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A Mössbauer study of the magnetic coupling in iron phosphorous trisulfides*

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The polycrystalline sample of layered compound $FePS_3$ has been investigated by using Mössbauer spectroscopy (12K to 300K), magnetic susceptibility measurements, x-ray diffraction and FTIR spectroscopy. The antiferromagnetic order exists below T_N=120.5±1K. The Mössbauer spectra below T_N indicate that the magnetization axis is perpendicular to the layer of $FePS_3$, and the divalent iron cations are in their high spin configurations. By fitting the hyperfine field parameters near the Néel temperature, we obtain information on the nature of magnetic interactions in the material. The results show that the magnetic coupling can be treated by the two-dimensional Ising model, and it can be interpreted on the basis of a crystal-field effect.

Keywords: layered compound, Mössbauer spectroscopy, magnetic coupling, Ising model
PACC: 0785, 0660E, 0630C, 0570J

1. Introduction

Low-dimensional magnetic systems have received considerable attention in recent years because of their interests in chemical and physical properties. In the low-dimensional magnetic systems, the layered transition metal thiophosphates, MPX_3 (M=Mn, Fe, Ni and X=S or Se), belong in the few layered systems known in which both the magnetic and the crystallographic lattices are two-dimensional (2D).[1]

The compound $FePS_3$ was prepared by Hahn and Klingen for the first time.[2] From x-ray crystal structure analysis, the structure of $FePS_3$ is monoclinic with the $C2/m$ space group. The conventional unit cell contains four units of $FePS_3$ formula with unitary iron and phosphorous positions and two nonequivalent sulfur positions. Sulfur atoms form a cubic close-packed array with the iron cations and phosphorous–phosphorous pairs occupying the octahedral vacancies. The iron cations within a layer have a honeycomb arrangement and the MS_6 octahedra show a small trigonal distortion. Although the crystalline structure,[3] magnetism,[1,4] and conductivity[5] of $FePS_3$ have been widely investigated, the quantitative study on magnetism is still open.

The transition metal thiophosphates form a layered structure, in which the magnetic MPX_3 layers are separated by a van der Waals gap, therefore they are intercalated by a variety of guest molecules or ions.[6] Subsequent to intercalation, the magnetic properties are considerably changed: for instance, the intercalated compounds show field-dependent susceptibility and are weakly ferromagnetic.[7] It has been considered as an alternative approach to the design of ferromagnets.[8,9] Three mechanisms have been suggested to explain the change in magnetism on intercalation: (1) a dilution effect, which results from random vacancies in the layer,[8] (2) a change in the local symmetry of metal cations around a vacancy, which leads to a canting of spins arising from a Dzyaloshinsky–Moriya-type interaction and/or zero-field splitting,[10] (3) through-space dipolar interactions, which may promote 2D magnetic ordering at a non-zero temperature.[11] However, the mechanisms

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of magnetic alteration have not as yet been well understood.

In the present work, we have studied the temperature dependence of the hyperfine field of the ^{57}Fe in $FePS_3$ in the vicinity of a critical point by Mössbauer spectroscopy to obtain the detailed information on the magnetic interactions, which is a prerequisite to the understanding of magnetism in the intercalated compounds.

2. Experiments

Polycrystalline $FePS_3$ was synthesized from the corresponding high purity (99.9%) elements powders according to the standard solid state method.[3] Iron metal powder, phosphorus and sulfur in their stoichiometric amounts, with phosphorus and sulfur being in slight excess, were sealed in an evacuated quartz tube and heated up to 700°C then kept at this temperature for 2 weeks. After the reaction had been completed, the reacted matter was slowly cooled down to a room temperature. Homogeneous and well-crystalline materials were obtained after having been ground and reheated. Subsequently, excess phosphorus and sulfur were distilled out at 300°C in air. The compound was characterized by powder x-ray diffraction recorded on a D/max-RA diffractometer using Cu$K\alpha$ radiation.

