© 1999 The Chemical Society of Japan *Bull. Chem. Soc. Jpn.*, **72**, 2249—2252 (1999) 2249

X-Ray Diffraction and Mössbauer Spectroscopic Studies of $FePS_3$–Alkylamines Intercalation Compounds

Hiroshi Sakai,* Ryoko Ukita, Nobuya Machida, and Toshihiko Shigematsu

Department of Chemistry, Faculty of Science, Konan University, Okamoto 8-9-1, Higashinada-ku, Kobe 658-8501

(Received April 30, 1999)

We succeeded in preparing $FePS_3$ intercalated with *n*-alkylamines, such as propylamine, butylamine, pentylamine, and hexylamine. The XRD patterns of the intercalation compounds indicate that the molecular axes of propylamine and butylamine are orientated parallel to the van der Waals layers, whereas those of pentylamine and hexylamine are perpendicular to the layers. The Mössbauer spectra of the intercalates, distinct from that of pure $FePS_3$, suggest a charge transfer from alkylamines to the Fe–S e_g^* antibonding orbitals of the $FePS_3$ host lattice

The transition-metal phosphorus trisulfides MPS_3, where M is a divalent metal cation, form a class of lamellar materials with crystal structures of the $CdCl_2$ type.[1] A number of MPS_3 compounds are known to intercalate organic and organometallic molecules, such as alkylamines, pyridine, and cobaltocene, in their van der Waals gaps as well as the transition-metal dichalcogenides.[1] The charge-transfer mechanism from the guest molecules to the host lattices has been widely accepted as a driving force for the intercalation reaction in these materials. Yamanaka et al.[2] prepared some intercalation compounds of MPS_3 (M = Mg, Zn, and Mn) with *n*-alkylamines, and found that the interlayer spacing increases linearly with the number of carbon atoms in *n*-alkyl chains. The slope of the linear line is about 2.5 Å per carbon atom, which is twice the increase in the length of an alkyl chain per carbon atom. In the $MnPS_3$–alkylamines system the interlayer spacings reduce to about 10.5 Å upon rinsing with acetone, irrespective of the length of the amine chains. These results suggest that the alkyl chains are oriented parallel to the sulfide layers in the stable intercalation compounds. On the other hand, Foot and Shaker[3] found that the interlayer spacings increase in $NiPS_3$ intercalated with alkylamines such as ethyl-, propyl-, butyl-, and hexylamine, in which the alkyl chains of ethyl- and propylamines are oriented parallel to the sulfide layers, whereas those of butyl- and hexylamines perpendicular to the layers from the interlayer expansions.

In order to obtain more detailed information on the orientation of the alkylamines and on the mechanism of charge transfer to the host lattice, we prepared $FePS_3$–alkylamines intercalation compounds, and measured their Fe-57 Mössbauer spectra. The Mössbauer spectra give much information on the electronic states of iron atoms and the interaction between the $FePS_3$ host lattice and guest molecules. Recently we have reported on the Mössbauer spectra of $FePS_3$–allylamine and $FePS_3$–pyridine intercalation compounds.[4] The spectra were completely different from that of $FePS_3$, suggesting charge transfer from the guest molecules to the host lattice.

Experimental

$FePS_3$ was prepared by reacting stoichiometric amounts of high-purity elements (99.9% or better) in an evacuated quartz tube at 700 °C for 1 month. The intercalation of alkylamines, such as propylamine, butylamine, and pentylamine, was carried out by immersing a fine powder (100 mesh) of $FePS_3$ in neat amines, and keeping at 45 °C for propylamine, 70 °C for butylamine, and 100 °C for pentylamine for 3 d. The amines were purchased from Wako Pure Chemical Industries, Ltd. and used as received without further purification. After withdrawal out of the amines, the intercalation compounds were thoroughly dried under vacuum for 1 d. The contents of amines per $FePS_3$ were determined to be 0.7, 0.6, and 1.5 for propylamine-, butylamine-, and pentylamine-intercalated $FePS_3$, respectively, from measurements of the weight gained by the sulfide. The intercalation compounds were characterized by X-ray powder diffraction (XRD) using graphite-monochromated Cu $K\alpha$ radiation. ^{57}Fe Mössbauer spectra were measured at room temperature 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.

