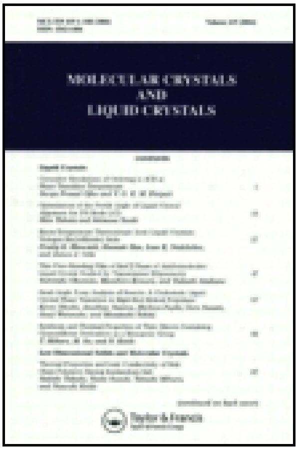

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Hiroshi Sakai [a] , Takashi Yamazaki [a] , Nobuya Machida [a] , Toshihiko Shigematsu [a] & Saburo Nasu [b]

[a] Department of Chemistry, Faculty of Science, Konan University, Okamoto 8-9-1, Higashinada, Kobe, 658-8501, Japan

[b] Department of Material Physics, Faculty of Engineering Science, Osaka University, Machikaneyama 1-3, Toyonaka, 560-8531, Japan

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HIROSHI SAKAI[a], TAKASHI YAMAZAKI[a], NOBUYA MACHIDA[a], TOSHIHIKO SHIGEMATSU[a] and SABURO NASU[b]

[a]*Department of Chemistry, Faculty of Science, Konan University, Okamoto 8–9–1, Higashinada, Kobe 658–8501, Japan and* [b]*Department of Material Physics, Faculty of Engineering Science, Osaka University, Machikaneyama 1–3, Toyonaka 560–8531, Japan*

Mössbauer spectra of the $FePS_3$-cobaltocene intercalation compound were measured in the temperature range of 300K to 10K. The spectra, distinct from those of pure $FePS_3$, suggest the charge transfer from cobaltocene to Fe-S antibonding orbitals of the $FePS_3$ host lattice.

Keywords: Mössbauer spectra; intercalation; layered compound; $FePS_3$; charge transfer

INTRODUCTION

The transition metal phosphorus trisulfides (MPS_3; M=transition metal) form a class of layered materials with crystal structures of the $CdCl_2$ type.[1] The layers are composed of arrays of $[P_2S_6]^{4-}$ units coordinated to the M^{2+} cations through M-S bonds, so that the M^{2+} cations are in a trigonally distorted octahedral environment. The transition metal layers are separated by two planes of sulfur atoms, bound together by relatively weak van der Waals interactions. Because of the weak interaction, various chemical species may be intercalated into the van der Waals gap between the adjacent sulfur layers.

Intercalations of neutral metallocenes like $[Co(\eta^5C_5H_5)_2]$ and $[Cr(\eta^5C_6H_6)_2]$ into MPS_3 (M=Mn, Zn, Fe, and Ni) were carried out by Clement and Green.[2] They found the increase of the basal spacings of *ca* 5.3 Å and the stoichiometries of *ca* x=1/3 in $MPS_3[Co(\eta^5C_5H_5)_2]_x$, suggesting the formation of "first-stage"

compounds. The IR spectra of these intercalation compounds clearly indicated that the intercalated guest metallocenes were essentially cationic. The results suggest that the driving force for the intercalation is a charge transfer from guest molecules to the host matrices. However, the reduction sites or the acceptor levels of the host are not established yet in the intercalation compounds. Whangbo et al.[3] calculated the band electronic structure of an $FePS_3$ slab by employing the tight-binding band scheme based on the extended Hückel method. They concluded that the metal 3d-block bands, which are partially filled with high-spin d^6 electrons, must be responsible for the acceptor capability.

Mössbauer spectroscopy gives much information on the electronic states of iron atoms in the matrices. Fatseas et al.[4] measured Mössbauer spectra of Li-intercalated $FePS_3$, which showed a new quadrupole doublet in addition to the host $FePS_3$. The new doublet, increases with lithium intercalation, was identified as an iron site reduced with intercalation. Recently we have reported on the Mössbauer spectra of $FePS_3$ intercalated with pyridine and allylamine.[5] The spectra were completely different from those of $FePS_3$ intercalated with Li. The spectra, consist of low spin Fe^{2+} and high spin Fe^{2+} states, suggest the charge transfer from the guest molecules to $[P_2S_6]^{4-}$ units of the host matrix. It is necessary to have more detailed information on the reduction sites of the host and the mechanism of the charge transfer. In this paper we have reported on the Mössbauer spectra and the mechanism of charge transfer in the $FePS_3$-cobaltocene intercalation compound.

