Intermultiplet transitions in filled skutterudite $SmFe_4P_{12}$

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Abstract. The intermultiplet transitions in filled skutterudite $SmFe_4P_{12}$ are studied by magnetization and time-of-flight inelastic neutron scattering experiments. In neutron scattering experiments by using high energy neutrons for reducing huge neutron absorption of natural Sm, a small inelastic peak has been observed around ∼80 meV at low temperature. The scattering vector dependence of intensity of this peak agrees with the theoretical inelastic structure factor for the intermultiplet transition from the ground $J = 5/2$ multiplet to the excited $J = 7/2$ multiplet in Sm^{3+} ion. Interestingly, the energy splitting is much smaller than the free Sm^{3+} ion value. This is also comparable with that estimated by the inverse magnetic susceptibility. This large reduction of the energy splitting might be due to the strong c–f mixing in $SmFe_4P_{12}$.

1. Introduction

Filled skutterudites RT_4X_{12} (R = rare-earth, T = transition metal, X = pnictogen) have been intensively studied because they exhibit unusual low temperature properties, such as the heavy fermion (HF) behavior, the multipolar ordering and the unconventional superconductivity [1]. Among them, $SmFe_4P_{12}$ is reported to be the first Sm-based ferromagnetic Kondo-lattice compound exhibiting a ferromagnetic transition at the Curie temperature 1.6 K [2]. It shows the unconventional HF state with the large electronic specific-heat coefficient $\gamma = 370$ mJ/mol K^2, which is the second heaviest in Sm-based compound next to $SmOs_4Sb_{12}$ [3, 4]. As is the case with $SmOs_4Sb_{12}$, the γ value of $SmFe_4P_{12}$ also seems to be robust against magnetic fields. The electrical resistivity of $SmFe_4P_{12}$ shows the characteristic feature of Kondo lattice with Kondo temperature of about 30 K [2, 5]. It shows the clear metamagnetism at 22 T and the magnetization does not saturate even at high magnetic fields up to 42 T [6]. The magnetization $0.4\mu_B$ at 42 T is considerably less than the free Sm^{3+} value of $0.71\mu_B$. The valence of Sm ions is reported to be almost trivalent [2, 10], in contrast to the intermediate valence state of $SmOs_4Sb_{12}$ [10]. The ground J multiplet of Sm^{3+} ion is the $^6H_{5/2}$ multiplet, which splits to a Γ_5 doublet and a Γ_{67} quartet by the crystal field (CF) with T_h symmetry [7], where the characteristic 6th-order term in the CF Hamiltonian does not affect the ground multiplet. The CF level scheme of $SmFe_4P_{12}$ is considered to be the Γ_5 ground state and the Γ_{67} excited state with the energy separation of about 6 meV by the specific heat [8] and NMR measurements [9].

In general, the energy from the ground J multiplet to the first excited J multiplet in Sm and Eu compounds is known to be not large compared to k_BT at room temperature [11]. Therefore it is necessary to consider the influence of the excited J multiplet for these compounds. Although it is reported that the local environment surrounding rare-earth ions has little effect on the energy between the J multiplets split by the spin-orbit interaction [12], it may be important to examine the energy splitting in the Sm-based HF compounds for understanding the unusual electronic states of these materials.

2. Experimental

Single crystals of $SmFe_4P_{12}$ were grown by the tin-flux method using the raw materials of 99.9%(3N)-pure naturally occurring Sm, 3N-Fe, 6N-P and 5N-Sn. Dimensions of most crystals were less than 1 mm. X-ray powder diffraction measurements confirmed that our sample has the filled skutterudite crystal structure (space group Im$\bar{3}$) with a lattice parameter $a = 7.803$Å, which agrees with the reported values [2, 13, 14], and no impurity phase except small amount of FeP_2 less than about 3% in volume. Magnetization measurement on the single crystal in a constant magnetic field 1 kOe parallel to [100] was performed in Quantum Design SQUID magnetometer between 2 K and 300 K. Inelastic neutron scattering (INS) experiments were done by using the time-of-flight high resolution chopper spectrometer HRC at J-PARC [15]. Many small single crystals of $SmFe_4P_{12}$ were combined for a total mass of 2.38 g. They were wrapped in thin Al foil and formed into a thin plate (30 mm×30 mm×1 mm) with the main plate plane perpendicular to the direction of the incident neutron beam. Then, it was enclosed in an Al container and mounted in a closed cycle refrigerator. Usually it is difficult to do INS

