Magnetic properties in spinel-type compounds $M\mathrm{Yb_2S_4}$ (M = Mg, Mn)

Shuji Ebisu [1], Taku Iwasa, Sachi Tamaki, Shoichi Nagata

Department of Materials Science and Engineering, Muroran Inst. of Tech., Mizumoto-cho 27-1, Muroran 050-8585, Japan

Abstract

The spinel-type compounds $M\mathrm{Yb_2S_4}$ (M = Mg, Mn) have been prepared and magnetic susceptibility measurements have been carried out. Two types of sample for $\mathrm{MnYb_2S_4}$ were obtained. The stable phase has a normal-spinel structure and the newly found metastable phase has a modified spinel structure which is not the inverse spinel. Susceptibility data show clearly the difference between both samples of $\mathrm{MnYb_2S_4}$, which reflects the difference of the crystal field on Yb^{3+} ions. Moreover, the magnitude of the FC susceptibility data for each type of $\mathrm{MnYb_2S_4}$ is slightly larger than that of ZFC below about 50 K, while such difference is not observed for $\mathrm{MgYb_2S_4}$.

Key words: $M\mathrm{Yb_2S_4}$; spinel; magnetic susceptibility; frustration

1. Introduction

Rare-earth thiospinels $M\mathrm{Yb_2S_4}$ (M = Mg, Mn) were firstly prepared by Patrie *et al.* [1]. So far as $\mathrm{MnYb_2S_4}$ is concerned, the crystal structure has been known just as normal-spinel type [2]. Paramagnetic behavior in these compounds has also been reported [2–5]. A detailed study of crystal structure and magnetic properties in these compounds will be presented. We emphasize the anomaly of the magnetic susceptibility for $\mathrm{MnYb_2S_4}$ is associated with the magnetic frustration.

2. Experimental

The samples were prepared by solid-state reaction among the appropriate molar-ratio elements in evacuated quartz tubes. Weighing, grinding and mixing of the elements were made in Ar gas. The sample was heated to 1273 K for 24 h after keeping at 673 K for 4 h, then quenched in air. After grinding in Ar gas, the product was reheated to 1473 K for 24 h and quenched in air. Powder X-ray diffraction data using Cu K_α radiation were taken. The dc magnetic susceptibility was measured with a SQUID magnetometer.

3. Results and Discussion

The X-ray diffraction peaks for each sample closely resemble those of spinel phase shown in the PDF cards No. 20-1396 for $\mathrm{MnYb_2S_4}$ (phase A) and No. 30-804 for $\mathrm{MgYb_2S_4}$. For $\mathrm{MnYb_2S_4}$, however, the other phase (B) having fcc structure with the lattice parameter a = 10.985 Å was also detected when only one cycle of heating up to 1423 K and air-quenching was done. Rietveld analyses using RIETAN-2000 [6] gave many structural information including site occupancy of ions, although the reliable factors R_{wp} were not so good as 13 % in all cases owing to slight amount of impurities. It has been confirmed $\mathrm{MnYb_2S_4}$ (phase A) has a normal-spinel structure with a = 10.950 Å. It was turned out that complicated distribution of cations among the sites of space group $Fd\bar{3}m$ takes place in phase B of $\mathrm{MnYb_2S_4}$, namely the 71 % of Mn and 25 % of Yb oc-

[1] Corresponding author. Fax: +81-143-46-5601.
E-mail: ebisu@mmm.muroran-it.ac.jp

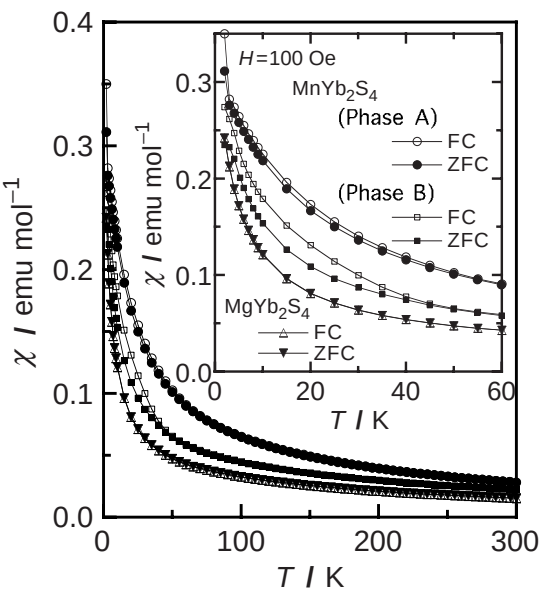

Fig. 1. Temperature dependence of dc magnetic susceptibility for $M\mathrm{Yb_2S_4}$ (M = Mg, Mn). The inset is an enlargement below 60 K and solid curves are guides to the eye.