EXPERIMENTAL

$FePS_3$ was prepared by reacting stoichiometric amounts of the high purity elements (99.9% or better) in an evacuated quartz tube at 700°C for 1 month. The intercalation of cobaltocene was carried out by dispersing the fine powder of $FePS_3$ and cobaltocene (in the molar ratio of $FePS_3$:cobaltocene=1:1) into toluene in an ampoule sealed under vacuum and keeping at 105°C for 1 week, which was the same as the method of Clement and Green.[2] The content of the intercalated cobaltocene was not determined clearly because an excess of cobaltocene was not removed completely from the intercalation compound. The stoichiometry was roughly estimated to be $x=0.3 \sim 0.4$ in $FePS_3[Co(\eta^5C_5H_5)_2]_x$ using thermogravimetric and X-ray fluorescence analyses. The intercalation compound, which is stable in air, was characterized by the X-ray powder diffraction (XRD) using graphite monochromated Cu-K α radiation. ^{57}Fe Mössbauer spectra of the intercalation compound were measured in the temperature range of 300K to 10K, using a constant-acceleration type spectrometer with a $^{57}Co/Rh$ matrix source.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of pure $FePS_3$ and cobaltocene-intercalated $FePS_3$, indicating sharp diffraction peaks of (00L) lines. The diffraction peaks corresponding to pure $FePS_3$ were completely missing in the pattern of intercalated $FePS_3$, suggesting that the intercalation are performed completely with cobaltocene. The shift to lower angle in the intercalation compound implies an increase in the interlayer spacing. The basal spacing is estimated to be 11.77Å, which is close to 11.74Å of the previous work.[2] The interlayer expansion of 5.35Å, in agreement with the values of cobaltocene-intercalated ZrS_2 and SnS_2,[6] suggests that the cobaltocene molecule is oriented with the C_5 axis parallel to the van der Waals layers, as shown in Fig. 2. Wong et al.[7] have established from X-ray and neutron diffraction studies on single crystals of ZrS_2 and $SnSe_2$ intercalated with cobaltocene that the C_5 axis of cobaltocene lies parallel to the layers. The area of a neutral cobaltocene molecule is estimated to be *ca.* 47 Å^2 (6.96 Å in length and 6.76 Å in width[7]) which compares with an interlayer area of *ca.* 16.3 Å^2 per iron atom in $FePS_3$. Such a geometric limitation suggests that the maximum uptake of cobaltocene is approximately 0.35 per iron atom. The intercalation compound obtained in this work, therefore, may be taken as $FePS_3[Co(\eta^5C_5H_5)_2]_{0.35}$ with maximum occupancy of the interlayer spacing.

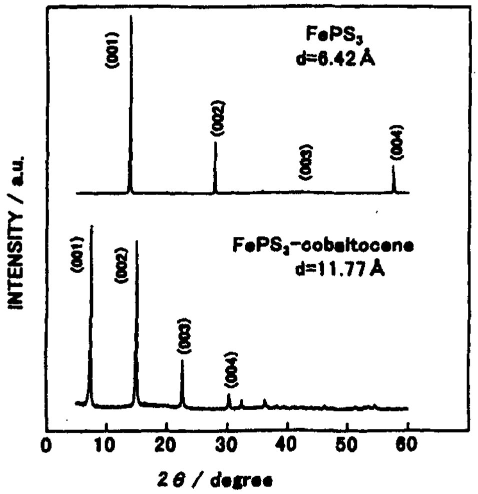

FIGURE 1 X-ray diffraction patterns of pure $FePS_3$ and $FePS_3[Co(\eta^5C_5H_5)_2]_{0.35}$.