Mössbauer experiments were carried out using a ^{57}Co/Pd source on a constant-acceleration spectrometer. The transmission spectra were recorded in the temperature range 12–300K using a closed-cycle REF-399-D22 refrigerator with helium being an exchange gas. The spectrometer was calibrated with a standard α-Fe foil and reported isomer shifts (I.S.) were relative to the centre of the α-Fe spectrum at a room temperature. The MossWinn program was used to determine the Mössbauer parameters.[12]

The magnetic susceptibility measurement was performed on polycrystalline samples between 4.2K and a room temperature in a constant magnetic field with a strength of 0.8T, using a vibrating sample magnetometer (VSM). The sample was cooled in zero external fields.

Infrared spectra were recorded on a Fourier transformed Nexus 870 FT-IR spectrometer in the spectral range 100–650cm^{-1}. The spectra of the powders were recorded in KBr pellets containing a small amount of the compound.

3. Results and discussion

The x-ray pattern for this compound is shown in Fig.1, the main indices are assigned in the figure. The sharp reflections imply a good crystallinity and homogeneity phase. All reflections could be indexed using the monoclinic unit cell with lattice parameters a=0.595nm, b=1.030nm, c=0.672nm, β=107.19°. This is identical with that reported in Ref.[3].

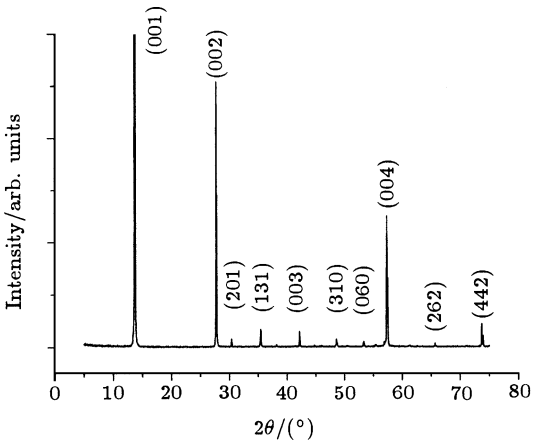


Fig.1. X-ray powder diffraction patterns (Cu$K\alpha$) for $FePS_3$, only indices of strong peaks are assigned in the figure.

The infrared spectrum (650–100cm^{-1}) for $FePS_3$ is illustrated in Fig.2. The band assignments are interpreted in terms of internal modes of PS_3 and by combining their in-phase and out-of-phase translational and rotational motions. The degenerate stretching band $\upsilon_d(PS_3)$ occurs at 570.9cm^{-1}, the υ(P-P) at 445.6cm^{-1}, the symmetric PS_3 bending band $\delta_s(PS_3)$ at 300.3cm^{-1} and 183.4cm^{-1}, the $\delta_d(PS_3)$ vibrations at 256.2cm^{-1}, and the translational motion band of Fe^{2+} ions at 151.9cm^{-1}. The values are the same as those reported in Ref.[6]. Both XRD and FTIR data can confirm that the synthesized sample is purely polycrystalline $FePS_3$ with a remarkable orientation effect, and the FeS_6 octahedra show a small distortion.

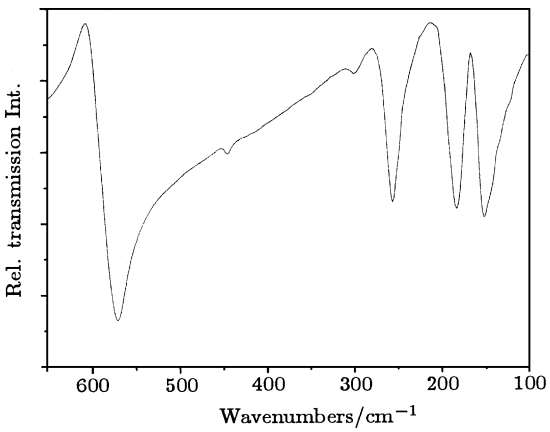


Fig.2. FTIR spectrum of $FePS_3$.

