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2009 J. Phys.: Condens. Matter 21 124214

(http://iopscience.iop.org/0953-8984/21/12/124214)

J. Phys.: Condens. Matter **21** (2009) 124214 (5pp) doi:10.1088/0953-8984/21/12/124214

High energy excitations measured by neutron spectroscopy in $FePS_3$

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Received 15 September 2008, in final form 22 January 2009
Published 25 February 2009
Online at stacks.iop.org/JPhysCM/21/124214

Abstract
The quasi-two-dimensional antiferromagnet $FePS_3$ has been investigated using inelastic neutron spectroscopy with the time-of-flight spectrometer HET at the ISIS spallation neutron source. In the paramagnetic regime, two clearly resolved, high energy excitations were observed in the low scattering angle detector banks at 195(5) meV and 430(10) meV. The absence of these transitions from the high angle detector banks indicates that they are likely to be due to the crystal fields and magnetic in origin. The two transitions most probably represent electronic transitions in the Fe^{2+} ion among the low lying crystal field and spin–orbit split levels raised from the ground state. It has not yet been determined why the energies are greater than those observed in a comparable Raman experiment.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Iron thiophosphate belongs to a class of layered materials in which the metal ion layers are separated by a van der Waal's gap. This gap is also responsible for the quasi-two-dimensional (2D) nature of the magnetism in these materials. Le Flem *et al* [1], originally proposed an ordered magnetic structure for $FePS_3$ where the Fe^{2+} moments formed ferromagnetic chains coupled antiferromagnetically within the honeycomb lattice. The proposed structure indicated that the planes were also antiferromagnetically coupled along c. We recently investigated the magnetic structure of $FePS_3$ using neutron diffraction and found that it was actually better described as a two-dimensional Ising antiferromagnet [2]. Our studies revealed incomplete long-range magnetic order along the c^*-direction below a Néel temperature of 117.5 K. Furthermore the integrated intensity of the magnetic short-range order peaks showed a temperature dependence similar to a two-dimensional Ising system on a honeycomb lattice. This type of magnetic order is not unusual in this class of materials [3].

The magnetic susceptibility in $FePS_3$ has also been found to be highly anisotropic. The work of Joy and Vasudevan [4] indicate that the susceptibility of $FePS_3$ above the Néel temperature is best described by a Curie Weiss law for temperatures greater than 200 K. They analysed the high temperature susceptibility with a mean field model which incorporated spin–orbit split atomic states. In this model they assumed that the Fe ions had low lying electronic levels which could be populated at a few hundred kelvin. However, their analysis produced inconsistent and contradictory exchange parameters. In particular, this model gave different signs for the effective first neighbour exchange interaction from the perpendicular and parallel susceptibilities. This result is naturally unphysical and highlights how mean field theory fails to describe the low-dimensional nature of the magnetism of $FePS_3$.

A more sophisticated model, developed later by Chandrasekharan and Vasudevan [5], involved calculating the electronic level scheme for $FePS_3$ combining this with a correlated effective field (CEF) model. The CEF model is suitable for describing low-dimensional materials and thus it was considered appropriate for $FePS_3$. The calculated electronic level scheme was displayed as a function of the ratio of the trigonal crystal field parameter Δ' and spin–orbit coupling parameter λ. The

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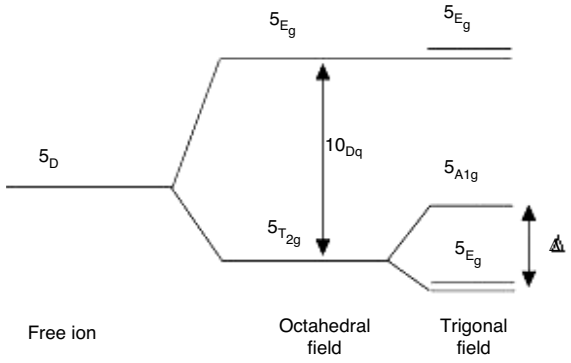