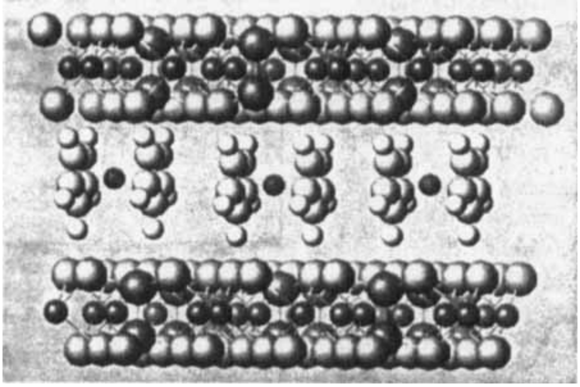

FIGURE 2 Model of the arrangement of cobaltocene in the van der Waals regions of $FePS_3$.

Figure 3 shows the Mössbauer spectra of $FePS_3$ intercalated with cobaltocene at various temperatures. The spectra are distinct from those of pure $FePS_3$, suggesting a charge transfer from cobaltocene to $FePS_3$. The paramagnetic spectra at 300K and 80K in the intercalation compound consist of three sets of quadrupole doublets. Table I gives the Mössbauer parameters such as isomer shift (IS), quadrupole splitting(QS), and line width (Γ), obtained by the least-squares fitting of the paramagnetic spectra. The outer two doublets (designated as **A** and **B**) and the inner doublet (**C**) are identified to be two kinds of high spin Fe^{2+} states and a low spin Fe^{2+} state, respectively, from the values of isomer shift and quadrupole splitting. The iron site corresponding to the doublet **B** is not so much influenced by the intercalation of cobaltocene, because the values of isomer shift and quadrupole splitting are close to those of pure $FePS_3$. The iron site is also observed in the pyridine-intercalated $FePS_3$, but not observed in the allylamine-intercalated $FePS_3$, depending on the content of intercalants.[5] As the content of cobaltocene (*ca.*0.35 per iron atom) is less than that of the pyridine (*ca.*0.66) intercalated in $FePS_3$, the intensity of the doublet **B** is fairly large compared with that of the pyridine-intercalated $FePS_3$.

The high spin Fe^{2+} species corresponding to the quadrupole doublet **A**, larger values of isomer shift and quadrupole splitting than the doublet **B** or pure $FePS_3$, is more ionic than the Fe^{2+} ion in pure $FePS_3$. The Fe^{2+} species, observed in $FePS_3$ intercalated with pyridine and allylamine, may result when the interaction between the iron and sulfur atoms becomes weak. The results suggest that the charge transfer arises partially from cobaltocene to the antibonding orbitals of the Fe-S bonds.

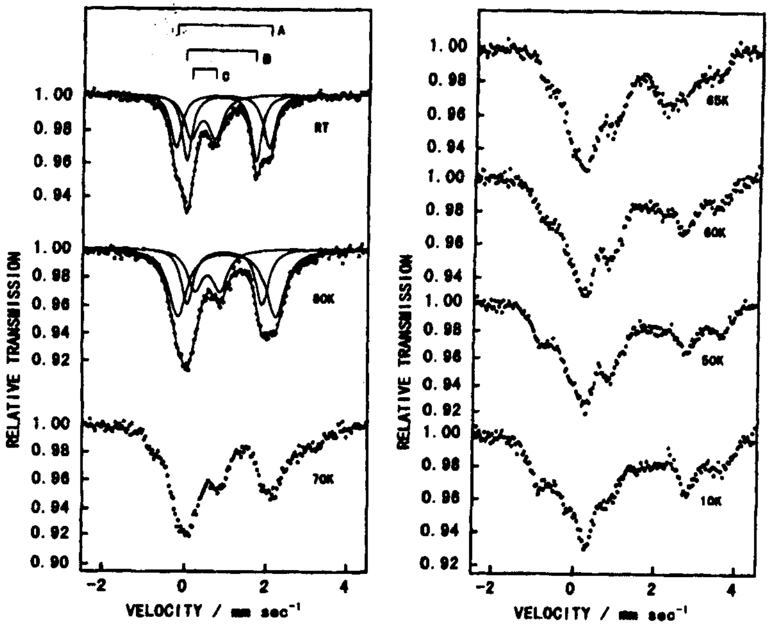

FIGURE 3 Mössbauer spectra of $FePS_3[Co(\eta^5C_5H_5)_2]_{0.35}$ at various temperatures.