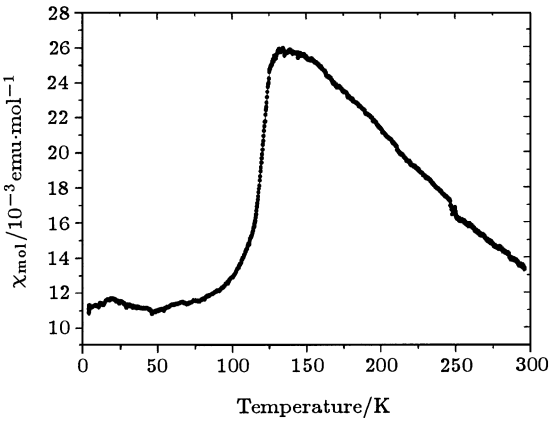


Fig.3. Magnetic susceptibility of $FePS_3$ as a function of temperature.

The magnetic susceptibility of $FePS_3$ as a function of temperature is shown in Fig.3. The susceptibility curve shows that the behaviour is indicative of typical antiferromagnetism of a two-dimensional system with a broad susceptibility maximum. The Nèel temperature, the temperature at which the slope of χ vs T is maximal, is 122±0.5K. The high-temperature paramagnetic susceptibility obeys the Curie–Weiss law. From the experimental data, the effective moment $\mu_{\rm eff}$= 5.84$\mu_{\rm B}$ and the Weiss constant Θ=120K can be obtained. The experimental $\mu_{\rm eff}$ is larger than the spin-only theoretical value (4.90$\mu_{\rm B}$), indicating a sizable spin-orbit contribution. A positive Θ and an Nèel temperature $T_{\rm N}$ show the simultaneous presence of ferromagnetic and antiferromagnetic interactions in $FePS_3$. Below the Nèel temperature, there is no hysteresis.

Mössbauer spectra at selected temperatures are shown in Fig.4. Above $T_{\rm N}$, the spectra consist of one doublet. In the immediate vicinity of the Nèel point, the spectra comprise a doublet and a magnetic sextet. Far below the $T_{\rm N}$, the spectra are composed of a magnetic sextet. Due to the magnetic interaction being comparable with the quadrupole interaction, we have fitted the magnetic subspectra to a nonlinear model, which is based on a hyperfine field $H_{\rm hf}$. The model is used to calculate the magnetic subspectra by solving the exact Hamiltonian mixed magnetic and quadrupole interactions with an arbitrary relative orientation. The z-axis is assumed to be parallel to the hyperfine magnetic field. β(EFG) denotes the polar, where EFG stands for electric field gradient, and α(EFG) denotes the azimuthal angle of V_{ZZ} relative to the direction of the magnetic field. The fitted results are summarized in Table 1.

Table 1. Mössbauer parameters measured for $FePS_3$ at various temperatures. I.S. denotes the isomer shift relative to the metallic iron at 300K (error is ±0.02mm·s^{-1}). Hyperfine field ($H_{\rm hf}$) is within an error of ±0.05T and the relative intensity within an error of ±1%.