Results and Discussion

Figure 1 shows the XRD patterns of (a) pure $FePS_3$, (b) propylamine-intercalated $FePS_3$, (c) butylamine-intercalated $FePS_3$, and (d) pentylamine-intercalated $FePS_3$, indicating sharp diffraction peaks of (00*l*) lines due to the layer structures. The basal spacing of pure $FePS_3$ is estimated to be 6.42 Å, in agreement with our previous result.[4] In the XRD patterns of the intercalated $FePS_3$ the diffraction peaks corresponding to pure $FePS_3$ were completely missing, suggesting that the intercalations are performed completely with alkylamines. The shifts to lower angle in the intercalation compounds imply increases in the interlayer spacings, which are estimated to be 10.30, 10.36, and 17.25 Å for the propylamine-, butylamine-, and pentylamine-intercalated compounds, respectively. The interlayer expansions of 3.88 and

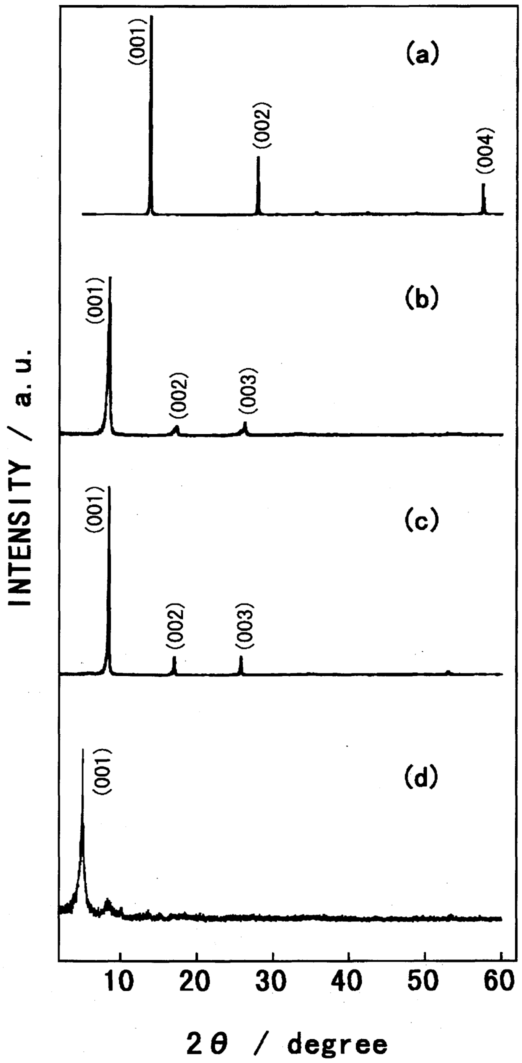

Fig. 1. X-Ray diffraction patterns of (a) pure FePS$_3$, (b) propylamine-intercalated FePS$_3$, (c) butylamine-intercalated FePS$_3$, and (d) pentylamine-intercalated FePS$_3$.

3.94 Å for propylamine- and butylamine-intercalated FePS$_3$ are close to the values of *n*-alkylamines-intercalated MnPS$_3$.[2] The results suggest that the molecular axes of propylamine and butylamine are oriented parallel to the van der Waals layers. In this configuration the increase in the alkyl chain length reduces the number of alkylamine molecules per FePS$_3$. The occupied areas in the van der Waals region are estimated to be ca. 23.2 Å^2 for propylamine (7.74 Å in length, 3.0 Å in width, and 3.7 Å in height) and ca. 27.0 Å^2 for butylamine (9.00 Å in length, 3.0 Å in width, and 3.7 Å in height), which compare with an interlayer area of ca. 16.3 Å^2 per FePS$_3$. Such a geometric limitation suggests that the maximum uptakes of propylamine and butylamine are approximately 0.7 and 0.6 per FePS$_3$, respectively, which are in fair agreement with the experimental values. In the butylamine-intercalated NiPS$_3$ the basal spacing is reported to be 14.5 Å, corresponding to the interlayer expansion of 8.16 Å.[3] The result suggests that the butylamine molecules are oriented perpendicular to the sulfide layers. We also observed such a diffraction peak at low angle in the preparation of butylamine-intercalated FePS$_3$, but the peak disappeared upon drying of the intercalated solids.