Figure 1. Electronic level diagram of an Fe^{2+} ion. This demonstrates the splitting from the cubic and trigonal components of the crystal field. This diagram is valid for all Fe^{2+} ions in these environments.

ratio of Δ'/λ was calculated by fitting the level scheme to the measured susceptibility via the correlated effective field model. At the fitted value of the ratio, $\Delta'/\lambda = 3.9$, the energy levels of the upper two of the three bands from the ground multiplet (from $M_J = 0$ to 1) are about 55 and 90 meV. From the schematic diagram of the Fe^{2+} ion in figure 1, these two energies represent the transitions from the lowest multiplet in the trigonally split T_{2g} level, to the upper two modes. Fitting the susceptibility is however a very indirect measure of the electronic levels and it is necessarily dominated by the ground state multiplet where the populations are most affected by temperature.

Both models described here are based on calculating the low lying electronic levels of $FePS_3$ by modelling the susceptibility data. While not without merit, a more direct method of investigation is required to accurately and consistently determine the energy of the low lying excitations. We present here a neutron spectroscopy study of $FePS_3$ as a direct probe of these excitations. We shall compare the results of this investigation with the previous susceptibility results as well as to Raman spectroscopy data.

2. Experimental details

Single crystals of $FePS_3$ were produced according to the method described earlier [9]. Due to the plate-like nature of the crystals, crushing the samples into a truly randomized powder was difficult. Instead a pseudo-random sample was produced by grinding the single crystals and then compressing the resulting powder into three cylindrical pellets each with a volume of approximately 1 cm^3. Thus each pellet was a powder with a high degree of preferred orientation where the c^*-axis, which is normal to the platelets, would be more likely to be coaxial with the cylinder axis. Finally the sample used for the inelastic neutron scattering experiment consisted of three pellets stacked with mutually orthogonal axes. To ensure that the sample was indeed homogeneous, all measurements were taken at two perpendicular sample orientations. There were no significant differences in these measurements, confirming the random orientation of the sample.

Table 1. Incoherent elastic linewidths (in meV) of vanadium for each detector bank and incident energy.

E_i (meV)	3°–7° bank	9°–29° bank	110°–140° bank
60	1.8	2.6	3.5
200	6.5	9.8	15
500	24	38	65
700	40	63	80

Inelastic neutron scattering measurements were performed using the high energy transfer (HET) chopper spectrometer at ISIS spallation neutron source at Rutherford Appleton Laboratory, UK. On the HET spectrometer, neutrons are scattered from the sample into two forward detector banks with low and medium scattering angles, and into two high scattering angle detector banks which are located underneath the sample position. The low scattering angle detectors range from 3° to 7° and are located at a distance of 4 m from the sample position, while the medium scattering angle bank ranges from 9° to 29° and is located 2.5 m from the sample. The two high angle detector banks range from 110° to 125° and 130°–140° at a distance of 4 m and 2.5 m from the sample respectively. With many more detectors positioned in the low and medium detector banks, HET is optimized to measure high energy magnetic scattering. The energy of the incident neutrons was varied between 60 and 700 meV to optimize the resolution and intensity and to satisfy kinematic conditions for high energy excitations. The observed excitations were measured with a neutron energy loss. Measurements were performed at 200 K, which corresponds to ≈1.7 times the magnetic Néel temperature which was previously found for this sample to be 117.5 K [2].

3. Experimental results

Inelastic neutron scans were taken by varying the incident energy of the neutrons between 60, 200, 500 and 700 meV. The full vanadium line width at half the maximum intensity for each incident energy in each detector bank are listed in table 1. The combined results of the 60 and 200 meV scans can be seen in figure 2 while the 500 and 700 meV data are shown in figure 3. Both figures show the data taken in the low (a) medium (b) and high (c) scattering angle banks. Each data set is formed from the sum of all detector counts in the relative bank. Thus each plot represents an integration over a range of $|\mathbf{Q}|$ given by the kinematic constraints of the measurement such that there is no explicit Q-dependent information.