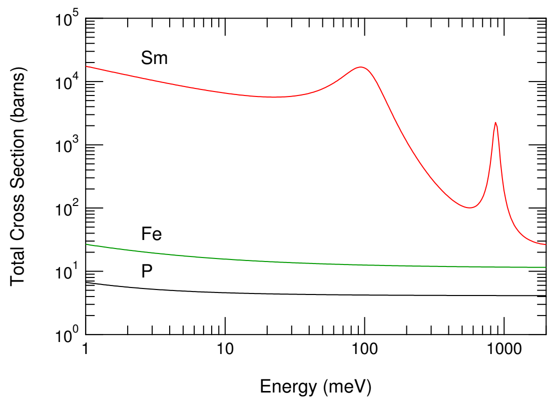

Figure 1. Energy dependence of the neutron cross sections of natural Sm, Fe and P.

experiments on the Sm containing materials because of huge thermal-neutron absorption by natural Sm, but, it is possible to reduce the effects of the neutron absorption by using higher energy neutrons. As shown in Fig. 1, there is a transmission window between the strong ^{149}Sm nuclear resonances which peak at ∼100 meV and ∼900 meV. Therefore we chose an high incident neutron energy of 514.1 meV and a chopper frequency of 600 Hz, where the scattered neutrons also have low absorption cross sections. In this experimental set up, the instrument resolution at zero energy transfer was a full width at half maximum of 19 meV.

3. Results and discussion

The temperature dependence of inverse magnetic susceptibility $1/\chi(T)$ is shown in Fig. 2. At low temperatures, there is a broad hump at ∼12 K as denoted by the arrow in the inset of Fig. 2.

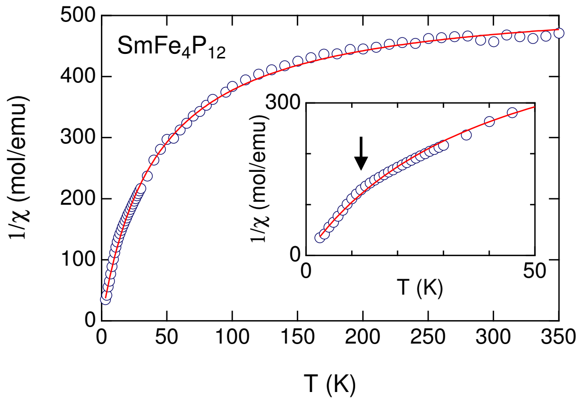

Figure 2. Temperature dependence of inverse magnetic susceptibility $1/\chi(T)$ of $SmFe_4P_{12}$. The line denotes a fit of Eq. (1) to the $1/\chi(T)$ data. The low temperature behavior is shown in the inset.

This may be due to the CF effects. Assuming that the Γ_5 ground doublet and the Γ_{67} excited quartet with the energy splitting of 6 meV, the CF calculation of the temperature dependence of $1/\chi(T)$ reproduces the observed hump. This is another piece of evidence that the Γ_5 doublet is a CF ground state because the CF calculation assuming the Γ_{67} quartet as a CF ground state does not reproduce such hump of $1/\chi(T)$. In order to get microscopic information about this CF splitting, we have tried to do INS experiment by using thermal neutrons with $E_i = 30$ meV, but, no signal was observed because of the influence of neutron absorption of Sm.