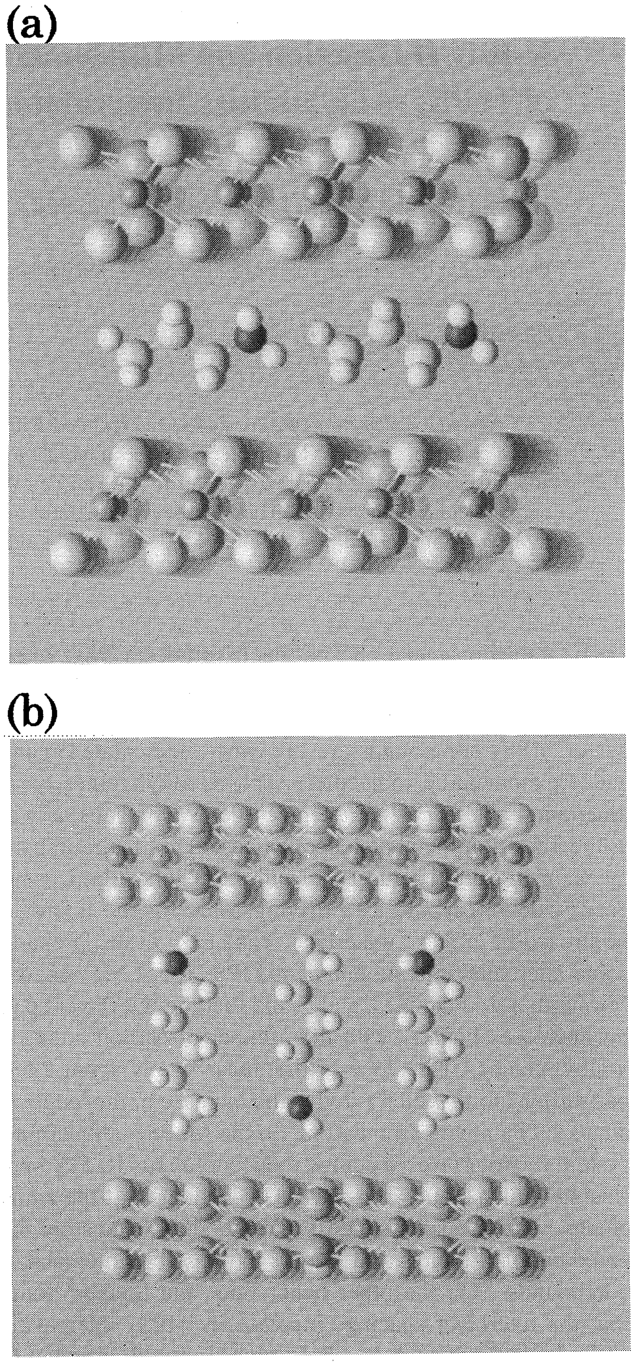

Fig. 2. Models of the arrangements of alkylamines in the van der Waals regions of FePS$_3$; (a) propylamine and (b) pentylamine.

On the other hand, in the pentylamine-intercalated compound the interlayer expansion is 10.8 Å, close to the length of pentylamine with the all *trans* geometry. The fact suggests that the molecular axis of pentylamine is oriented perpendicular to the van der Waals layers. In this configuration, since the occupied area is ca. 11.1 Å^2 for pentylamine (10.26 Å in length, 3.0 Å in width, and 3.7 Å in height), the maximum occupancy of the interlayer spacing is estimated to be approximately 1.5 per $FePS_3$. This value is also in agreement with the experimental one. If the configuration is maintained for alkylamines with longer alkyl chains, the interlayer spacing increases along with an increase in the number of carbon atoms in alkyl chains. We tried to prepare hexylamine-intercalated $FePS_3$, but the content of hexylamine could not be determined because of low vapor pressure of hexylamine. A preliminary value of the basal spacing is about 18.86 Å, which corresponds to the interlayer expansion of 12.44 Å, longer by 1.6 Å than the pentylamine-intercalated compound. It is noteworthy that propylamine and butylamine are intercalated parallel to the layers, whereas pentylamine and hexylamine are intercalated perpendicular to the layers, as shown in Fig. 2. Similar phenomena have been observed for alkylamine-intercalated TaS_2.[5]