At low energies (figure 2) the scattering is most obviously dominated by the incoherent elastic signal although a contribution from inelastic paramagnetic scattering is also significant. In the 200 meV data for the 9°–29° detector bank this scattering can be seen as a broad feature extending up to about 120 meV on the side of the incoherent elastic peak. At higher incident neutron energies, with poorer energy resolution, this feature becomes enveloped by the elastic peak (figure 3). The high angle results in figure 2(c) do not show clear evidence of the low energy inelastic feature although the statistics and resolution are also poorer in figures 2(c) than (b).

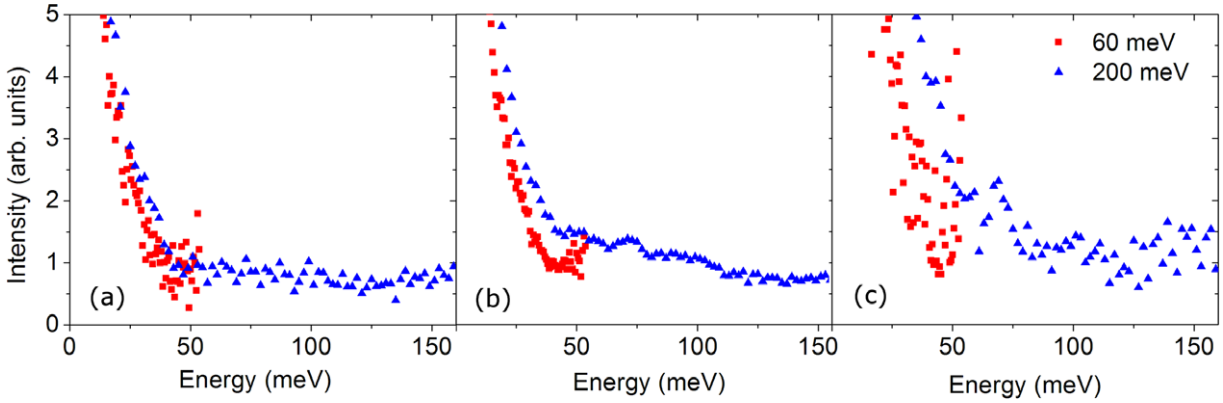

Figure 2. Inelastic neutron scattering results for $FePS_3$ taken at 200 K. Showing data collected in (a) the 3°–7° detectors, (b) the 9°–29° detectors and (c) the detectors with a scattering angle greater than 110°. The legend indicates the incident energy of the neutrons.