Overall temperature dependence of $1/\chi(T)$ in $SmFe_4P_{12}$ apparently does not follow the simple Curie-Weiss law. This is consistent with the small energy gap Δ between the ground $J = 5/2$ multiplet and the first excited $J = 7/2$ multiplet in the Sm^{3+} ion. Therefore a fit of the data was made with the modified Curie-Weiss law without considering the small CF splitting

$$\chi(T) = \frac{N{\mu_{\mathrm{eff}}}^2}{3k_{\mathrm{B}}\,(T-\Theta)} + \chi_0 \tag{1}$$

where N is Avogadro's number, μ_{eff} is the effective magnetic moment, Θ is the Curie-Weiss temperature and χ_0 is a temperature-independent Van-Vleck term due to coupling with the excited $J = 7/2$ multiplet, which is calculated to be $\frac{20N{\mu_{\mathrm{B}}}^2}{7\Delta k_{\mathrm{B}}}$. The fit yields $\Theta = 0.1$ K, $\mu_{\mathrm{eff}} = 0.79\mu_{\mathrm{B}}$, which is relatively less than $0.85\mu_{\mathrm{B}}$ expected for the Sm^{3+} free ion, and the energy splitting $\Delta = 569$ K (49 meV). This Δ value is much less than the free Sm^{3+} ion value ~ 130 meV [11]. For more exact estimation of Δ, the contribution of the Pauli paramagnetism of conduction electrons to χ_0 should be taken into account. Such small energy splitting is also reported in another Sm-based HF skutterudite $SmOs_4Sb_{12}$ by the bulk magnetic susceptibility measurement [4].

Figure 3 shows the INS energy spectra of $SmFe_4P_{12}$ at temperature 6.5 K and 280 K for $2\text{Å}^{-1} \leq Q \leq 6\text{Å}^{-1}$ and $6\text{Å}^{-1} \leq Q \leq 10\text{Å}^{-1}$, where Q is the magnitude of the scattering vector. At low Q region, one small inelastic peak was observed around $\sim$80 meV at 6.5 K as denoted by the arrow in Fig. 3. The peak almost disappears at high Q region, indicating its magnetic origin. Except for this small peak around $\sim$ 80 meV, no clear difference between the data at 6.5 K and 280 K was seen. If the small peak corresponds to the intermultiplet transition between the ground $J = 5/2$ multiplet and the excited $J = 7/2$ multiplet in Sm^{3+} ion, interestingly, the energy is much smaller than the free Sm^{3+} ion value $\sim$130 meV [11] and the reported values

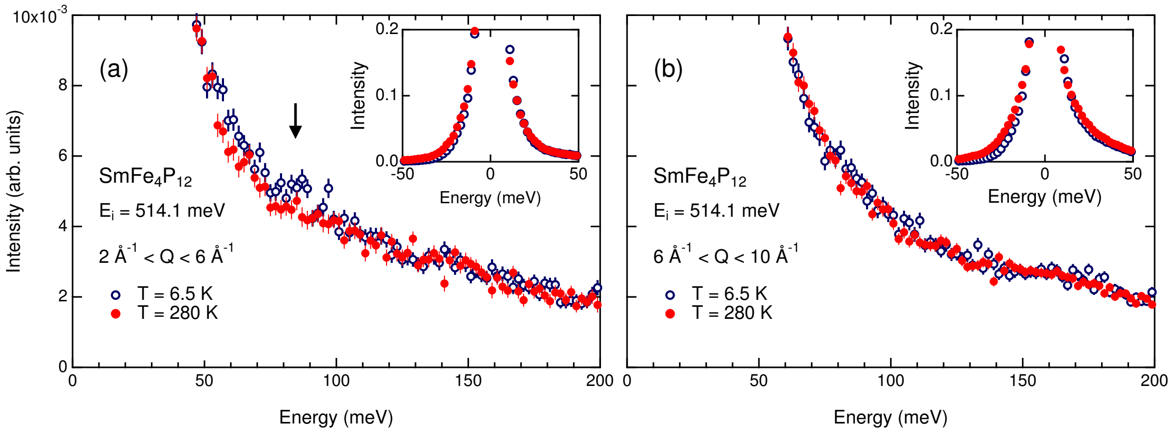

Figure 3. Energy spectra of neutrons scattered from $SmFe_4P_{12}$ measured with $E_{\rm i} = 514.1$ meV at lowest temperature 6.5 K and 280 K for (a) $2\text{Å}^{-1} \leq Q \leq 6\text{Å}^{-1}$ and (b) $6\text{Å}^{-1} \leq Q \leq 10\text{Å}^{-1}$. The arrow denotes the small inelastic peak at 6.5 K. The insets show the data below 50 meV.

