

X-ray Absorption Study of Zigzag-Antiferromagnetic Iron Phosphorus Trisulfide (FePS₃)

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Transition metal phosphorus trichalcogenide materials have received considerable attention recently. Rising as one of the most promising material in this family of magnetic van der Waal materials is iron phosphorus trisulfide (FePS₃). It crystalizes in the monoclinic symmetry, space group of C_{2m}^[1], exhibits a zigzag-antiferromagnetic ordering^[2], Ising-like spin dimensionality and Neel temperature of 118K independent of thickness^[3,4]. Electronic, magnetic and electrochemical studies have been done^[4-6] and was found to be a good candidate for strain and intercalation studies due to its large vdW gap^[1,7]. However, some properties of the material remain to be elusive up to present time of which can be probed using x-ray absorption spectroscopy (XAS), x-ray magnetic circular dichroism (XMCD) and x-ray magnetic linear dichroism (XMLD).

The iron L₃ and L₂ peaks were found to be at 706.6 and 719.3 eV which corresponds to the excitation energy of an electron from the spin-orbit split 2p core shell, 2p_{3/2} and 2p_{1/2} respectively to an empty state in the conduction band likewise revealing a spin-orbit coupling value of 12.7 eV in the 2p level. XAS measurements were performed in the room and low temperature (T=110 K) as shown in Fig.1. No asymmetry was observed using circularly polarized light. Instead, the linear dichroism, taken in the out-of-plane and in-plane polarization of x-rays, for both peaks were clearly observed, which could be caused by the antiferromagnetic or the orbital orders in the material. The difference in the spectra in the room and low temperature was already expected since the spin-orbit and exchange interaction are both in the order of k_BT.

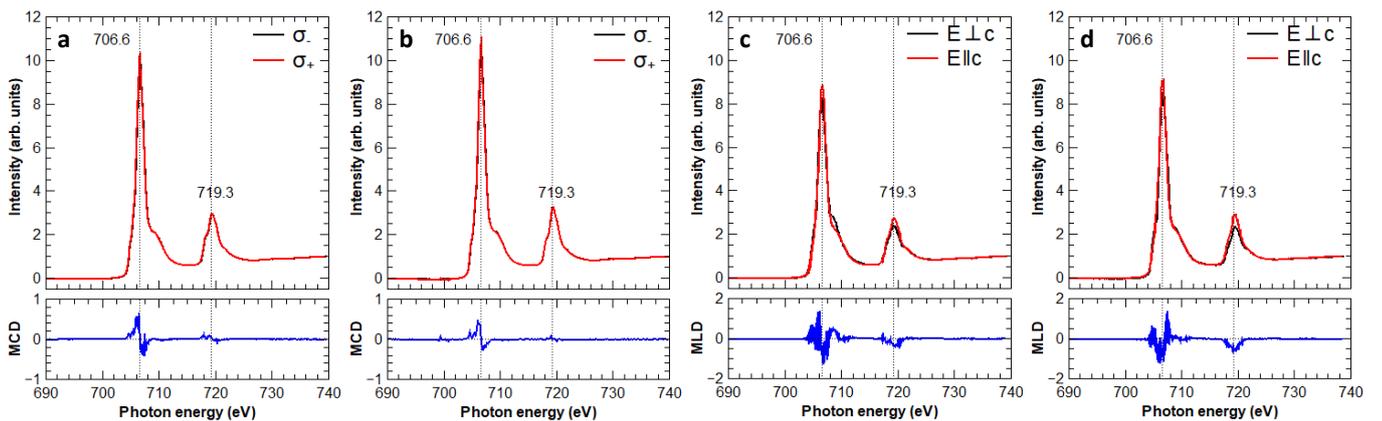


Figure 1. XAS and the corresponding XMCD spectra in the lower panel for (a) room temperature, (b) low temperature. XAS and the corresponding XMLD spectra in (c) room and (d) low temperature.

The branching ratio, which represents the fraction of the L_3 transition to the total transition probability $\frac{I_{L_3}}{I_{L_3}+I_{L_2}}$ [8], gives information on whether a material undergoes spin state transition. Quantitative measurement was done after removing the background using a two-step arctangent function [9] as shown in figure 2(a). The isotropic branching ratio in the Fe L-edge is 0.788 and 0.793 for room and low temperature, respectively. The value obtained represents the Fe^{2+} ions in FePS_3 which is near to the theoretical branching ratio of 0.78 for $\text{Fe } d^6 \ ^5T_2$ high spin magnetic ground state [10]. The lowered temperature contracts the coordination symmetry, enhance the crystal-field splitting and thus increase the likelihood of a high-spin to low-spin transition. A drastic change in the spectral line shape and a decrease in the branching ratio will occur if such spin transition happened [11]. However, no spin crossover occurred within the experimental temperature.

