Articles

A Theoretical Study on the Electronic Structures of MOCl (M=Ti, V and Fe) and Their Relationship with Physical Properties

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In order to find out the relationship between electronic structures of metal oxychlorides (MOCl) and their physico-chemical properties, we have carried out the tight-binding band electronic structure calculations with Extended Hückel (EH) method for TiOCl, VOCl and FeOCl. The relative contribution of metal atom to DOS at Fermi level increases in the order of Ti, V and Fe, which is parallel to the reactivities of MOCl toward guest species. The M^{2+} ion plays a crucial role in the electric conductivity of MOCl and its intercalation compounds. Hopping conduction theory is applied to explain the increase of conductivity after intercalation.

Introduction

When layered materials take up foreign chemical species (atoms, ions or molecules) into their interlayer spaces, the process is called as topochemical reaction, which is classified into intercalation and topochemical substitution.[1] In intercalation, the accessible types of guest species and reaction patterns are governed almost entirely by the bonding types of layered structures[1~3] For example, when the interlayer interaction is coulombic, ionic guest species are preferably intercalated into the host. Clay-organic complexes belong to this category.[4~6] In case of van der Waals type, electron donors are easily intercalated.[6~13] In contrast to intercalation, topochemical substitution is the reaction in which new covalent bonds are formed between host and guest by replacing the surface atoms of the layers. FeOCl,[14~15] γ-AlOOH[16~17] and zirconium phosphates[1,18] show this type of reaction.

Metal oxychlorides (MOCl) are investigated in this study because of at least the following two reasons. First, though many experimental studies have been performed, theoretical analysis to understand the intrinsic properties and reactivity to guest species of these materials are very few.[19~22] Secondly, the five MOCl (M=Ti, V, Cr, Fe and In) are mutually isomorphous so that the central metals experience almost

equivalent ligand fields.[23] However, their physico-chemical properties are somewhat different depending on the central metals. Thus calculations of the electronic structures of MOCl may help us to better understand their physico-chemical properties.

Various theoretical approaches have been attempted to investigate the electronic structures of two-dimensional solids[24~33] In any case, a good knowledge of the band structure in the vicinity of the Fermi level is required for qualitative analysis. Though not accurate in general, the theoretical calculations based upon the single electron approximation can give us very useful information about the band structure near the Fermi level. Thus we have applied the extended Hückel tight-binding (EHTB) method[33~36] to calculate the band structure of MOCl. Really, a number of compounds such as metal oxides, metal chlorides, and metal chalcogenides have been studied using this method.[22,33,37~39]

In the present work, in order to elucidate the basic differences among MOCl, we examine and compare the electronic structures of three of these compounds, TiOCl, VOCl and FeOCl, by the EHTB method. In section 2, we will summarized the structural features of MOCl. And then, from the energy band strcutures and DOS curves, the reactivities of MOCl will be discussed in section 3. Finally, the increase

Table 1. Cell parameters of MOCl (M=Ti, V and Fe) (Å)

P_{mmn}	Ti [40]	V [41]	Fe [42]
a	3.79	3.78	3.780
b	3.38	3.30	3.302
c	8.03	7.91	7.917
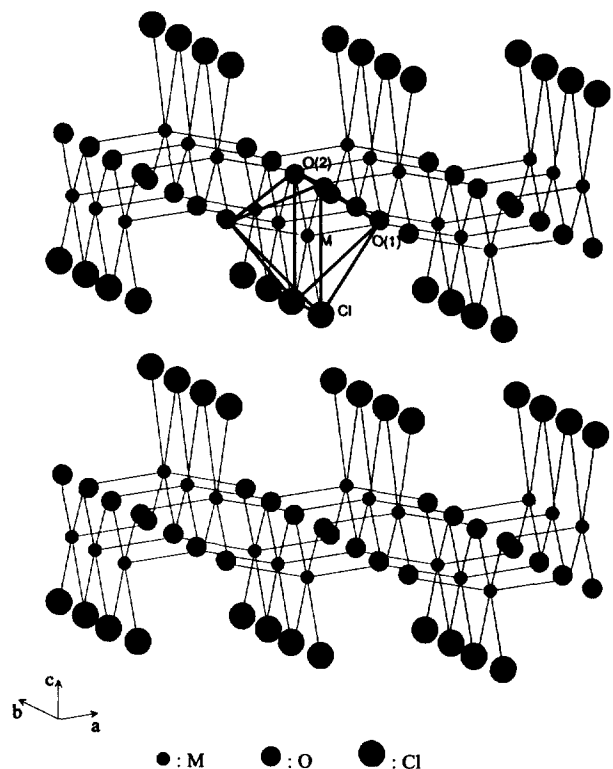
Figure 1. Structure of two layers of MOCl. The heavy solid lines denote the MCl_2O_4 distorted octahedron.

