Mössbauer Spectra of $FePS_3$ and Its Intercalation Compounds

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We succeeded in preparing $FePS_3$ intercalated with pyridine and allylamine. In the XRD patterns of the intercalates the diffraction peaks corresponding to $FePS_3$ were completely missing. The Mössbauer spectra are changed significantly by the intercalation, suggesting the charge transfer from guest molecules to the host matrix.

Metal phosphorus trisulfides with the formula MPS_3, where M is a divalent metal cation, crystallize in layered structures. Klingen et al.[1] determined the crystal structure of $FePS_3$ and found it to have a monoclinic unit cell (space group C2/m) with the lattice parameters a=5.934 A, b=10.28 A, c=6.722 A, and β =107.16°. The structure is related to that of cadmium chloride, with iron ions and phosphorus-phosphorus pairs occupying the cadmium positions and sulfur ions occupying the chloride positions. However, the bond distances of P-P and P-S bonds are 2.19 A and 2.03 A, respectively, closed to covalent bond distances, which suggest that the phosphorus and sulfur atoms exist as $[P_2S_6]^{4-}$ anions. The Fe^{2+} ion is octahedrally coordinated by six sulfur atoms of three $[P_2S_6]^{4-}$ anions.

The layered $FePS_3$ compound is known to be able to intercalate alkali metals[2] and metallocenes[3] in the interlayer spacings. The driving force for intercalation has been accepted as the charge transfer from guests to the host matrices. However, the reduction sites or the acceptor levels of $FePS_3$ are not established yet in the intercalation compounds. Whangbo et al.[4] 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. Fatseas et al.[5] measured Mössbauer spectra of Li intercalated $FePS_3$, which showed a new quadrupole doublet in addition to that corresponding to the host $FePS_3$. The new doublet, increases with lithium intercalation, was identified as an iron site reduced with intercalation.

In order to clarify the acceptor levels of intercalations, we have prepared $FePS_3$ intercalated with pyridine and allylamine and measured their Mössbauer spectra. Mössbauer spectroscopy gives much information on the electronic states of iron atoms in the matrices. It is, therefore, interesting to compare the Mössbauer spectra of pure and intercalated $FePS_3$.

Pure $FePS_3$ was prepared by reacting stoichiometric amounts of the high purity elements (99.99% or better) in an evacuated quartz tube at 700 ℃ for 3 weeks to 1 month.[6] The intercalation of pyridine or allylamine was carried out by the following procedure: The fine powder of $FePS_3$ was sealed in an evacuated glass ampoule together with liquid pyridine or allylamine. Then, the ampoule was kept at 105 ℃ for pyridine or 50 ℃ for allylamine for 2 weeks. The pure and intercalation compounds were characterized by the X-ray powder diffraction (XRD) using graphite monochromated Cu-K α radiation. ^{57}Fe Mössbauer spectra were measured at room temperature and 80K, using a constant-acceleration type spectrometer with a ^{57}Co / Rh matrix source. The velocity scales for the spectrometer were calibrated with an α-Fe foil.

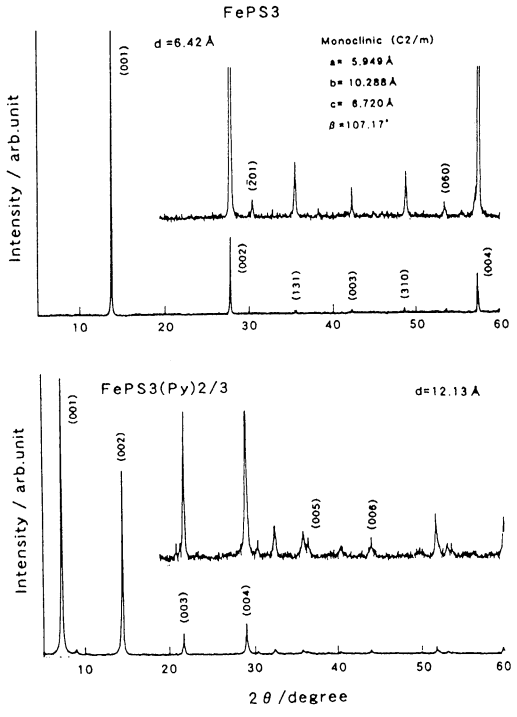

Figure 1. X-ray diffraction patterns of $FePS_3$ and $FePS_3(Py)_{2/3}$.