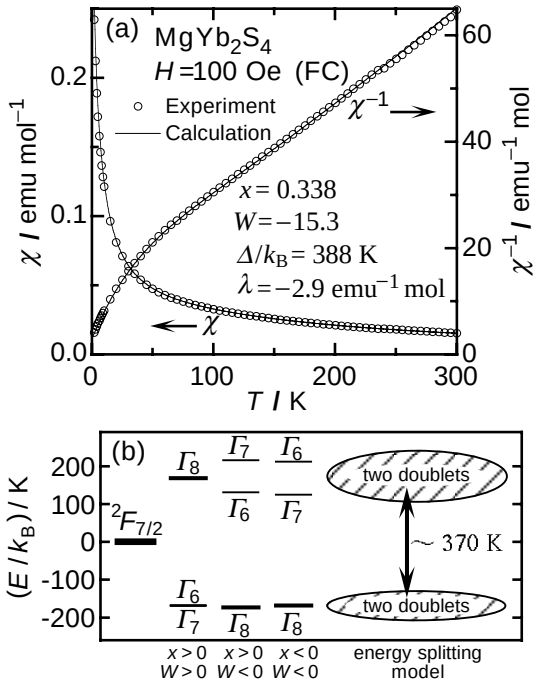

Fig. 2. (a) An example of optimized fits to χ and χ^{-1} for $\mathrm{MgYb_2S_4}$ obtained through a cubic crystal field analysis. (b) Energy level splitting; evaluated values and a model.

cupy $16c$ site. Such anomalous distribution of cations in spinel was observed in $\mathrm{Fe}R_2\mathrm{S_4}$ (R = Yb, Lu) [7]. We found $\mathrm{MgYb_2S_4}$ (a = 10.967 Å) also has modified spinel structure in which 35 % of Mg occupy $16c$ site.

Temperature dependence of dc magnetic susceptibility χ for each sample is shown in Fig. 1. Here both susceptibility data under the field of 100 Oe applied after cooling to 2 K (ZFC) and before cooling (FC) are shown. The inset demonstrates clearly the FC data are larger than those of ZFC below 50 K in both phases of $\mathrm{MnYb_2S_4}$, while these FC and ZFC data of $\mathrm{MgYb_2S_4}$ show fairly good agreement down to 2 K. These FC effects are associated with geometrical frustration between B site cations coupled antiferromagnetically in spinel-type compounds. However, no FC effect in Mg compound suggests the competition of magnetic interactions among the cations plays an important role for the magnetic frustration in $\mathrm{MnYb_2S_4}$.

Fig. 2 shows an optimized fit to the magnetic susceptibility for $\mathrm{MgYb_2S_4}$ determined through a cubic crystal field analysis. Here x and W are LLW parameters [8] and λ stands for a molecular field constant which comes mainly from the exchange interactions. Three sets of parameters corresponding to the splittings in Fig. 2(b) are able to reproduce the experimental result. A prediction based on a simple point-charge model considering only nearest neighbors comprising six $\mathrm{S^{2-}}$, which requires a negative x and positive W, is not valid. It may originate from the two points. The first is the disregard of covalency for the chemical bond and the second is the influence of crystal field from the next nearest neighbors. If we assume the value of $\lambda = -2.9$ $\mathrm{emu^{-1}mol}$ comes from the exchange interaction, the Weiss constant is estimated as -15 K. Thus the antiferromagnetic interaction exists between $\mathrm{Yb^{3+}}$ ions, however, the geometrical frustration is not sufficiently strong to bring about the FC effect at 2 K in $\mathrm{MgYb_2S_4}$.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (No. 12740193) from the Japan Society for the Promotion of Science.

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