of conductivity after intercalation will be explained briefly by the hopping conduction theory.

Structural features of MOCl

Three MOCl (M=Ti, V, and Fe) of interest are mutually isomorphous and belong to the orthorhombic space group Pmmn with Z=2 (Table 1).[40~42] The crystal structures consist of a stack of double sheets of *cis*-MCl_2O_4 distorted octahedra linked together by shared edge within the **ab** plane (Figure 1). The outermost atoms of a layer are chlorines bridged with central metals, so that each layer is bound with weak van der Waals interaction extended along the c-axis. An oxygen atom is surrounded by four metal atoms whereas the central metal is coordinated to four oxygen and two chlorine atoms. In MOCl, there are three types of bonds: M-O(1), M-O(2) and M-Cl (bond length: M-Cl>M-O(2)>M-O(1)) (Table 2). The M-O(1) bond runs along the **a**-axis whereas M-O(2) and M-Cl along the **b**-axis. (Figure 2)

In transition metal oxides and halides, delocalization is primarily governed by the degree of direct metal-metal overlap, rather than by the d-p cation-anion hybridization.[19~21] Hence

Table 2. Inter-atomic distances of MOCl and ionic radii sum of the constituting elements (unit: Å)

	Ti [40]	V [41]	Fe [42]
M-O(1)	1.950	1.967	1.964
M-O(2)	2.261	2.082	2.100
M-Cl	2.320	2.359	2.368
O(1)-O(1)	3.380	3.300	3.302
O(1)-O(2)	2.745	2.611	2.624
O(1)-Cl	3.124	2.956	2.995
O(2)-Cl	3.092	3.358	3.357
R_a (Cl-Cl)[1]	3.790	3.780	3.780
R_b (Cl-Cl)[2]	3.380	3.300	3.302
R_a (M-M)[3]	3.790	3.780	3.780
R_b (M-M)[4]	3.380	3.300	3.302
R_{nn} (M-M)[5]	3.207	3.097	3.107
M-O[6]	2.27	2.02	2.03 (HS)
			1.93 (LS)
M-Cl[6]	2.70	2.45	2.46 (HS)
			2.36 (LS)

[1,2] The Cl-Cl distances along *a* and *b* axes. [3,4] The M-M distances along *a* and *b* axes. [5] The nearest neighbor M-M distance in the unit cell. [6] The ionic radii sums calculated from Shannon values [44]: Ti^{3+} (1.025 Å), V^{3+} (0.78 Å), Fe^{3+} (0.785 Å (high spin) and 0.69 Å (low spin)) for octahedral metal ions; O^{2-} (1.24 Å) for tetrahedral oxygen; Cl^- (1.67 Å).
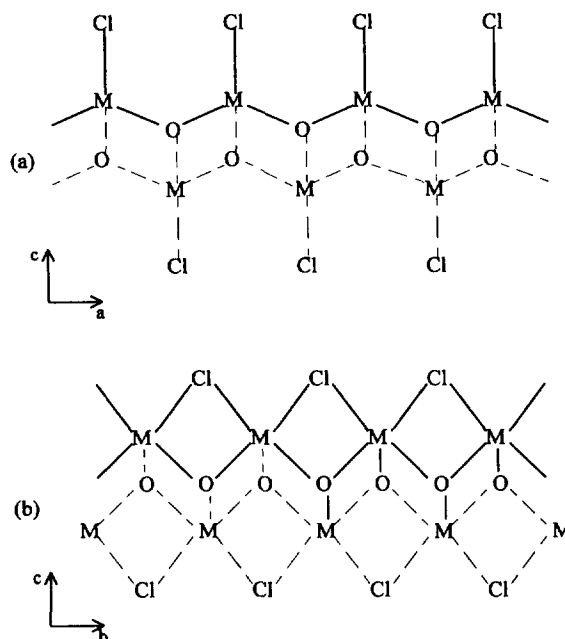
Figure 2. The building block of MOCl layers. The atoms connected by dashed lines lie in the plane b= −1/2 in (a) and a= − 1/2 in (b). (a) in *a*-direction. (b) in *b*-direction.