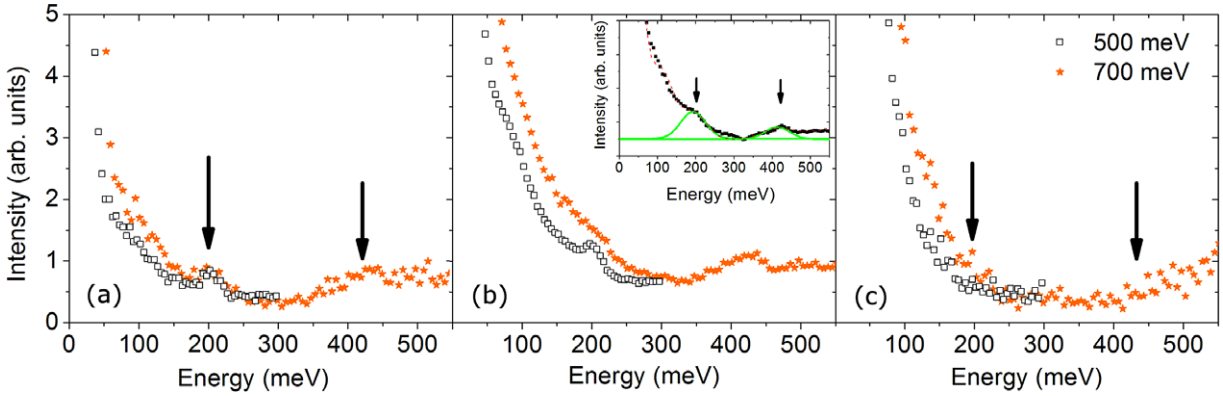

Figure 3. High energy inelastic neutron scattering results for $FePS_3$ taken at 200 K showing data collected in (a) the 3°–7° detectors, (b) the 9°–29° detectors and (c) the detectors with a scattering angle greater than 110°. The inset of (b) shows an example of the Gaussian profiles used to fit the two excitations in the 700 meV data. The arrows in (a) and (b) indicate the position of the two high energy excitations which were found from a simple Gaussian fit at 195(5) meV and 430(10) meV. The well-defined peaks from (a) and (b) are clearly absent from the data in (c). The legend indicates the incident energy of the neutrons.

Thus due to poor resolution there is no clear or consistent evidence of magnetic transitions for energy transfers less than 150 meV.

In contrast to the low energy feature, two high energy peaks are clearly resolved in figure 3 at 195(5) meV and 430(10) meV. The Q-ranges for these two peaks are listed in table 2. The data from the low and medium angle detector banks have the same features (as indicated by the arrows in figure 3(a)), however the statistics of the data from the low bank are poorer since it is located further from the sample and covers a smaller solid angle. These data were fit with Gaussian profiles (e.g. see inset of figure 3(b)) where the linewidths were constrained to be equal to that of the incoherent elastic line (table 1). As seen in figure 3(c), the two high energy transfer peaks which dominated the spectra in the low and medium detector banks were absent from high scattering angle detectors. This is highlighted by the arrows in figure 3(c) at which no obvious peaks are present.

It is highly likely that the two clearly observed excitations at 195(5) and 430(10) meV are magnetic in origin. The absence of these excitations from the high angle bank suggests that the scattering decreases rapidly with increasing Q. This is typical of magnetic scattering, where the intensity at large Q is suppressed by the square of the magnetic form factor. From the plot of the Fe^{2+} magnetic form factor squared as a function of Q (not shown) it is clear that no magnetic intensity remains beyond 10 $Å^{-1}$.

Table 2. Calculated Q-range for the peaks with an energy transfer (ΔE) 195 and 430 meV as observed with neutrons of incident energy 500 and 700 meV.

E_i (meV)	$\Delta 2\theta$	ΔE (meV)	$\|Q\|$ range ($Å^{-1}$)	ΔE (meV)	$\|Q\|$ range ($Å^{-1}$)
700	3°–7°	195	2.91–3.46	430	3.48–3.79
	9°–29°		3.84–8.92		4.03–7.67
	110°–140°		27.89–31.96		22.75–26.02
500	3°–7°	195	7.01–7.19	430	not observed
	9°–29°		7.33–10.06		
	110°–140°		24.73–28.10		

One could also believe that these excitations are phonons. The single phonon process is the only one likely to give a sharp feature in the energy. With multiphonon processes the conservation of wavevector and energy results in a large range of energy transfers and so will not be considered here.

The single phonon intensity is proportional to $Q^2 \exp(-Q^2\langle x^2\rangle)$ where $\langle x^2\rangle$ is the mean square excursion of

the scattering atom from its equilibrium position. For $FePS_3$, the value of this mean squared displacement at 300 K can be taken as $\langle x^2 \rangle = 0.88$ from Ouvrard *et al* [6]. It is unlikely that there will be phonon frequencies from $FePS_3$ as high as 195 and 430 meV. The most likely mechanical origin of these excitations would be from hydrogen impurity local modes. We calculated this for each excitation and found that scattering vectors corresponding to the high angle detector banks were beyond the maximum in this factor. Nevertheless in almost all cases significant intensity would be observable in these modes at the high angle detector banks since for $FePS_3$ this function gives a peak at 20 $Å^{-1}$ which is positioned within the high angle detector bank (table 2). It is clear from the data in figure 3(c) that this is not the case. The calculation also predicts that the intensities in the 3°–7° detectors should be much less than in the 9°–29° banks which was also not observed. Thus it is unlikely that these are hydrogen local modes even in the unlikely event that there were hydrogen incorporated in the $FePS_3$.