Temp. T/K	Magnetic sextet								Doublet		
	I.S./ mm·s^{-1}	Hyperfine Field /T	V_{ZZ} /10^{21}V·m^{-2}	η	β(EFG)	α(EFG)	Q.S./ mm·s^{-1}	Relative Intensity/%	I.S./ mm·s^{-1}	Q.S./ mm·s^{-1}	Relative Intensity /%
12	1.02	9.75	9.63	0.28	0	0	1.90	100			
22	1.03	9.74	9.64	0.28	0	0	1.90	100			
32	1.02	9.75	9.65	0.29	0	0	1.91	100			
42	1.05	9.63	9.59	0.29	0	0	1.90	100			
52	1.04	9.55	9.59	0.28	0	0	1.89	100			
62	1.01	9.45	9.56	0.30	0	0	1.89	100			
72	1.03	9.27	9.44	0.32	0	0	1.87	100			
82	1.03	9.09	9.39	0.34	0	0	1.87	100			
92	1.03	8.86	9.37	0.34	0	0	1.86	100			
103	1.02	8.22	9.40	0.33	0	1	1.87	100			
108	1.02	8.00	9.13	0.45	0	31	1.84	100			
111	1.03	6.89	9.00	0.41	0	34	1.80	74	1.03	1.59	26
112	1.03	6.80	9.12	0.41	0	36	1.83	73	1.03	1.59	27
113	1.03	6.73	9.01	0.37	0	36	1.80	71	1.03	1.59	29
114	1.03	6.54	9.17	0.35	0	42	1.82	62	1.03	1.59	38
115	1.03	6.29	9.25	0.35	0	43	1.84	53	1.03	1.59	47
116	1.03	6.04	9.34	0.37	0	44	1.86	48	1.02	1.59	52
117	1.03	5.85	9.28	0.38	0	46	1.85	36	1.02	1.58	64
118	1.04	5.70	9.11	0.40	0	46	1.82	35	1.02	1.58	65
119	1.03	5.11	9.27	0.35	0	48	1.84	8	1.01	1.58	92
121									1.01	1.58	100
123									1.01	1.57	100
300									0.90	1.53	100

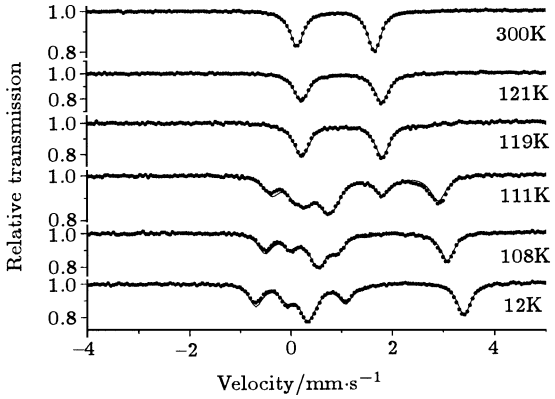


Fig.4. Mössbauer spectra for $FePS_3$ at some measuring temperatures.

In the region from 108 to 121K, the relative absorption intensity of the magnetic sextet varies with temperature from 100% down to 0%. By using a polynomial to fit the data, the Nèel temperature T_N=120.5±1K can be obtained (see Fig.5). This value is slightly deviated from that determined by the magnetic susceptibility curve (122K) because of the short-range ordering near the critical point in the compound.

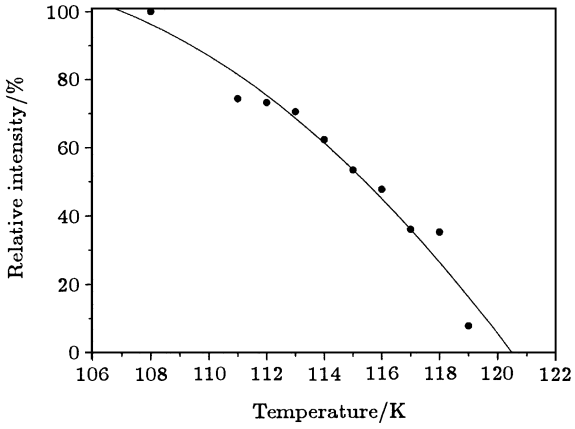


Fig.5. The absorption peak area of magnetic component as a function of temperature (dots denote the experimental data and the solid line denotes the fitting values).