the shorter M-M distance is, (the stronger the inter-cell interaction is) the more disperse the band structure becomes. Otherwise, the band becomes flat and localization of *d* elec-

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Table 3. Extended Hückel parameters

Element	orbital	H_{ii}	$\zeta_1{}^a$	$\zeta_2{}^b$	$C_1{}^a$	$C_2{}^b$
Ti	4s	−10.82	1.50			
	4p	−6.06	1.50			
	3d	−12.71	4.55	1.40	0.4206	0.7839
V	4s	−10.89	1.30			
	4p	−7.05	1.30			
	3d	−13.35	4.75	1.50	0.4560	0.7520
Fe	4s	−11.23	1.90			
	4p	−6.82	1.90			
	3d	−14.58	5.35	2.00	0.5505	0.6260
O	2s	−32.3	2.275			
	2p	−14.8	2.275			
Cl	3s	−30.0	2.033			
	3p	−15.0	2.033			
	3d	−9.0	2.033			

^{a} Exponents in a double-ζ expansion of the metal d-orbitals.
^{b} Coefficients in a double-ζ expansion of the metal d-orbitals. Ref. [45-47]

trons is expected.[43] Another factor determining the electronic structures of the solid state materials is the ligand effect. Metal-ligand (M-L) interaction can be regarded as a perturbation to the band structures of the metal. If the M-L interaction is strong, the band structure also becomes disperse and the electrons are delocalized in -M-L-M-L-M- array, where ligand acts as a bridge connecting metal and metal.

In our system, because the M-M distances are longer than their ionic radii sum, M-M interaction may be weak. M-L interaction in the distorted MCl_2O_4 would be quite different from and more complex than those in corresponding MO_6 and MCl_6 octahedra. We can expect that M-Cl interaction is a little bit stronger than M-O interaction because, compared to their effective ionic radii sum,[44] M-Cl distance is shorter than M-O distance.

Energy Band Structures and DOS curves of MOCl

The band structures of three MOCl (M=Ti, V and Fe) were obtained by the EHTB method. In Table 3, we summarize the atomic parameters employed in our calculations. The VSIP (Valence State Ionization Potential; H_{ii}) values were obtained through the Self-Consistent-Charge-Iteration method.[45-47] Figure 3 plots the band dispersion relation for a slab of MOCl layer along the XΓYMX symmetry line, where Γ=(0, 0), X=(a^*/2, 0), Y=(0, b^*/2), and M=(a^*/2, b^*/2).

