electrons on Co and Pc macrocyclic ligand, some experiment with the cation radical of CoPc(OBu)<sub>8</sub> which is soluble to organic solvents were made to estimate the magnetic exchange energy between them. In this study, a ferromagnetic interaction in the neutral CoPc(OBu)<sub>8</sub> compound at low temperature was unexpectedly found. This property is attractive from the viewpoint of the comparison with the antiferromagnetic property of the  $\beta$ -polymorph of CoPc. Since the ferromagnetic interaction is rare even in the molecules involving transition metals, the study of this material may give an insight into the molecular ferromagnetism.

## 論文の審査結果の要旨

山門英雄君の博士論文内容は、1) 高周波伝導度測定装置の製作、立ち上げ、および2) コバルトフタロシアニン部分酸化塩の物性研究である。

まず、試料を破損しやすいという四端子伝導度測定法の欠点を解決するため、高周波伝導度測定装置を製作した。製作過程における最も重要な点は、空洞共振器自身の高周波損失を少なくすることにある。この問題点を克服するにあたって、空洞共振器本体に誘起された損失が空洞共振器の機械的精度に大きく依存することなどの現象面を明らかにし、共振器の損失の少ない装置を完成させた。本装置により、これまで測定困難であった試料の低温での伝導度測定を可能とした。

次に、白金、ニッケル、コバルトを含むフタロシアニンの部分酸化塩を作成し、結晶構造および光学的性質、磁化率、電気伝導度などを測定し、その基本物性を明らかにした。従来からの研究により、コバルトフタロシアニン塩は、白金、ニッケル、銅フタロシアニン塩とは異なり、中心金属のコバルトが酸化を受けているとされていた。この考えはこの物質だけが他と異なって半導体的な挙動を示すことを説明するために導入されていた。この論文では、新たに作成したコバルトフタロシアニン塩の電子スペクトルと振動スペクトルの研究から、 $\pi$ 電子系部分の有機配位子であるフタロシアニン環が酸化を受けていることが特異な物性と重要な相関があることを明らかにした。これはこれまでの考え方を覆す実験事実を提供したものであり、この実験結果に基づき半導体的な挙動の原因が、伝導電子と不対電子のカップリングに由来する可能性があるという新しい考え方を導入した。

以上の研究は数物科学研究科構造分子科学専攻の博士学位論文としての内容に値し、更に、実験装置の立ち上げ、新しい物質の作成、各種固体物性の研究、および新しい考えの提案と専門的にも総合的にも極めて優秀な研究業績を上げていると判断した。