Above T_N, the spectra consist of a doublet with I.S. varied from 0.90mm·s^{-1} (300K) up to 1.01mm·s^{-1} (121K). This increased value originates from the second-order Doppler effect. In this temperature range, the quadrupole splitting (Q.S.) is seen to be only weakly temperature-dependent with an indication of a slightly increase in a low temperature range. From the values of I.S. and Q.S., it is reasonable to deduce that the Fe^{2+} ions are in their high spin states.

Far below T_N (below 108K), the spectra are composed of a magnetic sextet with β(EFG)=0 and α(EFG)=0, the values of Q.S. calculated from $\frac{1}{2}eQV_{zz}(1+\eta^2/3)^{1/2}$ slightly increase with the decrease in temperature. In $FePS_3$, Fe^{2+} and P–P pairs occupy the octahedral vacancies formed by sulfur atoms. The FeS_6 octahedra show a small trigonal distortion, the trigonal axis being perpendicular to the layer.[1] Namely, the major component of the asymmetric electric field gradient (EFG) tensor in $FePS_3$ is perpendicular to the layer. Therefore, according to the fact that β(EFG)=0 and α(EFG)=0, it is concluded that the hyperfine field H_{hf} is perpendicular to the layer in a low temperature range. The value of H_{hf} (T=0) can be extracted from a linear extrapolation of H_{hf} versus T to T=0 using data below 42K. The extrapolation yields H_{hf} ($T\rightarrow$0)=9.75T.

In the vicinity of the Nèel temperature T_N (111–119K), the spectra can be fitted by a doublet and a magnetic sextet. For the doublet, the values of I.S. and Q.S. are almost unchanged as the temperature decreases. For the magnetic spectra, the values of $\frac{1}{2}eQV_{zz}(1+\eta^2/3)^{1/2}$ are around 1.8mm·s^{-1}, the values of I.S. are about 1.03mm·s^{-1}. These values remain nearly unchanged with the decrease in temperature. The coexistence of paramagnetic and antiferromagnetic phases in this transition region, implies that the magnetic hyperfine fields in different parts of the sample suddenly drop down to zero in a range of temperatures. The ratio of paramagnetic phase to antiferromagnetic phase varies with the temperature decreasing from a high region to the transition region. This ratio also changes with the temperature increasing from the transition region up to a high region. And the two ratios are found to be slightly different, which implies that a small thermal hysteresis is present.[4] The results indicate that not crystallographic transition but magnetic transition takes place when the temperature decreases from a room temperature down to 12K.

It is generally found that the sublattice magnetization below the critical point may be expressed in the form

$$M(T) = M(0)D(1 - T/T_N)^{\beta}. \qquad (1)$$

An important parameter is the critical exponent β. The coefficient D is introduced because the validity of this expression is limited to a region near the critical point, so that the magnetization at $T\rightarrow$0 given by this expression is not equal to the measured value $M(0)$.[13] The value of β implies the type of the magnetic interaction in magnet: e.g., β=1/3 for spin wave

model, β=1/8 for 2D Ising model.

As the hyperfine field is directly proportional to the spontaneous sublattice magnetization in the material, the following equation holds true:

$$H_{\rm hf}(T) = H_{\rm hf}(0)D(1 - T/T_{\rm N})^{\beta}. \qquad (2)$$

Therefore, the critical exponent can be determined by fitting Eq.(2) to the data in the immediate vicinity of the Nèel point. With $T_{\rm N}$=120.5K, $H_{\rm hf}(0)$=9.75T, Figure 6 shows a plot of $\log_{10} H_{\rm hf}(T)$ versus $\log_{10}((T_N - T)/T_{\rm N})$ for $FePS_3$. With the data fitted to a linear function in the least-square fitting, the best values β=0.16±0.01 and D=1.06±0.03 are obtained. This indicates that the magnetic interaction in $FePS_3$ satisfies the two-dimensional Ising model. The result is in good agreement with that obtained from magnetic susceptibility of single crystal $FePS_3$.[1]