In the band structures of MOCl, there exist one or more bands intersecting the Fermi level, which suggests these materials are metallic. However, MOCl have been reported to be semiconductive.[1] Such a breakdown of normal band theory have been widely observed.[48,49] When electron-electron repulsion is large enough to cause an electron localization, the metallic state does not appear against the expectation with
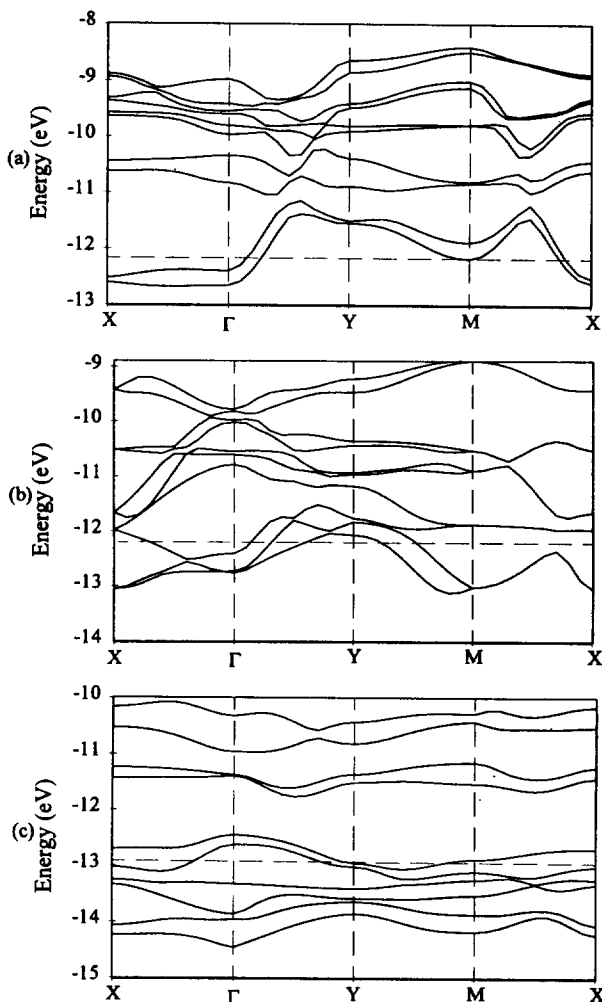

Figure 3. The d-block band structures of three MOCl. The horizontal dashed lines refer to the Fermi level. (a) TiOCl (E_f= −12.10 eV), (b) VOCl (E_f= −12.20 eV) and (c) FeOCl (E_f= −12.92 eV).

the normal band theory.[50] When the band width is much smaller than the on-site Coulomb repulsion, for example, the electrons will stay apart to reduce the Coulomb repulsion, and be localized. It may be necessary to calculate the on-site Coulomb repulsion and to compare it with the band width in order to confirm whether the localized state is more stable or not. In the present case, however, it is not feasible to calculate the on-site Coulomb repulsion term. Therefore, we should simply infer the electronic structures of MOCl only from the band width.

The dispersional widths of the d bands cutting the Fermi level of MOCl are somewhat narrow, which are varied as 1.62, 1.54, and 0.69 eV for M=Ti, V and Fe, respectively. Such narrow width results from the relatively long M-M distances compared with their effective ionic radii sum. The M-M orbital interactions exponentially decrease as their distances get longer. The narrow band width of MOCl suggests that these MOCl could be classified into Mott-Hubbard insulators. It has been generally accepted that TiOCl and VOCl are Mott-Hubbard insulators,[19-21] which is in good agreement with our suggestion. However, in the case of d^5 system such
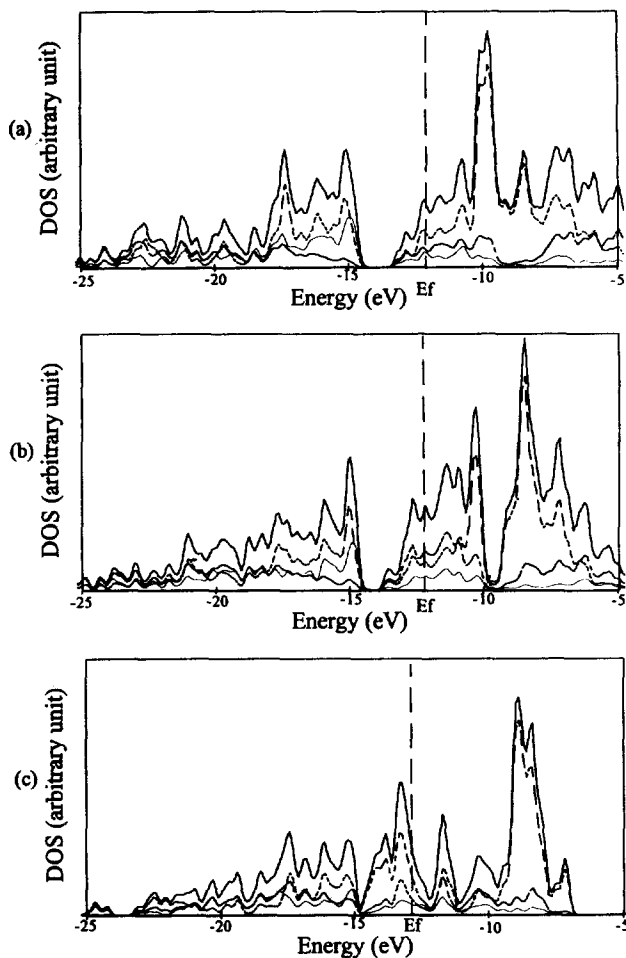
Figure 4. DOS curves of three MOCl. Vertical dashed lines refer to the Fermi level (E_f) of MOCl. Heavy solid lines indicate the total DOS, dotted lines projected DOS onto metal atoms, dashed lines Cl atoms and solid lines O atoms. (a) TiOCl (b) VOCl (c) FeOCl