in usual trivalent Sm compounds, for example, 131.5 meV in Sm^{3+} ion doped in LaF_3 [16] and 129 meV in $SmPd_3$ [17]. The small energy is comparable with the Δ value estimated by the fit of $1/\chi(T)$. We also confirmed the existence of the small excitation below ∼100 meV and the absence of the excitation around ∼130 meV at low Q and low temperatures by a tentative INS experiment with the incident energy $E_i = 300$ meV.

The INS intensity for the intermultiplet transitions from the J multiplet to the $J+1$ multiplet is proportional to the inelastic structure factor

$$G(Q; J, J+1) = \sum_{k,l} C^{k,l} \langle j_k(Q) \rangle \langle j_l(Q) \rangle \quad (2)$$

where $C^{k,l}$ are constants, which tabulated in appendix of [18], and $\langle j_k(Q) \rangle$ are averages of spherical Bessel functions. The inelastic structure factor $G(Q; \frac{5}{2}, \frac{7}{2})$ of Sm^{3+} monotonically decreases with increasing Q, in contrast to the elastic magnetic form factor which has a maximum at finite Q. Figure 4 shows the Q dependence of the integrated intensity of the small peak, which is the sum of the difference between the data at 6.5 K and 280 K in Fig. 3, and the inelastic structure factor $G(Q; \frac{5}{2}, \frac{7}{2})$ expressed by Eq. (2) , where the integrated intensity is normalized in a way that the intensity at $Q = 4\text{Å}^{-1}$ corresponds to $G(4\text{Å}^{-1}; \frac{5}{2}, \frac{7}{2})$. The observed rapid decrease of the intensity with increasing Q agrees with the theoretical inelastic structure factor of Sm^{3+}.

The intermultiplet transitions in many Sm-based compounds have been studied by INS experiments. Especially, large changes of INS spectra are reported in intermediate valence compounds such as $Sm_{1-x}Y_xS$ [12, 19, 20]. If the valence of Sm ions in $SmFe_4P_{12}$ deviates from trivalent slightly, the $J = 0$ to $J = 1$ excitation around 36 meV for Sm^{2+}, which has the largest inelastic structure factor in the rare-earth ions, may be expected. However no significant difference between the data at 6.5 K and 280 K around 36 meV was observed as shown in the inset of Fig. 3. This is consistent with the results of the magnetic susceptibility [2] and the X-ray absorption spectra [10].

The observed large reduction of the energy splitting between the J multiplets has not been reported so far. Here we discuss the origin of the small energy splitting. Firstly, we consider

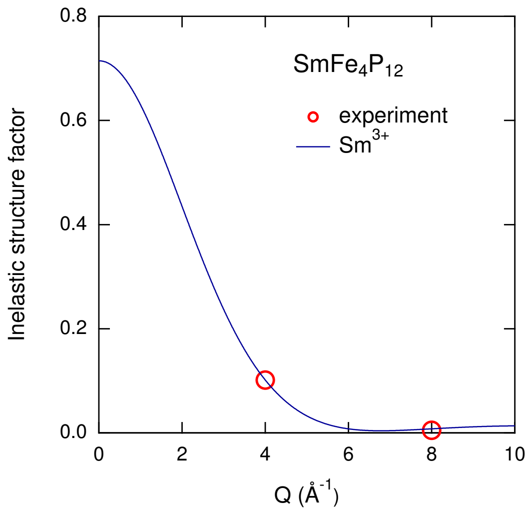

Figure 4. The scattering vector dependence of the integrated intensity of the small peak around 80 meV. The line denotes the theoretical inelastic structure factor of Sm^{3+} expressed by Eq. (2).