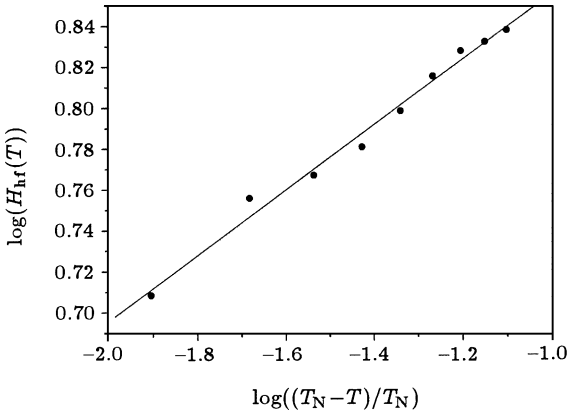


Fig.6. Plot of $\log_{10} H_{\rm hf}(T)$ versus $\log_{10}((T_{\rm N} - T)/T_{\rm N})$ with $T_{\rm N}$=120.5K (Dots denote the experimental data and the solid line denotes the fitting values).

The result can be interpreted by the effect of spin-orbit coupling and the effect of the trigonal distortion of the FeS_6 octahedra. In $FePS_3$ the Fe^{2+} ions are in the high spin ^{5}D ground state, in such a weak octahedron crystalline-field environment, which transforms into the triply degenerate $^5T_{2g}$ and a doubly degenerate ^5E_g orbital. Furthermore, the trigonal distortion of the FeS_6 octahedra splits the low-energy $^5T_{2g}$ states into a doublet (^5E_g) and a singlet ($^5A_{1g}$). The trigonal distortion of the FeS_6 octahedra in $FePS_3$ is manifested as a trigonal elongation,[1] so that the doublet will be lower in energy compared to the singlet. The magnetic property depends upon the energy levels of states populated within a given temperature range and also the levels which may mix significantly with the ground state under perturbations such as spin-orbit coupling or Zeeman effect. Therefore, the difference was created between $g_{//}$ and $g_{\perp}$, resulting in the anisotropic magnetism.

4. Conclusion

The magnetic property of $FePS_3$ has been investigated by magnetic measurement and Mössbauer spectroscopy. The behaviours of $FePS_3$ in the immediate vicinity of critical point give the critical exponents β=0.16±0.01, and D=1.06±0.03. The magnetic interaction in $FePS_3$ satisfies the Ising model and can be interpreted by the effect of spin-orbit coupling and the effect of anisotropy of the single ions originating from the trigonal distortion of FeS_6 octehedra.

References

[1] Joy P A and Vasudevan S 1992 *Phys. Rev.* B **46** 5425
[2] Hahn H and Klingen W 1965 *Naturwissenschaft* **52** 494
[3] Taylor B E, Steger J and Wold A 1973 *J. Solid State Chem.* **7** 461
[4] Jernberg P, Bjarman S and Wäppling R 1984 *J. Mag. Mag. Mat.* **46** 178
[5] Grasso V, Neri F, Patanè S and Silipigni L 1990 *Phys. Rev.* B **42** 1690
[6] Brec R 1986 *Solid State Ionics* **22** 3
[7] Joy P A and Vasudevan S 1992 *J. Am. Chem. Soc.* **114** 7792
[8] Lomas L, Leaustic A, Audiere J P and Clement R 1992 *Mater. Sci. Forum* **91-93** 641
[9] Dai Y D, He Y, Huang H B, Shao T and Xia Y F 2003 *Acta Phys. Sin.* **52** 3020 (in Chinese)
[10] Joy P A and Vasudevan S 1993 *J. Chem. Phys.* **99** 4411
[11] Drillon M and Panissod P 1998 *J. Mag. Mag. Mat.* **188** 93
[12] lencsár Z K, Kuzmann E and Vértes A 1996 *J. Radioanal. Nucl. Chem.* **210** 105
[13] Wertheim G K and Buchanan D N 1967 *Phys. Rev.* **161** 478