Figure 3 shows the Mössbauer spectra of (a) pure $FePS_3$, (b) propylamine-intercalated $FePS_3$, (c) butylamine-intercalated $FePS_3$, and (d) pentylamine-intercalated $FePS_3$ at room temperature. The spectrum of pure $FePS_3$ is similar to our previous one,[4] in which the asymmetry is due to the preferred orientation of the plate-like crystals. The spectra of alkylamine-intercalated $FePS_3$ are distinct from that of pure $FePS_3$, suggesting a charge transfer from alkylamine to the $FePS_3$ host lattice. The spectra of $FePS_3$ intercalated with propylamine and butylamine consist of three sets of quadrupole doublets, whereas two quadrupole doublets are observed in pentylamine-intercalated $FePS_3$. Table 1 gives the Mössbauer data, such as the isomer shift (IS), quadrupole splitting (QS), line width (Γ), and area ratio, obtained by least-squares fittings of these spectra.

In the spectra (b) and (c), similar to the spectrum of pyridine-intercalated $FePS_3$ in our previous paper,[4] 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 the isomer shift and the quadrupole splitting. The iron sites corresponding to the doublet B in both spectra are not so much influenced by the intercalation of alkylamines, because the values of the isomer shift and the quadrupole splitting are close to those of pure $FePS_3$. The occurrence of such iron species may be dependent on the content of the intercalated alkylamines. That is, the iron species decreases along with an increase in the charge transfer from alkylamines to the $FePS_3$ host lattice. As the content of butylamine (ca. 0.6 per $FePS_3$) is less than that of the propylamine (ca. 0.7) intercalated in $FePS_3$, the former intensity of the doublet B is fairly large

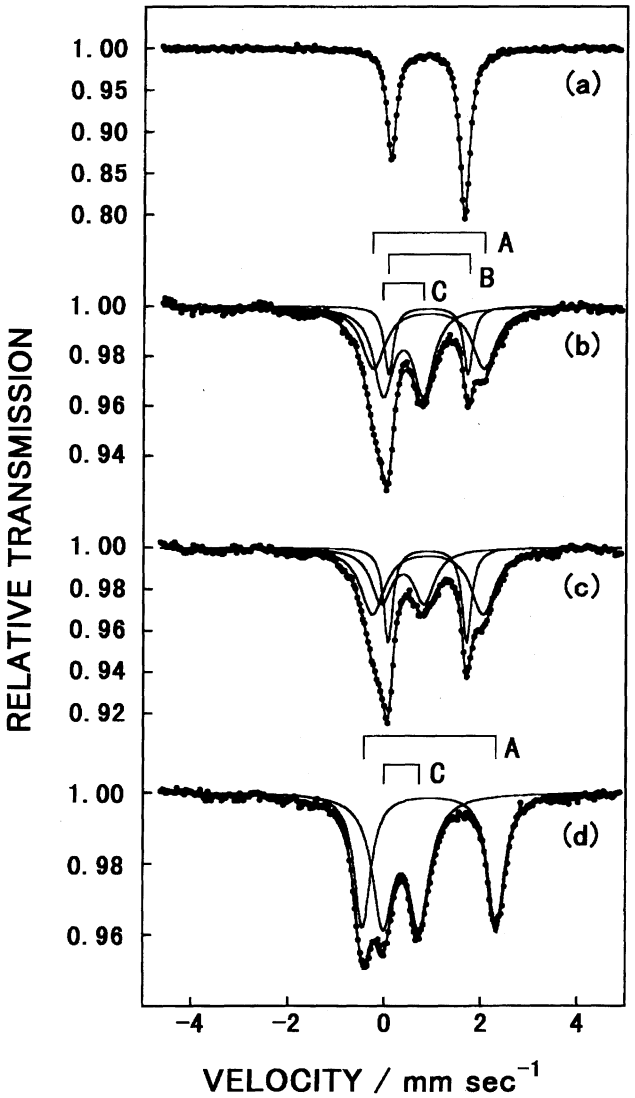

Fig. 3. Mössbauer spectra of (a) pure $FePS_3$, (b) propylamine-intercalated $FePS_3$, (c) butylamine-intercalated $FePS_3$, and (d) pentylamine-intercalated $FePS_3$ at room temperature.