TABLE I Mössbauer Parameters of $FePS_3$, $FePS_3[Co(\eta^5C_5H_5)_2]_{0.35}$, and $FePS_3(Py)_{2/3}$.

Compounds	T(K)		IS(mms^{-1})	QS(mms^{-1})	Γ(mms^{-1})	
$FePS_3$	290		0.864	1.527	0.285	ref.[5]
$FePS_3[Co(\eta^5C_5H_5)_2]_{0.35}$	300	A	0.893	2.293	0.342	
		B	0.871	1.718	0.301	
		C	0.410	0.601	0.418	
$FePS_3(Py)_{2/3}$	290	A	0.931	2.336	0.547	ref.[5]
		B	0.846	1.747	0.321	
		C	0.437	0.616	0.470	

According to the extended Hückel tight-binding calculations of $FePS_3$ [3,8], the 3d band of Fe is divided into three sublevels in the density of state (DOS) diagram: a strong peak centered at -11.9 eV and two smaller peaks at -13.8 and -10.2 eV. Whereas the 3p lone-pairs orbitals of S are predominantly located at -13.8 and -10.2 eV. This results immediately suggest that the highest peak at -10.2 eV in the total DOS contains the Fe-S e_g* antibonding orbitals, the peak at -11.9 eV contains the Fe t_{2g} nonbonding orbitals, and the lowest peak at -13.8 eV contains the Fe-S e_g bonding orbitals. This is confirmed by the Fe-S crystal orbital overlap population curves.[8] Therefore, it is quite reasonable that the antibonding orbitals of the Fe-S bonds may be responsible for the acceptor capability of the charge transfer.

On the contrary, the low spin Fe^{2+} species corresponding to the doublet C, which is also observed in $FePS_3$ intercalated with pyridine and allylamine, is more covalent than the Fe^{2+} ion in pure $FePS_3$. The origin of the low spin Fe^{2+} species is not clear. We note that the quantity of the low spin Fe^{2+} species is close to that of the high spin Fe^{2+} species in the Mössbauer spectra. By the charge transfer from cobaltocene to a part of the antibonding orbitals of Fe-S bonds (e.g., the Fe-S bonds become weak), the adjacent Fe-S bonds seem to become strong, that is, the adjacent Fe^{2+} ions undergo stronger ligand field of sulfur atoms than the Fe^{2+} ion in pure $FePS_3$. The presumption may lead to the formation of the low spin Fe^{2+} species. The Mössbauer paramagnetic spectra of the cobaltocene-intercalated $FePS_3$ are quite similar to those of $FePS_3$ intercalated with pyridine. The experimental results suggest that the intercalation mechanism of cobaltocene is the same as that of pyridine. Mössbauer data of the pyridine-intercalated $FePS_3$ are also given in Table 1 for comparison.

References

[1] R. Brec, *Solid State Ionics,* **22,** 3 (1986).
[2] R. Clement and M. L. H. Green, *J. Chem. Soc. Dalton Trans.,* **1979,** 1566.
[3] M.-H. Whangbo, R. Brec, G. Ouvrard, and J. Rouxel, *Inorg. Chem.,* **24,** 2459 (1985).
[4] G. A. Fatseas, M. Evain, G. Ouvrard, R. Brec, and M.-H. Whangbo, *Phys. Rev.,* **B35,** 3082 (1987).
[5] H. Sakai, T. Yamazaki, T. Shigematsu, S. Nakashima, T. Hinomura, and S. Nasu, *Chem. Lett.,* **1997,** 1101.
[6] D. O'Hare, W. Jaegermann, D. L. Williamson, F. S. Ohuchi, and B. A. Parkinson, *Inorg. Chem.,* **27,** 1537 (1988).
[7] H.-V. Wong, J. S. O. Evans, S. Barlow, and D. O'Hare, *J. Chem. Soc., Chem. Commun.,* **1993,** 1589.
[8] H. Mercier, Y. Mathey, and E. Canadell, *Inorg. Chem.,* **26,** 963 (1987).