Figure 1 shows typical XRD patterns for pure $FePS_3$ and intercalated $FePS_3$ with pyridine, indicating sharp diffraction peaks of (00L) lines. The patterns indicate that the

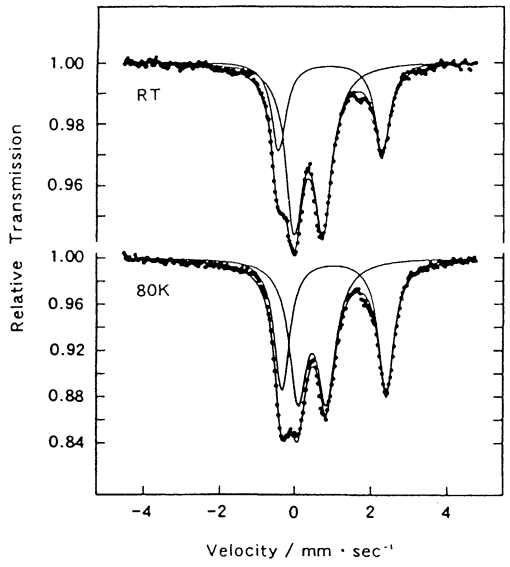

Figure 2. Mössbauer spectra of $FePS_3(Aa)_{3/4}$ at RT and 80K.

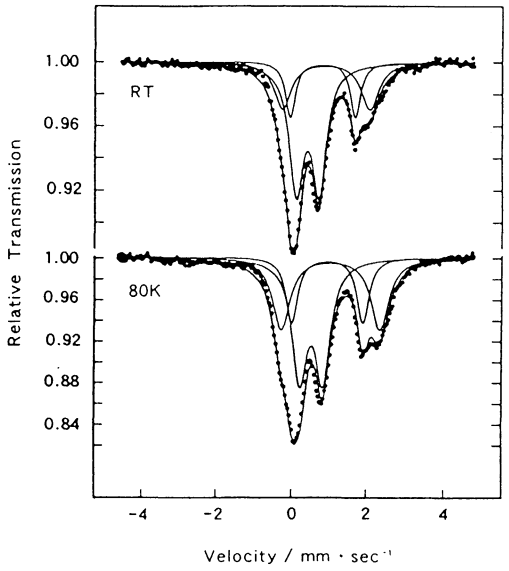

Figure 3. Mössbauer spectra of $FePS_3(Py)_{2/3}$ at RT and 80K.

intercalation compounds maintain layered structures and the interlayer distances are estimated to be 12.13 A for pyridine and 10.60 A for allylamine, being larger than that of the pure $FePS_3$ crystal (6.42 A). The diffraction peaks corresponding to pure $FePS_3$ were completely missing for intercalated $FePS_3$, suggesting that the intercalations are performed completely with pyridine and allylamine. The compositions of these intercalates are obtained to be $FePS_3(pyridine)_{2/3}$ and $FePS_3(allylamine)_{3/4}$ using a thermogravimetric analysis.

Mössbauer spectra of pure $FePS_3$ were similar to those reported by Taylor et al.[6], consisting of a paramagnetic quadrupole doublet at room temperature and a magnetically ordered spectrum at 80K. Figure 2 shows the Mössbauer spectra of $FePS_3$ intercalated with allylamine at room temperature and 80K, distinct from those of pure $FePS_3$ at both temperatures, suggesting the charge transfer from guest molecules to the host matrix. The spectra consist of two quadrupole doublets, while three quadrupole doublets are observed in the pyridine intercalation compound, as shown in Figure 3. It suggests that pyridine is intercalated ununiformly in the host crystal. Table 1 gives the values of the isomer shift (I.S.), quadrupole splitting (Q.S.), and line width (Γ), obtained by the least-squares method of those spectra. From these values, the inner and outer doublets (two doublets in the pyridine intercalate) are identified to be low spin Fe^{2+} and high spin Fe^{2+} states, respectively. That is, the iron atom in the $FePS_3$ host matrix is not reduced by the intercalation of allylamine or pyridine. In the case of the intercalation of amines, a covalent bond may be formed between lone pair electrons in the amines and sulfur 3d orbitals, and the bond influences Fe^{2+}-S interactions of the host matrix. If Fe^{2+}-S interaction becomes stronger, Fe^{2+} takes the low spin state. This is the reason why the low spin Fe^{2+} and high spin Fe^{2+} states exist in the amine intercalates.

Table 1. Mössbauer Data of $FePS_3$ and $FePS_3$ intercalated with allylamine and Pyridine

Compounds	T(K)	I.S.(mm s^{-1})	Q.S.(mm s^{-1})	Γ(mm s^{-1})
$FePS_3$	290	0.864	1.527	0.285
$FePS_3(Aa)_{3/4}$	290	0.937	2.752	0.477
		0.384	0.767	0.564
	80	1.054	2.743	0.501
		0.492	0.760	0.571
$FePS_3(Py)_{2/3}$	290	0.931	2.336	0.547
		0.846	1.747	0.321
		0.437	0.616	0.470
	80	1.054	2.626	0.547
		0.973	1.908	0.376
		0.547	0.621	0.492

The Mössbauer spectra of Li intercalated $FePS_3$ are quite different from our spectra of amine intercalates, presumed to be due to another mechanism of charge transfer.

References

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