Table 4. The relative contribution of the constituting atoms to DOS at Fermi level.[a]

MOCl	M	Cl	O
Ti	31.0%	48.3%	20.7%
V	48.6%	32.4%	18.9%
Fe	61.3%	25.8%	12.9%

[a] Considering the electron-electron repulsion, the true Fermi level would be located above the calculated one. However, the relative contributions to DOS will not be changed considerably around the Fermi level.

dispersiveness of the HO bands depends both on the M-M and M-L interactions. In MOCl, however, we must consider the latter much seriously, because the M-M distances are longer than M-L distances (See Table 2). Thus it is considered that the low-lying HO-band of TiOCl interacts more efficiently with the ligands p-bands than that of FeOCl does and thus has much more ligands characters.

Figure 4 represents the DOS curves of three MOCl. The amounts of orbital mixing between ligands (O or Cl) and metals can be estimated in the projections of DOS (PDOS) onto the three constituent atoms. In the PDOS curves onto O atom, we can see that the contribution of O atom to the DOS at the Fermi level is much smaller than that of the Cl atom. In other words, M-O interaction is weaker than M-Cl interaction at the Fermi level. This is explained by the two factors of M-L distance and the energy gap between the metal d-orbital and the ligand p-orbital bands. In the present case, the O $2p$ orbital is located a little bit closer to the metal $3d$ orbitals than Cl $3p$ orbital (Table 3). However, M-Cl interaction is stronger than M-O interaction because M-Cl distance is much shorter than their effective ionic radii sum (Table 2). Consequently, we expect that the Cl atom makes much larger contribution to the DOS at the Fermi level than O atom.

In TiOCl, the extent of contribution to the DOS at the Fermi level is the following order: Cl>Ti>O. In VOCl and FeOCl, the order is changed as M>Cl>O. As given in Table 4, the relative contribution of metal atoms to the DOS at Fermi level increases in the order of Ti, V and Fe. In intercalation reaction, the reactivity of pristine MOCl against guest species is, in general, the largest in FeOCl and followed by VOCl and TiOCl in decreasing orders.[1,53] This trend is parallel to that of metal contribution to DOS at the Fermi level. Thus the metal contribution at the Fermi level provides a crucial role in the reactivity of MOCl. In fact, it is well known that the transferred electron from guest species is localized in the central metal in MOCl.[54~59]