4. Experimental discussion

Interestingly, the high energy crystal field excitations at 195 and 430 meV were not predicted by the work of either Joy and Vasudevan [4] or Chandrasekharan and Vasudevan [5]. On the other hand resolved transitions at 55 and 90 meV are not observed in our data. The broad feature extending up to about 120 meV is more likely to be the expected inelastic paramagnetic scattering. Observed as a shoulder on the elastic scattering it is too broad to be modelled as electronic excitations centred on 55 and 90 meV. Also it must be noted that the susceptibility based studies are very indirect and the prediction of transitions of about 55 and 90 meV may be quite speculative.

Another direct method for measuring the splittings between electronic levels is provided by Raman spectroscopy. One Raman experiment has been performed on $FePS_3$ by Sanjuán *et al* [7] where the spectra show transitions of 110, 170 and 260 meV. In this study, the higher energy transitions at 170 and 260 meV were interpreted as phonon sidebands of the mode at 110 meV. None of these modes correspond to the transitions at 195 and 430 meV which we have observed with inelastic neutron scattering. However, features in Raman spectra can be difficult to interpret with an added complication that the Raman spectra were taken at temperatures well below the Néel temperature. Thus it is possible that the data of Sanjuán *et al* were influenced by an additional monoclinic distortion which has previously been associated to the magnetically ordered state of $FePS_3$ [8].

We must point out that significant differences also exist between neutron scattering and Raman spectroscopy. In particular the electronic transition selection rules are different for Raman and neutron spectra, the latter being magnetic dipole in origin. This difference however cannot entirely explain the difference between the observations from the two techniques. The resolution of both spectra is such that transitions to individual levels cannot be clearly distinguished. Transitions between bands of multiplets however can be seen and the selection rules for both spectroscopies should yield transitions between these bands even though the details will not be the same. It is still unclear what the true nature of the discrepancy between the data from these two techniques really is.

As a means to understanding the discrepancy between the Raman and neutron results of $FePS_3$ and to understand the peaks at 195 and 430 meV, it is useful to look at other materials containing Fe^{2+} ions in similar environments. Raman spectra for FeF_2 were taken by Hoff *et al* [10] at 80 K and at room temperature. Well above the Néel temperature two broad peaks are visible at about 130 and 180 meV. This is consistent with the picture of the Fe^{2+} ion in $FePS_3$. In both cases the T_{2g} ground state in an octahedral crystal field is split into three bands of multiplets by the combined effects of a further trigonal crystal field and spin–orbit coupling (figure 1). The antiferromagnetic material $FeCO_3$ may also shed some light on the Fe^{2+} in $FePS_3$, with a trigonal field environment influencing the splitting of the energy levels for Fe^{2+} similar to that plotted in figure 1. In fact, in $FeCO_3$ the splitting of the Fe^{2+} ion levels ^5E_g and ^5A_1g in a trigonal field has been estimated to be approximately 200 meV [11]. This corresponds to our observed excitation at a similar energy.

Finally, it is difficult to imagine that the higher transition at 430 meV could be explained as a transition between the ground and higher states. The next state is the E_g split from the ground state by the octahedral component of the crystal field (figure 3). Estimates of this splitting place it at more than 1000 meV. Optical absorption experiments [12] identify a line at 1090 meV as this $^5T_{2g}$–E_g transition which is well above the higher transition observed in this experiment. Thus we do not at present know the origins of this mode, which has only been seen in our neutron scattering work.

5. Conclusion

Using neutron spectroscopy we have observed two clear transitions at 195(5) and 430(10) meV in paramagnetic $FePS_3$ which we believe to be magnetic in origin. These excitations are only present at low scattering angles which strongly supports this belief. The excitations are thus most likely to be electronic transitions in the Fe^{2+} ion among the low lying crystal field and spin–orbitally split levels raised from the ground state. From comparisons with other Fe^{2+} materials, the peak at 195 meV may represent a splitting of the ^5E_g and ^5A_1g crystal field levels in a trigonal environment.

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