the effects of the CF on the excited $J = 7/2$ multiplet. Under the CF with T_h symmetry, the $J = 7/2$ multiplet splits into two doublets and one quartet, where the 6th-order term in CF Hamiltonian also contributes to the splitting. Since the $\Gamma_5 - \Gamma_{67}$ energy splitting in the ground $J = 5/2$ multiplet is about 6 meV, the overall energy splitting in the $J = 7/2$ multiplet due to the CF effects is estimated to be the same order of magnitude, as reported by INS experiments on some Sm-based compounds [21, 22]. This means that the energy reduction due to the CF effects may be at most ∼20 meV. Therefore the CF effects alone cannot explain the observed large reduction of the energy. Secondly, we might need to think the effect of the ferromagnetic interaction in $SmFe_4P_{12}$. It shifts the energy of excitations, for example, as reported in the permanent magnet Sm_2Fe_{17} [23]. However, the ferromagnetic interaction in $SmFe_4P_{12}$ is very weak compared to the energy between the J multiplets and shifts rather higher energy. Thus, this interaction cannot explain the small energy splitting. Finally, we consider the strong mixing between $4f$ electrons and conduction electrons and the rattling motion of Sm ions, resulting from the characteristic cage structure in filled skutterudites. Since the cage formed by the pnictogen X in RT_4X_{12} becomes smaller as changing X = Sb → As → P, the effects of the former may be more important in $SmFe_4P_{12}$. In fact, the band calculation shows that RFe_4P_{12} systems have the strongest $c - f$ mixing [24]. On the other hand, the latter was not seen in $SmFe_4P_{12}$ [25, 26], in contrast to $SmOs_4Sb_{12}$ [26, 27, 28]. Therefore, this strong $c - f$ mixing might renormalize the spin-orbit transition between the J multiplets.

In summary, we have performed magnetization measurement and INS experiments on filled skutterudite $SmFe_4P_{12}$ by using high energy neutrons. The results indicate that the energy splitting between the ground $J = 5/2$ multiplet and the excited $J = 7/2$ multiplet is very small compared to usual Sm-based compounds. This large reduction of the energy might originate from the strong $c - f$ mixing in $SmFe_4P_{12}$. The present study suggests that the contribution of the excited $J = 7/2$ multiplet should be taken into account for understanding the electronic states in the Sm-based filled skutterudites.