Conductivities of MOCl

As mentioned above, the d electrons of MOCl are localized into unit cell. Electronic conductivities of MOCl vary with the central metal and the amount of transferred electron from the guest. In order to understand these, at first, let us consider the conductivities of pure MOCl. Commonly MOCl are prepared by the chemical vapor transport method under the appropriate temperature gradient in an evacuated

as FeOCl, the situation is not so simple. Several quantitative informations such as the charge transfer energy (Δ), the d-d Coulomb interaction (U), the anion valence band width (W), the d band width (w) and the hybridization interaction (T) are required to explain the electronic behavior of this system. According to the Zaanen-Sawatzky-Allen (ZSA) model,[51] insulating compounds arising from the correlation between d electrons can be catagorized into either of two classes, Mott-Hubbard insulators or charge-transfer insulators. From the discussion of Zaanen *et al.*,[51] it is expected that FeOCl falls into the intermediate region of the ZSA phase diagram. Since there are no reported numerical data about the above parameters at present, we infer the electronic feature of FeOCl from considering those of Fe_2O_3 and $FeCl_3$. Since Fe_2O_3 and $FeCl_3$ belong to Mott-Hubbard regime,[20,43] it is considered that FeOCl bahaves as a Mott-Hubbard insulator, which is supported by its conductivity data.[52]

The Highest Occupied bands (HO-bands) are getting flatter as the metal changes from Ti to Fe, which results from the interactions between the bottom of metal d-block bands and the upper portion of ligand (O or Cl) p-block bands. The

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Table 5. Some physical properties of MOCl. (cited from ref. [1])

M=	electron configu- ration	Magnetism	[b]μ_{eff} (300 K)	[c]Resistivity	Standard Reduction Potential
Ti^{3+}	$3d^1$	A^a	$0.98\mu_B$(1.73)	–	-0.369eV
V^{3+}	$3d^2$	A	$2.06\mu_B$(2.83)	$5\times10^7\Omega$cm	-0.256eV
Fe^{3+}	$3d^5$	A	$2.78\mu_B$(5.92)	$10^7\Omega$cm	0.771eV

[a]A: Antiferromagnetic. [b]Effective magnetic momentum. Values in parantheses are the spin-only ones for high spin. [c]Room temperature

sealed tube.[40,53,59] In this method, small amounts of water molecules behave as a transporting agent to promote the formation of reaction product, so that oxychlorides are considered to have proton defects in the form of $H_xM_x^{2+}M_{1-x}^{3+}$-OCl.[59,60] That is, pure MOCl contains small amounts of built-in M^{2+} ions. If so, the liability to form M^{2+} ion would be a key to solve the conductivity problem. Table 5 represents the standard reduction potential of M^{3+} ion and conductivities and magnetic properties of MOCl. Here, standard reduction potentials show the same trend as the conductivities of hosts. Therefore, impurity, i.e. M^{2+}, can be regarded as a main factor determining the conductivity of MOCl.

During intercalation, the M^{3+} ion of MOCl is partially reduced to form M^{2+} ion depending on the amount of electrons transferred from the guest introduced between interlayer gaps.[54~58] The partial reduction of central metal will affect the electronic structure of MOCl.

In order to understand the effect of M^{2+} impurity on the electronic properties of MOCl, the hopping conduction model is applied. In this model, the temperature dependence of resistivity is often expressed by

$$\rho^{-1}(T) = \rho_1^{-1}\ \exp(-\varepsilon_1/kT) + \rho_3^{-1}\ \exp(-\varepsilon_3/kT) \qquad (1)$$

where ε_1 and ε_3 denote the ionization energy of an isolated donor and the activation energy in hopping process, respectively.[61] The first term corresponds to the band conduction and the second term the hopping one. For convenience, we assume that the impurity of host affects the band structure very slightly. In order to estimate the order of magnitude of ε_3 in MOCl and their intercalation compounds, we have used the conductivity data of FeOCl and FeOCl(FeCp₂)₁/₆ obtained by Villeneuve *et al.*[52] Figure 5 represents the conductivity data of these compounds and theoretical ones. For FeOCl and its ferrocene intercalation compound, conductivities are described as follows:
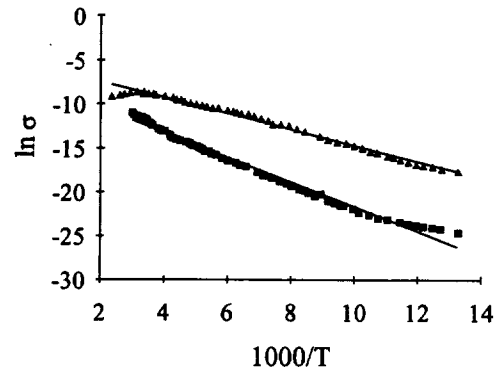
$$\rho_{FeOCl}^{-1}(T) = \rho_1^{-1}\ \exp(-\varepsilon_1/kT) + \rho_{3,FeOCl}^{-1}\ \exp(-\varepsilon_{3,FeOCl}/kT) \qquad (2)$$