Table 1. Mössbauer Data of $FePS_3$ and $FePS_3$ Intercalated with Propylamine, Butylamine, and Pentylamine

Compounds	T (K)		IS (mm s^{-1})	QS (mm s^{-1})	Γ (mm s^{-1})	Area ratio (%)	
$FePS_3$	290		0.864	1.527	0.285		**Ref. 4**
$FePS_3$–propylamine	290	A	0.899	2.299	0.588	40	
		B	0.892	1.645	0.229	17	
		C	0.374	0.833	0.493	43	
$FePS_3$–butylamine	290	A	0.892	2.292	0.604	43	
		B	0.887	1.629	0.232	24	
		C	0.375	0.888	0.520	33	
$FePS_3$–pentylamine	290	A	0.942	2.782	0.408	46	
		C	0.355	0.755	0.519	54	

compared with that of the latter. The iron species is absent in pentylamine-intercalated $FePS_3$, which contains many pentylamine molecules (ca. 1.5 per $FePS_3$) in the van der Waals regions.

The high-spin Fe^{2+} species corresponding to the quadrupole doublet A, having larger values of the isomer shift and the quadrupole splitting than the doublet B or pure $FePS_3$, are more ionic than the Fe^{2+} ion in pure $FePS_3$. Such Fe^{2+} species may occur when the interaction between the iron and sulfur atoms becomes weak. The results suggest that the charge transfer arises partially from alkylamines to the antibonding orbitals of the Fe–S bonds. According to the extended Hückel tight-binding calculations of $FePS_3$,[6,7] 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 calculated result immediately suggests 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.[7] 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 are more covalent than the Fe^{2+} ion in pure $FePS_3$. The origin of such 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 (doublet A) in the Mössbauer spectra (b) and (c). By charge transfer from alkylamines to a part of the antibonding orbitals of the 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 a stronger ligand field of the sulfur atoms than the Fe^{2+} ion in pure $FePS_3$. This presumption may lead to the formation of the low-spin Fe^{2+} species.

The Mössbauer spectrum (d) consists of two kinds of quadrupole doublets with an intensity ratio of about 1 : 1, similar to the spectrum of allylamine-intercalated $FePS_3$ in our previous paper.[4] The outer doublet (designated as A) and the inner doublet (C) have been identified to be high-spin Fe^{2+} and low-spin Fe^{2+} states, respectively, based on the values of the isomer shift and the quadrupole splitting. These high-spin Fe^{2+} and low-spin Fe^{2+} species may be identical to those observed in spectra (b) and (c). The high-spin Fe^{2+} species appear by a charge transfer from pentylamine to the antibonding orbitals of Fe–S bonds in a similar manner as that mentioned above. As a result of the occurrence of the high-spin Fe^{2+} species, the adjacent Fe^{2+} ions are changed to the low-spin states, undergoing the strong ligand field of the surrounding sulfur atoms. In the pentylamine-intercalated $FePS_3$, the high-spin Fe^{2+} and low-spin Fe^{2+} ions are expected to exist alternately in the iron layers.

References

1 See, for example: R. Brec, *Solid State Ionics*, **22**, 3 (1986), and the references cited therein.

2 S. Yamanaka, H. Kobayashi, and M. Tanaka, *Chem. Lett.*, **1976**, 329.

3 P. J. S. Foot and N. G. Shaker, *Mat. Res. Bull.*, **18**, 173 (1983).

4 H. Sakai, T. Yamazaki, T. Shigematsu, S. Nakashima, T. Hinomura, and S. Nasu, *Chem. Lett.*, **1997**, 1101.

5 F. R. Gamble, J. H. Osiecki, M. Cais, R. Pisharody, F. J. DiSalvo, and T. H. Geballe, *Science*, **174**, 493 (1971).

6 M.-H. Whangbo, R. Brec, G. Ouvrard, and J. Rouxel, *Inorg. Chem.*, **24**, 2459 (1985).

7 H. Mercier, Y. Mathey, and E. Canadell, *Inorg. Chem.*, **26**, 963 (1987).