References

[1] Sato H, Sugawara H, Aoki Y and Harima H 2009 *Handbook of Magnetic Materials* vol 18, ed K H J Buschow (Amsterdam: Elsevier) p 1
[2] Takeda N and Ishikawa M 2003 *J. Phys. Condens. Matter* **15** L229
[3] Sanada S, Aoki Y, Aoki H, Tsuchiya A, Kikuchi D, Sugawara H and Sato H 2005 *J. Phys. Soc. Jpn.* **74** 246
[4] Yuhasz W M, Frederick N A, Ho P C, Butch N P, Taylor B J, Sayles T A, Maple M B, Betts J B, Lacerda A H, Rogl P and Giester G 2005 *Phys. Rev.* B **71** 104402
[5] Kikuchi D, Sugawara H, Tanaka K, Aoki H, Kobayashi M, Sanada S, Kuwahara K, Aoki Y, Shishido H, Settai R, Ōnuki Y, Harima, H and Sato H 2008 *J. Phys. Soc. Jpn.* **77** 114705
[6] Takeda N and Ishikawa M 2008 *J. Phys. Soc. Jpn.* **77** Suppl. A 209
[7] Takegahara K, Harima H and Yanase A 2001 *J. Phys. Soc. Jpn.* **70** 1190
[8] Matsuhira K, Doi Y, Wakwshima M, Hinatsu Y, Amitsuka H, Shimaya Y, Giri R, Sekine C and Shirotani I 2005 *J. Phys. Soc. Jpn.* **74** 1030
[9] Hachitani K, Fukazawa H, Kohori Y, Watanabe I, Yoshimitsu Y, Kumagai K, Giri R, Sekine C and Shirotani I 2006 *J. Phys. Soc. Jpn.* **75** 124717
[10] Mizumaki M, Tsutsui S, Tanida H, Uruga T, Kikuchi D, Sugawara H and Sato H 2007 *J. Phys. Soc. Jpn.* **76** 053706
[11] Van Vleck J H 1932 *The Theory of Electric and Magnetic Susceptibilities* (London: Oxford University Press)
[12] Osborn R, Lovesey S W, Taylor A D and Balkar E 1991 *Hand- book of Physics and Chemistry of Rare Earths* vol 19, ed K A Gschneider Jr and L Eyring (Amsterdam: Elsevier) p 1
[13] Jeitschko W and Braun D J 1977 *Acta Cryst.* B **33** 3401
[14] Giri R, Shimaya Y, Sekine C, Shirotani I, Matsuhira K, Doi Y and Hinatsu Y 2003 *Physica* B **329-333** 458
[15] Itoh S, Yokoo T, Satoh S, Yano S, Kawana D, Suzuki J and Sato T J 2011 *Nucl. Instr. Meth. Phys. Res.* A **631** 90
[16] Carnall W T, Goodman G L, Rajnak K and Rana R S 1989 *J. Chem. Phys.* **90** 3443
[17] Williams W G, Boland B C, Bowden Z A, Taylor A D, Culverhouse S and Rainford B D 1987 *J. Phys.* F **17** L151
[18] Balcar E and Lovesey S W 1989 *Theory of Magnetic Neutron and Photon Scattering* (Oxford: Clarendon Press)
[19] Alekseev P A, Mignot J M, Link P, Hahn W, Ochiai A, Filippov V, Nefeodova E V and Clementyev E S 1999 *Physica* B **259-261** 351
[20] Alekseev P A, Mignot J M, Ochiai A, Nefeodova E V, Sadikov I P, Clementyev E S, Lazukov V N, Braden M and Nemkovski K S 2006 *Phys. Rev.* B **74** 035114
[21] Guillaume M, Henggeler H, Furrer A, Eccleston R S and Trounov V 1995 *Phys. Rev. Lett.* **74** 3423
[22] Rosenkranz S, Medarde M, Fauth F, Mesot J, Zolliker M, Furrer A, Staub U, Lacorre P, Osborn R, Eccleston R S and Trounov V 1999 *Phys. Rev.* B **60** 14857
[23] Sippel A, Jahn L, Loewenhaupt M, Eckert D, Kerschl P, Handstein A, Müller K H , Wolf M, Kuz'min M D, Steinbeck L, Richter M, Teresiak A and Bewley R 2002 *Phys. Rev.* B **65** 064408
[24] Sato H, Kikuchi D, Tanaka K, Ueda M, Aoki H, Ikeno T, Tatsuoka S, Kuwahara K, Aoki Y, Kohgi M, Sugawara H, Iwasa K and Harima H 2008 *J. Phys. Soc. Jpn.* **77** Suppl. A 1
[25] Nakanishi Y, Tanizawa T, Fujino T, Sugawara H, Kikuchi D, Sato H and Yoshizawa M 2006 *J. Phys. Soc. Jpn.* **75** 192
[26] Ogita N, Kojima R, Takasu Y, Hasegawa T, Kondo T, Udagawa M, Takeda N, Ikeno T, Ishikawa K, Sugawara H, Kikuchi D, Sato H, Sekine C and Shirotani I 2007 *J. Magn. Magn. Mater.* **310** 948
[27] Yanagisawa T, Ikeda Y, Saito H, Hidaka H, Amitsuka H, Araki K, Akatsu M, Nemoto Y, Goto T, Ho P, Baumbach R E and Maple M B 2011 *J. Phys. Soc. Jpn.* **80** 043601
[28] Tsutsui S, Uchiyama H, Sutter J P, Baron A Q R, Mizumaki M, Kawamura N, Uruga T, Sugawara H, Yamaura J, Ochiai A, Hasegawa T, Ogita N, Udagawa M and Sato H 2012 *Phys. Rev.* B **86** 195115