$$\rho_{inter}^{-1}(T) = \rho_1^{-1}\ \exp(-\varepsilon_1/kT) + \rho_{3,inter}^{-1}\ \exp(-\varepsilon_{3,inter}/kT) \qquad (3)$$

Subtraction of Equation (2) from Equation (3) gives

$$\rho_{inter}^{-1}(T) - \rho_{FeOCl}^{-1}(T) =$$
$$\rho_{3,inter}^{-1}\ \exp(-\varepsilon_{3,inter}/kT) - \rho_{3,FeOCl}^{-1}\ \exp(-\varepsilon_{3,FeOCl}/kT). \qquad (4)$$

We assumed that the first terms of the Equations (2) and (3) are approximately equivalent because they are independ-

Figure 5. Conductivity data of FeOCl (lower part) and FeOCl (FeCp₂)₁/₆ (upper part). The solid lines represent the least square fitting of experimental data.

ent of impurity concentration. The impurity (Fe^{2+} ion) concentration in FeOCl is negligible compared with that in FeOCl (FeCp₂)₁/₆. Then Equation (4) becomes

$$\rho_{inter}^{-1}(T) - \rho_{FeOCl}^{-1}(T) \cong \rho_{3,inter}^{-1}\ \exp(-\varepsilon_{3,inter}/kT) \qquad (5)$$

Taking logarithms one obtains,

$$\ln\{\rho_{inter}^{-1}(T) - \rho_{FeOCl}^{-1}(T)\} = -\ln\rho_{3,inter} - \varepsilon_{3,inter}/kT \qquad (6)$$

From the fitting of Equation (6) to observed data, we have obtained the value ε_3 as 0.078 eV. If FeCp₂ is an one-electron donor, we can say the one-third of electron is transferred to the unit cell of host (FeOCl)₂.[52,54] When transferred electron is delocalized in the host matrix to form an Fe^{2+} ion, the impurity band resulting from Fe^{2+} ion is located near above the HO-band. Thus the conductivities of MOCl increase as a result of intercalation.

Concluding remarks

The present work reveals that the long M-M distance in MOCl plays a crucial role for their characteristic electronic structures. Long M-M distance reduces the cation-cation inter-cell interaction. This causes a relatively flat band structures and is a main driving force for electron to be localized. Considering the conductivities, other experimental results[19~21] and the electronic structures of MOCl, we can categorize these compounds to be the Mott-Hubbard insulators.

It is known that FeOCl shows higher reactivity towards intercalation compared with TiOCl and VOCl. In our work, this is explained by the analysis of DOS. The metal contribution to DOS at the Fermi level is the largest in FeOCl. The metal contribution at the Fermi level accelerates the intercalation reaction of MOCl, which is the result of charge transfer from guests to the central metal.

The hopping conduction process is applied to explain the increase in conductivity upon intercalation. When some electron donating species are introduced into the van der Waals gap of host materials, charge transfer occurs to produce the M^{2+} ion. This M^{2+} ion, hopping in the layer of MOCl, causes an increase in conductivity. By comparing the conductivity data of FeOCl with that of FeOCl(FeCp₂)₁/₆, we have estimated the hopping activation energy. The existence

of M^{2+} ion plays a crucial role in characteristic physical properties of MOCl.

Further experimental studies are needed to confirm the conclusive relationship between electronic structures, conductivities and other physico-chemical properties.

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