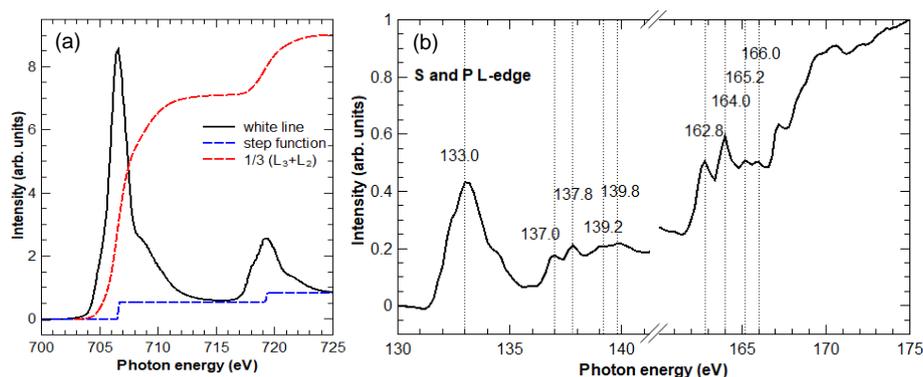


Figure 2. (a) Isotropic XAS of Fe in FePS_3 taken at room temperature at 0.1 eV energy resolution. The blue dashed line is the two-step function for the removal of the background while the red dashed line is the total intensity multiplied to a factor for visualization. (b) Large scan of sulfur and phosphorus L-edge taken using right circularly-polarized light at low temperature regime.

The sulfur and phosphorus L-edge feature of FePS_3 is shown in figure 2(b). Sulfur LS doublet was found at 162.8 and 164.0 eV with a second doublet in 165.2 and 166.0 eV. The second doublet was also observed in pyrite and native sulfur and was attributed to multiple scattering or transition to localized levels higher in the conduction band [12]. Phosphorus LS doublet in FePS_3 was found to be at 137.0 eV and 137.8 eV and a broad peak at ~ 139 -140 which was assigned to a $1s \rightarrow 3p$ antibonding state transition [12]. Aside from the transitions to the hybridized orbitals involving iron and the sulfur states, sulfur post edge feature in FePS_3 is also likely to be affected by P L_1 edge transitions at around 189 eV. The full width at half maximum in the Fe L_3 in FePS_3 is narrow compared to that of the pristine iron indicative of the decreased unfilled portion in the 3d band upon formation of sulfides [13]. Manifestation in the XMLD spectrum of the crystal-field splitting and its associated orbital occupation will be discussed along with other spectral and dichroism feature observed in FePS_3 .

Keywords: iron phosphorus trisulfide, antiferromagnetic van der Waal material, x-ray absorption spectroscopy, x-ray magnetic circular dichroism, x-ray magnetic linear dichroism.

References:

- [1] G. Ouvrard, R. Brec and J. Rouxel, *Mat. Res. Bull.* **20**, 1181-1189 (1985).
- [2] B. L. Chittari, Y. Park, D. Lee, M. Han, A. MacDonald, E. Hwang and J. Jung, *Phys. Rev. B* **94**, 184428 (2016).
- [3] J-U. Lee, S. Lee, J.H. Ryoo, S. Kang, T. Y. Kim, P. Kim, C-H. Park, J-G. Park and H Cheong, *Nano Lett.* **16**, 12, 7433 (2016).
- [4] P. A. Joy and S. Vasudevan, *Phys. Rev. B* **46**, 9, 5425 (1992).
- [5] A. Hashemi, H-P. Komsa, M. Puska, and A.V. Krashennnikov, *J. Phys. Chem. C* **121**, 27207 (2017).
- [6] C. C. M. Martinez, Z. Sofer, D. Sedmidubsky, S. Huber, A. Y. S. Eng and M. Pumera, *ACS Appl. Mater. Interfaces* **9**, 12563-12573 (2017).
- [7] R. Brec, *Solid State Ion.* **22**, 3-30 (1986).
- [8] B. T. Thole and G. van der Laan, *Phys. Rev. B* **38**, 5 (1988).
- [9] C.T. Chen, Y. U. Idzerda, H.-J. Lin, N.V. Smith, G. Meigs, E. Chaban, G. H. Ho, E. Pellegrin and F. Sette, *Phys. Rev. Lett.* **75**, 1 (1995).
- [10] G. van der Laan and B. T. Thole, *Phys. Rev. B* **43**, 16 (1991).
- [11] G. van der Laan and I. W. Kirkman, *J Phys.: Condens. Matter* **4**, 4189-4204 (1992).
- [12] G. S. Henderson, F. M. F. de Groot and B. J. A. Moulton, *Rev. Mineral. Geochem.* **78**, 75-138 (2014)
- [13] J. G. Chen. *Surf. Sci. Rep.* **30**, 1-152 (1997).